

A study of some organic compounds of boron

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A STUDY
OF SOME ORGANIC COMPOUNDS
OF BORON

K. G. O'BRIEN

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A STUDY OF SOME ORGANIC COMPOUNDS OF BORON

Thesis submitted for the Degree of Doctor of Philosophy of
The New South Wales University of Technology.

KEITH GEORGE O'BRIEN

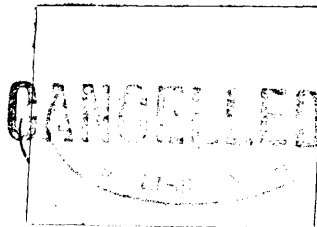
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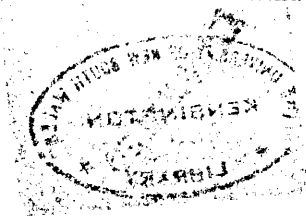
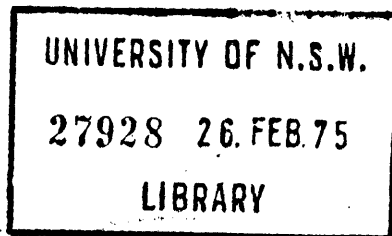
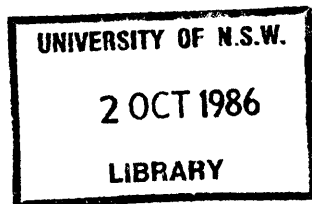


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Don. Prof. R. L. H. H. H.

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SUMMARY

The object of the thesis is to present the results of an investigation concerning the methods of preparation, chemical reactions and uses of some alkyl and aryl compounds of orthoboric acid.

The following is a brief summary of the contents of the thesis:-

SYMMETRICAL TRI-ALKYL AND TRI-ARYL ESTERS OF ORTHOBORIC ACID

The preparation of tri-alkyl borates using the azeotropic apparatus of Anderson et al (1952) was undertaken. By this method tri-n-butyl, tri-sec-butyl, tri-cyclohexyl and tri-phenyl borates were prepared. It was found that tri-tert-butyl borate could not be prepared under these experimental conditions.

Contrary to the literature reports (Etridge and Sudgen 1928, Scattergood et al 1945 and Thomas 1946) it was found possible to prepare tri-tertiary-butyl borate by fractional distillation. Using this technique the following esters of orthoboric acid were prepared.

Tri-n-aryl borate

Tri-tertiary-butyl borate

Tri-n-hexyl borate

Tri-n-heptyl borate

Tri-2-octyl borate

Tri-(2-ethyl)-hexyl borate

Triphenyl borate

Tri-p-cresyl borate

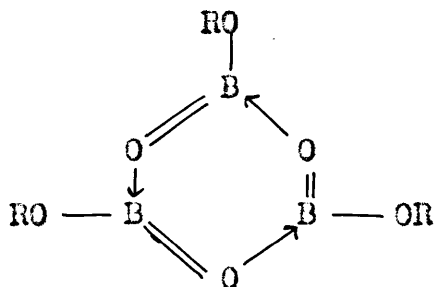
It was found that this fractional distillation method was inapplicable to the preparation of tri-methyl borate and tri-n-propyl borate. These esters were prepared by methods described by Etridge and Sudgen (loc.cit).

A literature survey showed that there was no record of the infra red spectra of tri-alkyl and tri-aryl borates. A representative group of the esters was submitted for examination and it was found that the tri-alkyl and tri-aryl esters both show characteristic strong absorption bands at 1340 cm^{-1} .

TRI-ALKOXY BOROXOLES

A series of experiments was carried out in order to determine whether it was possible to prepare tri-, di-, and mono-cyclohexyl borate.

Three mols of alcohol were found to react readily with one mol of boric acid to give a quantitative yield of tri-cyclohexyl borate. Two mols of cyclohexanol per mol of boric acid gave a mixture of indeterminate composition. Where the ratio of alcohol to boric acid was one to one, however, it was found that a class of compound, first described by Goubeau (1951) and called alkoxy boroxoles; was formed



TRI-ALKOXY BOROXOLE DERIVATIVE.

It was found that the partially alkylated esters of orthoboric acid could not be prepared under these experimental conditions.

In an attempt to prepare mono- and di- cyclohexoxy boroxole it was found that irrespective as to whether the ratio of alcohol to boric acid was two to three or one to three, the resultant products were tri-cyclohexoxy boroxole and metaboric acid. The ratio of three alcohol to three mols of boric acid led to the formation of tri-cyclohexoxy boroxole.

Similarly it was found that partially alkylated boroxole derivative could not be prepared under these experimental conditions.

A series of tri-substituted boroxole derivatives was prepared using the method of Goubeau and also by reacting one mol of alcohol with one mol of boric acid in presence of a suitable solvent, as described above. The following compounds were prepared for the first time.

Tri-tertiary butoxy boroxole

Tri-cyclohexoxy boroxole

Tri-n-propoxy boroxole

Tri-n-pentoxy boroxole

Tri-n-butoxy boroxole

Tri-n-hexoxy boroxole

Tri-(1-methyl)-n-heptoxy boroxole

Tri-(2-ethyl)-n-hexoxy boroxole

Tri-phenoxy boroxole

Tri-(p-methyl phenoxy)- boroxole.

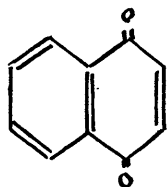
As with the tri-alkyl and aryl borate esters, a literature survey showed that there was no published work regarding the infra red spectra of these compounds. It was found, on infra red examination that these boroxole derivatives showed strong characteristic bands of absorption at 700 and 740 cm^{-1} , as well as the strong absorption bands at 1340 ± 10 which are present in the borate esters.

PREPARATION OF ALKYL ACETATES FROM TRI-ALKYL BORATES

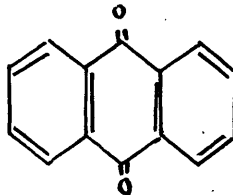
anhydride respectively, in benzene was carried out in order to test their suitability as reagents for the specific characterisation of compounds possessing naphthoquinone, anthraquinone and flavone structures in which there is an hydroxyl group occupying a position peri- to the quinoid group.

As a control, compounds were examined in which the hydroxyl group occupied a position other than that peri- to the quinoid group.

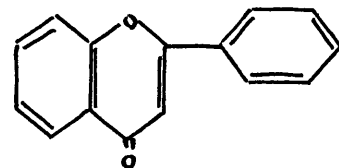
The reagents were found to be capable of allowing the detection of the presence of peri-hydroxy quinoid structures and related compounds down to a concentration of $1\mu/\text{cc}$. In all cases where the hydroxyl group was not in the peri- position, the reactions were negative.



NAPHTHOQUINONE



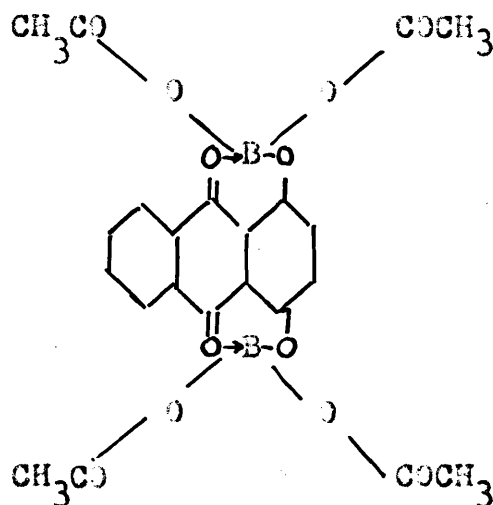
ANTHRAQUINONE



FLAVONE

BORON DERIVATIVES OF PERI-HYDROXY QUINONES

Dinroth (1921, 1926) had isolated intensely coloured compounds from the reaction between pyroboracetic anhydride and peri-hydroxy quinones, typical of which is the following compound from 1:4 di-hydroxy anthraquinone.



Now, where Dimroth used acetic anhydride as his solvent, in these series of experiments benzene was the solvent. Examination of the compounds isolated from the benzene solution showed that they were very susceptible to atmospheric moisture.

Although it was not possible to determine the exact structure of these compounds, sufficient evidence was discovered to show that they were definitely different from those prepared by Dimroth.

METABORIC ACID

It has been found that orthoboric acid may be readily dehydrated by azeotropic distillation with benzene, toluene or xylene, the rapidity of the reaction increasing with the increase in boiling point of the azeotrope. However, even at the high temperature of 144°C, the boiling point of xylene, it was not found possible to isolate boron oxide.

Because of the following facts:-

- (i) The ease of dehydration of orthoboric acid to metaboric acid.
- (ii) Tri-alkoxy boroxoles are intermediates in the formation of tri-alkyl borates.
- (iii) Metaboric acid may be formed by the dehydration of orthoboric acid with acetic anhydride and is the intermediate product in the formation of pyroboracetic anhydride, it is proposed that the reactions of orthoboric acid should be considered rather as those of a hydrate of metaboric acid. In each case quoted above, the reaction involves not the orthoboric acid but rather the initial dehydration product, namely metaboric acid.

A REVIEW OF METHODS OF PREPARATION OF
ORGANIC ESTERS OF ORTHOBORIC ACID

The development of suitable methods of preparation of the organic esters of orthoboric acid is a problem which has occupied the minds of chemists for over a hundred years. Up to the present time there has been no satisfactory method reported in the literature for the preparation and isolation in the pure state of the tri-tertiary alkyl esters of orthoboric acid. On the other hand, however, the preparation of esters of primary and secondary alcohols has not been such a difficult problem and quite a number have been prepared in the pure state.

The earliest technique of Ebleman and Bouquet (1846), in which the alcohol and boron trichloride were heated in a sealed tube, was not very successful. The product was recorded as having a boiling point of 73°C at 760mm. which, in view of later information, indicates that the compound was very impure since latest figures record the boiling point of trimethyl borate as 68°C at 760mm. The distillation of anhydrous borax with methyl potassium sulphite was attempted by Rose (1856) and Frankland (1862) independantly but without success. Pictet and Karl (1908) found that methyl alcohol and boryl disulphate

$((\text{SO}_3)_2\text{B}_2\text{O}_3)$ formed trimethyl borate. A poor yield of trialkyl borate was obtained by Counceler (1878a, b, c and d), from the interaction of the alcohol and borontrichloride, and in the attempt to prepare tribenzyl borate in this manner only benzyl chloride, dibenzyl and hydrogen chloride were obtained. Gasselin (1894), using dimethoxy boron fluoride or methoxy boron difluoride and sodium methoxide, prepared a compound with boiling range of $55-56^\circ\text{C}$ which was considered to be trimethyl borate; it would appear however that this compound was an azeotropic mixture of methanol and trimethyl borate, since Etridge and Sudgen (1928) found that in the preparation of dimethyl borate from boric oxide and methanol an azeotrope containing 30% of the ester was formed.

The most satisfactory method developed prior to 1900 for the preparation of organic esters of orthoboric acid was that of Schiff (1867), which was slightly modified later by Counceler (1878) and Copaux (1898). The general method was to react boron trioxide and the alcohols in a digester, generally at a pressure of two atmospheres, at temperatures ranging from 120 to 160°C , the time of reaction being 22 hours. Addition of ice cold sulphuric acid to the reaction mixture enabled the lighter trimethyl borate to be separated and distilled with boiling point of 68°C at 760mm. In the case of the triethyl borate it was found to be too soluble in sulphuric acid but could be separated by fractional distillation,

boiling point 120°C .

Pictet and Geleznoff (1903) claimed to have prepared trimethyl borate by the reaction between boracetic anhydride ($\text{B}(\text{OCOCH}_3)_3$) and methanol. It is considered by the author that there is some doubt as to the authenticity of the claim because Etridge and Sudgen (1928) made several unsuccessful attempts to prepare the ester by this method. They found that the crude product from the reaction between methanol and boracetic anhydride was ternary mixture of methyl alcohol b.p. 65°C , trimethyl borate b.p. 68°C and methyl acetate b.p. 57°C from which they were unable to obtain the pure ester by repeated fractionation. The separation was also complicated by the presence of the constant boiling mixture of the alcohol and methyl borate. Etridge and Sudgen (1928) also found that the method was of little value in the preparation of triethyl borate, b.p. 117°C since it could not be separated from the glacial acetic acid, b.p. 118°C ., by prolonged fractional distillation. Pictet and Geleznoff (1903) do not mention these difficulties and it is possible that the methyl and ethyl esters which they prepared were not pure substances. Attempts to prepare tritertiary butyl borate from the boracetic anhydride were also unsuccessful, leading to the formation of butyl acetate amongst other unidentified products. Dimroth (1921, 1926) endeavoured to prepare triacetyl orthoborate according to the method of Pictet and Geleznoff (1903) but found that

the resultant compound was pyroboracetic anhydride. The author has found that similar results to those of Dimroth were obtained, consequently it appears that the claim of Pictet and Geleznoff to have prepared trimethyl and triethyl borates is open to question.

Cohn (1911) improved the method of Schiff (1867) considerably by showing that in the presence of sulphuric acid it was possible to react a mixture of methyl alcohol and boric oxide at atmospheric pressure until the mixture became homogeneous and so avoiding the use of pressure vessels. The ester was then distilled as the azeotrope, separated by treatment with ice cold sulphuric acid and finally distilled to give pure trimethyl borate.

Etridge and Sudgen (1928) made a brief examination of the various methods used for the preparation of trimethyl and triethyl borates and concluded that Schiff's method (1867) was the best available. They modified the method somewhat. The appropriate anhydrous alcohol was heated in a sealed pressure vessel with boric oxide at 120°C for 12 hours in an oil bath. The contents of the flask were then fractionated, and after treatment with freshly ignited calcium chloride for 24 hours fractionally distilled again. By repetition of the process they were able to prepare pure esters. It would appear that these authors were not aware of the method of Cohn (1911) which is far more suitable than any methods involving the use

of pressure vessels.

Khotinski and Pupko (1929) revived the use of borax, as introduced by Rose (1856) and Frankland (1862) for the preparation of orthoboric acid esters. They heated a mixture of borax, anhydrous alcohol and hydrogen chloride and claimed that the method has the advantage that it eliminates the use of pressure vessels. Since, however, the paper was published in an obscure and unobtainable Ukrainian journal, it was impossible to obtain further information other than that contained in Chemical Abstracts.

The utilisation of the fact that borate esters of alcohols containing four or more carbon atoms were relatively non-volatile was made by Schmidt (1928) as a means of isolation of alcohols and phenolic compounds from essential oils. The total alcoholic and phenolic constituents were esterified by either excess pyroboracetic anhydride or by heating the oil with boric acid and removing the water of esterification under reduced pressure. The volatile components were then distilled to leave a residue of esterified alcohols and phenols which was then decomposed by steam or alkali to give the free alcohols and phenols unchanged. Schmidt made no attempt to investigate the nature of the resultant boric acid esters.

Wiberg and Sutterlin (1931) using a Stock high vacuum apparatus (1914) at low temperatures of approximately -80°C investigated the mechanism of the interaction of methyl and

ethyl alcohols respectively with boron trichloride and found that quantitative yields of the tri-esters were obtainable.

Sheffield (1936) found that the use of pyroboracetic anhydride as an esterifying agent was not to be recommended since it could possibly lead to the dehydration of tertiary alcohols. He preferred to treat the essential oil of long leaf yellow pine with boric acid under suitable conditions such that the secondary alcoholic terpenes were esterified and the tertiary alcoholic terpenes were dehydrated between the temperatures of 100 to 170°C. The secondary terpene alcohol borates were then separated and readily hydrolysed with water to give the original alcohols.

Kaufman (1933) treated anhydrous mixtures of essential oils, containing terpene alcohols, with neutral alkyl borate esters and obtained borate esters of the terpene alcohols which could be readily separated from the non-alcoholic constituents and recovered unchanged on hydrolysis with water. This method of transesterification was not a new contribution to the subject because Schiff (1867) had prepared diethylamyl borate and diamylethyl borate by heating ethyl borate with amyl alcohol or amyl borate with ethyl alcohol as the case may be and also prepared methyl diethyl borate by heating monomethyl borate with ethyl alcohol.

The technique of transesterification as a means of preparation of alkyl esters of orthoboric acid was extended by

Wuyts and Duquesne (1939). First they prepared tripropyl borate by the standard method using boric oxide and anhydrous alcohol, then heated the ester with various alcohols to form a series of alkyl borates. Using this method they were able to prepare the tri-ester of the tertiary alcohol dimethyl-butyl carbinol, which, apart from tri-tertiary butyl borate, which Kahovec (1938, 1939) prepared from pyroboracetic anhydride and tertiary butyl alcohol, is the only borate of a tertiary alcohol reported in the literature as having been isolated and identified. Using tri-ethyl borate, Haves (1949) esterified nerolidol, and Sutherland (1950) esterified α -terpineol with tri-n-butyl borate.

From 1930 onwards the knowledge already accumulated regarding the theory of fractional distillation as applied to industrial stills began to be used in the development of more and more efficient laboratory fractional distillation columns for batch distillations. With this resultant improvement in design it was a logical sequence of events that an attempt be made to apply these columns to the problem of separation of the organic esters of boron. Webster and Dennis (1933), prepared tri methyl borate from boric oxide, anhydrous methyl alcohol and sulphuric acid by a method practically identical with that of Cohn (1911). Since the authors make no reference to this earlier worker it can only be concluded that they, like Etridge and Sudgen (1928), were unaware of his

work. The main difference in the method was that the ester was distilled through a Johnson column (1950) then, after treatment with sulphuric acid and separation, was finally distilled through a fractionation column containing Jack Chain packing (Laubengayer and Corey 1926), to give very pure trimethyl borate. Triethyl borate was prepared in a similar manner.

Johnson and Tompkins (1950) heated a mixture of boric acid, n-butyl alcohol and benzene in a still pot, passing the vapours through an efficient fractionation column. The benzene removed the water as an azeotropic mixture with a little n-butyl alcohol. From time to time the n-butyl alcohol in the distillate was separated, dried and returned to the column until such time as there was no further evolution of water. In this way pure tri-n-butyl borate was prepared, being easily separated from the excess n-butyl alcohol by fractional distillation.

A series of new esters of orthoboric acid were prepared by Scattergood et al (1945), using the method of Bannister (1928) (U.S.P. 1,668,798). For each mole of boric acid three moles of the alcohol were used together with sufficient excess alcohol to remove three moles of water as the azeotrope plus an overall excess of 10% alcohol to ensure complete reaction. The mixture was distilled through a column 115cm. high, electrically heated, filled with helices,

and having a total condensation variable take off. The H.E.T.P. of the column was given as 2.5cm. under operating conditions. During the distillation of the water alcohol azeotrope it was found that a proper adjustment of the take-off returned the alcohol layer to the column so that an excess of the alcohol may not be necessary. After the excess of the alcohol had been distilled the borate was distilled through the column at atmospheric pressure unless it decomposed or boiled above 275°C, in which case the column was operated under reduced pressure. Several borate esters which had been reported in the literature as unstable were distilled successfully at atmospheric pressure. The most important conclusion resulting from this work was that whereas the method was applicable for all the primary and secondary alcohols studied it was entirely unsuccessful in the case of the three tertiary alcohols used, i.e. 2-methyl pentanol-2, 2-methyl butanol-2 and 3-methyl pentanol-3., which suggests that primary and secondary alcohols contaminated with tertiary alcohols may be purified through their borate esters.

Thomas (1946) prepared a series of tri-alkyl and tri-aryl esters of orthoboric acid by slight modifications to known methods. Firstly he refluxed a mixture of boric oxide and the alcohol in an inert solvent such as toluene and allowed the condensed vapours to percolate through anhydrous copper sulphate, held in the thimble of a soxhlet apparatus, to remove the water

of esterification as formed during the reaction according to the method of Johnson and Dupine (1936); secondly he used azeotropic distillation through an efficient fractionation column to remove the water of esterification as per method of Johnson and Tompkins (1950); finally he repeated the transesterification method of Schiff (1867) and Wuyts and Duquesne (1939). Again, in apparent confirmation of the results of previous workers, it was reported that all of these methods were inapplicable for the preparation of the tri-tertiary alkyl esters of orthoboric acid.

H.G. Cook et al (1950) prepared a number of esters of orthoboric acid by reaction between the appropriate alcohol and a compound which they considered as boron triacetate since it had been prepared according to the method of Pictet and Geleznoff (1903). In this way they were able to prepare tri-n-propyl, tri-n-butyl, tri(2-fluoro-ethyl), tribenzyl, and tricyclohexyl borates. Attempts to prepare isopropyl and tertiary esters by alcoholysis of the borontriacetate were not very successful. By the use of an autoclave, specially designed (Saunders and Stacey, 1948) to rotate, the time of heating of the boric anhydride and ethyl alcohol was reduced from 24 to 6 hours. In addition the yield was increased to 30% for triethyl borate and 25% for tri-2-propyl borate. Yet again it is to be noticed that no satisfactory method for tri-tertiary alkyl esters was

developed.

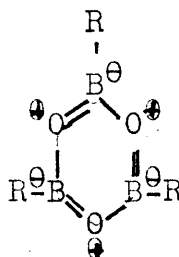
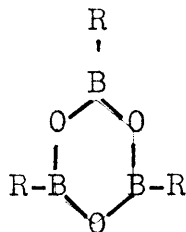
Gerrard and Lappert (1951) considerably improved the technique of previous workers who used borontrichloride for the esterification. They used n-pentane as a vehicle for the borontrichloride and found that with octan-2-ol and I-phenylethanol respectively, at -10°C , tri-2-octyl borate and tri-I-phenylethyl borate in 90% and 26% yields could be obtained. The yields could be increased if the pyridine-borontrichloride complex was used in chloroform solution. In a second paper (1952), the method was elaborated by preparing boron trichloride-pyridine complex by a slightly modified method and refluxing a chloroform solution for ten hours. By this method a 70% yield of tri-tertiary butyl borate was obtained and a 60% yield of I:I dimethylpropyl borate. This is the most satisfactory method for the preparation of esters of tertiary alcohols reported in the literature to date.

In 1950, a preliminary investigation was commenced by Anderson et al (1952) re the direct esterification of tertiary alcohols. All reports in the literature to that date intimated that the direct esterification process was inapplicable to the tertiary alcohols. It was subsequently shown that, by use of a specially designed azeotropic-distillation apparatus, it was possible to esterify primary, secondary and tertiary alcohols. In the case of the tertiary

alcohols no boric esters could be separated in the pure state. They neither could be sublimed nor distilled under vacuum. Their recrystallisation was extremely difficult owing to acute sensitivity to hydrolysis due to traces of atmospheric moisture. However, the fact that the products could not be obtained in a pure condition was of minor importance because the main point of the investigation was to establish indubitably the fact that esterification had taken place. The nature of the products of investigation were to be considered in later work. It was desired to make this method of esterification generally applicable for the separation of alcohols from mixtures. It was realised that low molecular weight alcohols, e.g. methyl, ethyl and propyl alcohols, form neutral trialkyl esters which possess sufficient volatility to make separation difficult, if not impossible. The method developed to overcome this difficulty arose from the observation that one mol of boric acid reacted with less than three moles of alcohol to form a completely non-volatile product. In all cases it was found that on removal of the solvent, a pasty semicrystalline mass remained which could not be satisfactorily recrystallised or distilled without decomposition even at 0.1mm. pressure. Hydrolysis of the reaction product yielded a quantitative yield of the alcohol. All tertiary alcohols were found to be esterified under the conditions used as demonstrated from the fact that the whole of the boric acid had gone into solution. It was not

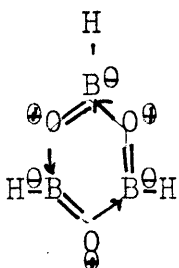
merely a case of physical solution as there was about a tenfold excess of benzene present, in which both ortho and meta boric acids are insoluble and, further, dilution of the mixture with benzene gave no precipitate of boric acid.

H.R. Snyder et al. (1938) and S.H. Bauer and J.V. Beach (1941) showed that tri-alkyl boric anhydrides (R-O-B-O) exist as trimers in a six membered ring and from electron diffraction studies suggested the structure to be a resonance hybrid as follows:-



R = Alkyl or aryl group.

Goubeau and Keller (1951) prepared a similar series of compounds in which R = Halogen, $-\text{CH}_3$, $-\text{N}(\text{CH}_3)_2$ and $-\text{OCH}_3$ and gave this series of compounds the generic name of boroxoles since they considered that these compounds were derivatives of the theoretical compound Boroxole which was given the following formula and to date has not been isolated.



The work of Goubeau which was of most importance with respect to this thesis was the preparation of tri-methoxy boroxole. He showed that tri-methyl borate, prepared according to the method of Cohn (1911) and treated with boric anhydride gave tri-methoxy boroxole rather than methyl meta-borate ($\text{CH}_3\text{O}-\text{B}=\text{O}$) as claimed by Schiff (1867). Goubeau has not as yet published any further work on the preparation of tri-alkoxy boroxoles.

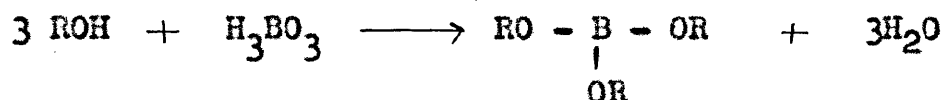
O'Connor and Nace (1955) described the preparation and properties of three compounds, 1-menthyl metaborate trimer, cyclohexyl metaborate trimer and n-butyl metaborate trimer. These compounds were prepared by reaction between one mol of boric acid and one mol of the appropriate alcohol. It was found that the compounds decomposed on distillation, were very easily hydrolysed and on infrared examination were found to fail to give $-\text{B}=\text{O}$ absorption.

O'Connor and Nace were apparently unaware of the work of Goubeau in the preparation of trimethoxy boroxole and related compounds since they persist in referring to their compounds as trimers of metaboric acid esters. The infra red examination was incomplete since a more detailed examination would have shown that the boroxoles have characteristic absorption bands at the 700 and 740cm^{-1} and 1340cm^{-1} region as discussed in this thesis.

SYMMETRICAL TRI-ALKYL AND TRI-ARYL
ESTERS OF ORTHOBORIC ACID.

(a) Discussion of methods of preparation

In the initial experiments the azeotropic apparatus of Anderson et al (1952) was used for the preparation of tri-alkyl and tri-aryl esters of orthoboric acid, being simple to operate and requiring very little attention. Tri-n-butyl, tri-secondary-butyl, tri-cyclohexyl and tri-phenyl borate were prepared in a pure condition by this method when using three mols of alcohol or phenol to one of boric acid in the presence of benzene as the azeotroping agent.



The preparation of tri-tertiary-butyl borate was not accomplished using this method. In all cases a white crystalline compound was obtained which decomposed on vacuum distillation, contained 10.8% boron instead of the 4.7 required for tri-tertiary-butyl borate. A benzene solution of the compound gave a positive development of colour with quinalizarin. This colour development was interesting because it indicated there was a possibility that the compound was the same as that prepared by Anderson (1950) and thought to be tri-tertiary-butyl

borate. Further discussion on this type of compound is contained in section of thesis devoted to TRI-ALKOXY BOROXOLES.

Although it is recorded as being impossible to prepare tri-tertiary butyl borate by fractional distillation, (Etridge and Sudgen 1928, Scattergood et al 1945 and Thomas 1946), it was considered that it might be possible to prepare the compound using a more modern laboratory fractionation column. A glass fractionation column two feet by one-half inch internal diameter was packed with $\frac{1}{8}$ th inch stainless steel Dixon ring packing, (Dixon 1949), and fitted with a McIntyre weir reflux ratio head (McIntyre 1933). A little benzene was added to the still head from time to time to facilitate the separation of the water from the azeotropic mixture of water and alcohol, a technique introduced by Johnson and Tompkins (1950). By operating at a fast boil up rate and high reflux ratio, it was found possible to remove all the water, the end of the reaction being indicated by the fact that the still head temperature rose to 82.5°C , the boiling point of the excess tri-tertiary butyl borate, which in this experiment was used in the ratio of 0.9 mol of alcohol to 0.1 mol of orthoboric acid.

This technique of fractional azeotropic distillation proved most satisfactory, consequently it was adopted for all further work involving the preparation of tri-alkyl and tri-aryl borates. The following esters were prepared:-

Tri-n-amyl borate
Tri-tertiary butyl borate
Tri-n-hexyl borate
Tri-cyclohexyl borate
Tri-n-heptyl borate
Tri-2-octyl borate
Tri-2-ethyl-hexyl borate
Tri-phenyl borate
Tri-cresyl borate

Tri methyl borate and tri-n-propyl borate were prepared according to method of Etridge and Sudgen (1928).

Attempts to prepare tri-tertiary butyl borate by the trans esterification of tertiary-butyl alcohol with pyroboracetic anhydride, as recommended by Cooke et al (1950), yielded only tertiary butyl acetate. However, it was found that tri-phenyl borate could be prepared by the transesterification of phenol with pyroboracetic anhydride. This method was not, however, further exploited.

PHYSICAL PROPERTIES AND ANALYTICAL VALUES OF SOME ALKYL BORATE ESTERS

Compound	Boiling Point (°C/mm)	$n_D^{22.5}$	Yield (%)	Molecular Composition	Mol. Wt.
Trimethyl borate, $C_3H_9O_3B$	69/750	1.3585	55	Calc. : C, 34.7 ; H, 8.7 ; B, 10.6% Found : C, 35.0 ; H, 8.8 ; B, 10.8%	Calc. 104 Found 100
Tri - <i>n</i> - propyl borate, $C_9H_{21}O_3B$	180-183/760	1.4266	45	Calc. : C, 57.5 ; H, 11.2 ; B, 5.8% Found : C, 57.3 ; H, 11.0 ; B, 5.9%	Calc. 188 Found 180
Tri - <i>tert.</i> - butyl borate, $C_{12}H_{27}O_3B$	65-66/11	1.3869	44	Calc. : C, 62.6 ; H, 11.8 ; B, 4.7% Found : C, 62.6 ; H, 11.9 ; B, 4.8%	Calc. 230 Found 234
Tri - <i>n</i> - amyl borate, $C_{15}H_{33}O_3B$	154/16	1.4205	80	Calc. : C, 66.2 ; H, 12.1 ; B, 4.0% Found : C, 64.6 ; H, 11.5 ; B, 3.9%	Calc. 271 Found 260
Tri - <i>n</i> - heptyl borate, $C_{21}H_{45}O_3B$	192/4-6	1.4355	88	Calc. : C, 70.8 ; H, 12.6 ; B, 3.2% Found : C, 70.8 ; H, 12.6 ; B, 3.3%	Calc. 355 Found 348
Tri - (2 - ethyl)- hexyl borate, $C_{24}H_{51}O_3B$	348-352/745	1.4365	73	Calc. : C, 72.4 ; H, 12.8 ; B, 2.8% Found : C, 72.1 ; H, 12.7 ; B, 2.8%	Calc. 397 Found 405
Tri - 2 - octyl borate, $C_{24}H_{51}O_3B$	170/1	1.4275	83	Calc. : C, 72.4 ; H, 12.9 ; B, 2.8% Found : C, 72.1 ; H, 12.9 ; B, 2.7%	Calc. 397 Found 400

PHYSICAL PROPERTIES AND ANALYTICAL VALUES OF SOME ALKYL BORATE ESTERS

Compound	Boiling Point (°C/mm)	$n_D^{22.5}$	Yield (%)	Molecular Composition	Mol. Wt.
Tri - <i>n</i> - butyl b o r a t e, $C_{12}H_{27}O_3B$	136/30	1.4806	80	Calc. : C, 62.6 ; H, 11.8 ; B, 4.7% Found : C, 62.6 ; H, 11.8 ; B, 4.8%	Calc. 230 Found 220
Tri - <i>sec.</i> - butyl b o r a t e, $C_{12}H_{27}O_3B$	92/10	1.3950	75	Calc. : C, 62.6 ; H, 11.8 ; B, 4.8% Found : C, 62.6 ; H, 11.9 ; B, 4.8%	Calc. 230 Found 236
Tri - <i>cyclohexyl</i> b o r a t e, $C_{18}H_{33}O_3B$	323-326/750	Solid, m.p. 56.4 °C	88	Calc. : C, 70.1 ; H, 10.3 ; B, 3.5% Found : C, 69.8 ; H, 10.5 ; B, 3.5%	Calc. 307 Found 306

SECTION IEXPERIMENTAL.(a) TRI-ALKYL AND TRI-ARYL ESTERS OF ORTHOBORIC ACID

(1) Azeotropic distillation.

Tri-n-, tri-sec- butyl and tri-cyclohexyl borates were prepared as follows:-

The alcohol (0.6 mol), boric acid (0.2 mol) and crystallizable benzene (300 ml.) were heated in the apparatus of Anderson et al (1952). The azeotropic distillate of benzene, alcohol and water was recycled until there was no further evolution of water. The solvent was then distilled off and the residual ester vacuum distilled. The following products were obtained.

Tri-n-butyl borate:- Colourless liquid, $n_D^{22.5}$ 1.4086 b.p. 136°C at 3mm
Analysis for boron Calculated for $C_{12}H_{27}O_3B$ 4.7% Found 4.8%

Molecular weight, boiling.

elevation method in cyclohexane " " " 229.8 Found 220

Elementary Analysis.

Calculated C, 62.61 H, 11.85

Found C, 62.59 H, 11.80.

Tri-sec-butyl borate:- Colourless liquid, $n_D^{22.5}$ 1.3950 b.p. 92°C at 10mm.

Analysis for boron Calculated for $C_{12}H_{27}O_3B$ B, 4.7% Found 4.73%

Molecular weight, boiling.

elevation method in cyclohexane " " " 229 Found 236

Tri-cyclohexyl borate:- White crystalline solid b.p. 323-6 at 760mm.
m.p. 56.4°C Yield.

Analysis for boron Calculated for $C_{18}H_{33}O_3B$ 3.5% Found 3.5%

Molecular weight, boiling.

Elevation of cyclohexane " " " 307 Found 306

Elementary Analysis.

Calculated C, 70.12 H, 10.79

Found C, 67.66 H, 10.42

Attempts to prepare tri-tertiary butyl borate by this method gave a thick oily residue which could not be distilled without decomposition even under vacuum. The method was unsatisfactory for the preparation of tri-tertiary butyl borate and was abandoned for that purpose.

(ii). Azeotropic fractional distillation

Tertiary butyl alcohol (0.9 mol, 66.6g) and boric acid (0.1 mol, 6.2g) were placed in a 100 ml. still pot fitted to a glass fractionation column two feet long by one-half inch internal diameter. It was packed with one eighth inch stainless steel wire gauze Dixon (1949) ring packing. At the top was fitted a MacIntyre weir reflux ratio head (1933). Although originally designed as a reflux time-off head, it was found that the weir could act as a trap in which water could be collected as it separated from the azeotropic mixture and run off at frequent intervals. The benzene alcohol azeotrope mixture was able to run over the top of the weir and return down the column. The reaction

mixture was retained at total reflux until the still head temperature was constant and then a little benzene (5 ml) added to the top of the column. Immediately water separated from the azeotropic mixture and continued to do so for a considerable time. When water was no longer observed a little more benzene was added and this process was continued until final addition of benzene did not yield further separation of water. Distillation was then continued under high reflux ratio until the temperature of still head rose to 82.5°C , the b.p. of tertiary butyl alcohol. The flask was then removed from column, most of excess alcohol removed at atmospheric pressure and finally at reduced pressure followed by the tri-tertiary butyl borate.

Tri-tertiary butyl borate:- Colourless liquid, b.p. $55-66^{\circ}\text{C}$ at 11mm. $n_{\text{D}}^{15} 1.3902$. Yield 10g (44%).

Boron Analysis:	Calculated for $\text{C}_{12}\text{H}_{27}\text{O}_3\text{B}$	4.7% Boron MW 229
	Found	4.7% Boron MW 226

Tri-sec-octyl borate:-

The alcohol (104g, 0.8 mol) was refluxed with boric acid (12.4g, 0.2 mol) in a packed fractionation column until there was no further evolution of water. The temperature at still head 178°C , the b.p. of sec-octyl alcohol. The excess alcohol was removed by distillation. The residual ester distilled at 179°C at 1mm. Yield 66g. (83%). Colourless liquid. $n_{\text{D}}^{21.5} 1.4275$, $d_{21.5}^{21.5} 0.842$.

a white compound. m.p. 56.4°C .

Boron content Calculated for $\text{C}_{18}\text{H}_{33}\text{O}_3\text{B}$ 3.5 % Found 3.6 %

Molecular weight, boiling.

elevation, cyclohexane as solvent " " 307 Found 297

Repetition of this method using toluene as solvent gave identical product m.p. 56.4°C which was not depressed on admixture with previously prepared compound.

(iii) Transesterification with pyroboracetic anhydride.

Tri-tertiary butyl borate (15.2g, 0.2 mol) was heated with pyroboracetic anhydride (14g, 0.05 mol) under a fractionation column one foot high and half inch internal diameter, packed with Fenske (1932) glass packing. To the still head was attached a McIntyre weir reflux ratio head. The distillation was carried out with fast boilup rate but operating at high reflux ratio. It was noticed that the majority of the distillate possessed a b.p. in vicinity of 106°C and a semi solid product was left in flask. Distillate was washed with sodium carbonate solution, then dried over calcium chloride and distilled.

Yield 18g, 78% calculated as tertiary butyl acetate, $n_{\text{D}}^{22.5}$ 1.388, b.p. 95°C at 760mm.

Tri-aryl Borates

(i) Tri-phenyl borate. Azeotropic distillation:-

The phenol (56.4g, 0.6 mol) was heated with boric acid (12.4g, 0.2 mol) and benzene (500 ml) in azeotroping apparatus of Anderson et al (1952). After fifteen hours there was no

evolution of water. The excess phenol and benzene were distilled off and the residue vacuum distilled at 1 mm. to give 25g of tri-phenyl borate, b.p. 170°C at 1 mm.

Molecular weight, boiling

elevation in cyclohexane Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{B}$ 289 Found 275.

Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{B}$ C, 74.51%; H, 5.21%; B, 3.7%

Found C, 72.13%; H, 5.27%; B, 3.7%.

Azeotropic fractional distillation

The phenol (140g, 0.5 mol) and boric acid (12.4g, 0.2 mol) were heated in fractionation column as for tri-alkyl esters. Benzene was used to facilitate the separation of the aqueous phase. When removal of water was complete, excess phenol was distilled off and residual tri-phenyl borate distilled at 171°C at 1 mm. Yield 30g.

Analysis for boron content. Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{B}$ 3.7% Found 3.9%

Transesterification with pyroboracetic anhydride

The phenol (232g, 3.0 mol) was heated with pyroboracetic anhydride (273g, 1 mol) for an hour then distilled at atmospheric pressure to remove the acetic acid and acetic anhydride. The residual tri-phenyl borate distilled at 171°C at 1 mm. Yield 200g. Analysis for boron. Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{B}$ 3.7% Found 3.9%.

Tri-cresyl borate

p-cresol (162g, 1.5 mol) and boric acid (22g, 0.3 mol) were heated in toluene in small fractionation still until there was no further evolution of water. Excess cresol distilled off at 3°C at 3 mm. Yield 38g. off and residue distilled at 222°C

Analysis for boron Calculated for $C_{21}H_{21}O_3B$ 3.27% Found 3.35%.

Tri-n-amyl borate

n-amyl alcohol (70.4g, 0.8 mol) was heated with boric acid (12.4g, 0.2 mol) until there was no further evolution of water at head of fractionation column. Excess alcohol was distilled off and the residual tri-alkyl borate distilled under reduced pressure.

Yield 44g. (80%) b.p. 154/16mm. (Johnson and Thompson, Organic Synthesis Vol. II p. 107 claim b.p. 146-8/16 mm.)

$n_D^{21.5}$ 1.4295 $d_{21.5}^{21.5}$ 0.8508

Analysis:-

Calculated for $C_{15}H_{33}O_3B$ C, 66.21; H, 12.14; B, 3.99 MW 271

Found C, 64.63; 11.43; 3.94 MW 270

Tri-n-heptyl borate

n-heptanol (46.4g, 0.8 mol) and boric acid (12.4g, 0.2 mol) were heated under fractionation column in the usual manner until there was no further evolution of water. Distillation was complete after four hours. Excess alcohol was removed at atmospheric pressure followed by the tri-alkyl borates at 4-6mm.

Yield 61g (88%) b.p. 192°C/4-6mm.

Analysis for Boron content. Calculated for $C_{21}H_{45}O_3B$ 3.03%B

Found 3.4%

Elementary Analysis Calculated for C, 70.83%; H, 12.65%; MW 355

Found C, 70.82%; H, 12.69%; MW 348.

ANALYSIS TECHNIQUES - GENERAL DISCUSSION

I. Boron determinations

(a) Tri-alkyl borates and boroxoles:- A sample of the compound (0.2-0.5g) was dissolved in 50 ml. of distilled water by gentle warming if necessary. 4 drops of 0.1% solution of neutral red indicator in 70% alcohol were added and the solution titrated to pale orange with N/10 Barium hydroxide solution. Mannitol (2g) was then added with 4 drops phenolphthalein indicator solution and titration concluded at development of first permanent faint pink colour of phenolphthalein. The difference between titration figure for neutral red and phenolphthalein gave titre equivalent to boron content. This technique has advantage that the end point cannot be easily over-shot since the change of neutral red to faint orange after addition of mannitol preceded the true end point for boron with the phenolphthalein by approximately half a cubic centimetre and so gives ample warning of approaching end point.

(b) Tri-aryl borates:- A sample of the compound (0.3-0.5g) was gently ignited in a platinum crucible in muffle furnace and the residue dissolved in N/10 sodium hydroxide. The alkaline solution was then made just acid to neutral red with N/10 acetic acid. The acid solution was titrated to pale orange with N/10 Barium hydroxide, mannitol added (2g) and

solution then titrated with phenolphthalein as indicator. Titration figure with phenolphthalein indicator was equivalent to boron content.

2. Molecular weight determinations.

Initially attempts were made to determine molecular weights by cryoscopic methods using benzene as solvent. Inconsistent results were obtained. Insertion of a mercury seal stirrer in order to exclude the entrance of moisture failed to give satisfactory results. Dioxane was more suitable as a solvent but was found to co-ordinate with the boron, so proved useless for molecular weight determinations. Neither of these solvents was satisfactory for ebullioscopic method and were replaced by cyclohexane which gave reproducible results.

3. Combustion analysis.

It was found that, providing care was taken to ensure that samples for analysis were handled quickly in order to avoid any contamination by atmospheric moisture, it was possible to obtain results which were acceptable especially when considered in relation to obtained molecular weights and boron content.

Once any particular method of preparation was established as giving a certain type of compound, combustion analyses were confined to a few selected representative samples of the compounds prepared.

(c) The Infra-red Spectra of Tri-alkyl and Tri-aryl Esters of Orthoboric Acid.

Although several investigators have reported on the Raman spectra of some esters of orthoboric acid, (Ananthrakrishnan 1936, Joglekar and Thatte 1936, Milone 1936, Kahovec 1938, 1939), the infra-red spectra of this class of compound have not been reported.

It was considered that the infra-red spectra of these compounds should be examined in order to determine whether or not there were any characteristic strong absorption bands which could be assigned to the asymmetrical stretching frequency of the BO_3 group.

The samples were submitted to Dr. R. Verner, Physical Chemistry Department, N.S.W. University of Technology for infra-red analysis.

Conclusion

From the discussion and experimental work of Dr. Verner which follows, it is quite apparent that, as expected, the infra-red spectra of the series of tri-alkyl and tri-aryl esters of orthoboric acid examined in the region from 1800cm^{-1} to 670cm^{-1} showed a strong characteristic absorption band at $1340 \pm 10\text{cm}^{-1}$. This band has been assigned to the asymmetric stretching frequency of the BO_3 group.

DISCUSSION

The absorption bands recorded in the range $670-1800\text{ cm}^{-1}$ are presented in table I and the relationship of the corresponding bands in the different compounds is shown by the means of a line graph (Fig. I).

By analogy with bands similar to B - O and by approximate calculations, it would appear likely that the BO_3 group absorbs in the region between 1000 and 1500 cm^{-1} . In this region there occur also bands due to C-O stretching and C-H in plane bending vibrations from which the B-O absorption must be differentiated. The C-O stretching frequency in the series studied is readily identified. In the esters of the primary alcohols it occurs close to 1060 cm^{-1} except for the first member of the series, namely tri-methyl borate, which is somewhat lower. As the degree of substitution of the carbon atom increases, the band would be expected to move to higher frequencies (Colthup 1950) and in agreement with this we find the band at 1130 and 1124 cm^{-1} in the secondary alkyl esters and still higher at 1216 and 1217 cm^{-1} in the aromatic esters. The band position in tri-cyclohexyl borate (1062 cm^{-1}) is slightly low but this may well be steric effect.

In the region between 1300 cm^{-1} and 1500 cm^{-1} there appear several bands, some of which must be due to hydrogen in-plane bending vibrations. A characteristic pattern of bands is discernible for the primary alkyl esters which differ from the secondary and tri-aryl compounds. These are assigned to

the hydrogen bending modes.

Common to all the spectra, whether alkyl or aryl, is the presence of a very strong band at $1340 \pm 10 \text{ cm}^{-1}$. This band in fact, is the strongest in this region of the spectrum in every case and its intensity is such that the capillary samples were necessary to prevent the complete absorption at the peak. There seems little doubt that this is due to the B-O linkages in the molecule. In support of this assignment we note that Bethell and Sheppard (1955) record value of 1450 cm^{-1} for the B-O stretching frequency in crystalline boric acid.

The narrow range over which the band falls (20 cm^{-1}) contrasts with the spread of the C-O bands (nearly 200 cm^{-1}) which are considerably influenced by the substituent. This suggests a partial double bond character and is in accord with the values of 1.40 for the bond order obtained by the application of Gordy's equation (1947)

$$N = \frac{a}{R^2} + b$$

where N is the bond order, a and b are constants 6.75 and -2.14 respectively and R is the interatomic distance, taken in this case from electron diffraction data, of Bauer and Beach (loc.cit) as 1.38 Å.

EXPERIMENTAL

The compounds readily hydrolysed, therefore precautions in handling were taken to ensure minimum hydrolysis. After

distillation under anhydrous conditions, the liquid samples were immediately sealed in glass tubing which had been previously baked out. Samples which condensed as solids on distillation were mulled with paraffin oil in a "dry box" and were safe to handle.

The spectra were run on liquid capillaries or pastes, between rock salt plates. By placing several drops on a plate and sliding a second plate over this with a wiping motion, the thin hydrolysed layer which was formed on the surface was effectively removed. That these precautions were sufficient was shown by the fact that in the spectra taken, only small hydroxyl bands were revealed in the 3 micron region, and these only on thick samples. Such small contaminations as may have occurred by the presence of hydrolysed products, can have had only a very minor effect on the spectrogram.

The spectra were obtained on a Perkin-Elmer 12-C single beam spectrometer with sodium chloride optics. Calibration was affected in the usual manner against the data of Getlen, Kao and Randall (1942).

THE INFRA-RED SPECTRA OF THE BORIC ACID ESTERS*

Trimethyl	Tri- <i>n</i> -propyl	Tri- <i>n</i> -butyl	Tri- <i>n</i> -amyl	Assignment
1484 (s)	1486 (m)	1483 (m)	1495 (m)	—CH ₂ — bending
1417 (m)	1417 (s)	1417 (s)	1417 (s)	—CH ₂ — bending
1377 (s)	1354 (s)	1360 (ms)		—CH ₃ bending
1348 (vs)	1334 (vs)	1336 (vs)	1340 (vs)	B—O stretching
	1298 (m)	1298 (ms)	1279 (m)	
	1280 (m)	1261 (m)	1243 (m)	
	1255 (m)	1232 (m)	1218 (w)	
1183, 1172 (m)				
1112, 1095 (vw)	1102 (vw)	1118 (w)	1119 (w)	
			1077 (m)	
1032 (s)	1072 (s)	1071 (s)	1056 (s)	C—O stretching
	1054 (m)	1031 (m)	1009 (m)	
	1016 (w), 997 (w)			
	973 (m)	969 (m)	987 (w)	
883 (w)	911, 895, 873 (w)	852 (vw)	893 (w), 843 (vw)	
815, 773 (w)	757 (w)	738 (w)	775, 730 (w)	
	693 (w)	692 (w)	690 (mw)	
	665 (m)		670 (m)	

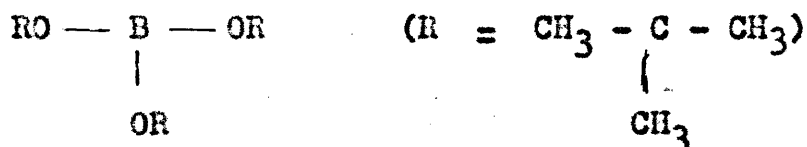
INFRA-RED SPECTRA OF THE BORIC ACID ESTERS*

Tri-sec.-butyl	Tri-2-octyl	Triphenyl†	Tricresyl†	Tricyclohexyl†	Assignment
		1593 (s)	1615 (m)		Phenyl
			1598 (w)		
		1486 (s)	1511 (s)		Phenyl
1453 (m)	1456 (m)				
1423 (ms)	1419 (m)	1400 (s)	1413 (m)	1424 (m)	C—H bending
1396 (s)	1396 (s)			1398 (s)	
1374 (s)	1376 (ms)		1367 (s)	1361 (s)	
1330 (vs)	1331 (vs)	1350 (vs)	1345 (vs)	1331 (vs)	B—O stretching
1303 (m)			1303 (w)		
1271 (w)		1242 (w)	1257 (w)	1257 (w)	
1173 (w)	1198 (w)		1233 (w)	1238 (w)	
1131 (s)	1124 (s)	1217 (s)	1216 (s)	1062 (ms)	C—O
1114 (m)	1074 (m)	1166,	1171 (m)		
		1153 (w)	1103 (m)		
1032 (m)	1040 (w)	1071 (m)	1044 (w)		
994 (m)		1024 (mw)	1018 (w)	1028 (w)	
973 (w)	976 (w)			969 (m)	
914 (m)	937 (w)			892 (w)	
	863 (vw)	854 (w)	852 (w)		
833 (w)		836, 822 (m)	○		
779 (w)		767 (s)	821 (s)		Phenyl
			812 (s)		
			757 (m)		
	724 (w)	723 (m)	738 (w)		
			714, 707, 703 (w)		
		692 (ms)			Monosubstituted phenyl
	690 (mw)				

TRI-ALKOXY BOROXOLES

(a) Introduction

Anderson (1950) reacted excess tertiary butyl alcohol in benzene with orthoboric acid in the azeotropic apparatus of Anderson et al (1952). The resulting product, presumed to be tri-tertiary butyl borate,



was not isolated but used in situ in benzene solution as a reagent for the preparation of characteristic colours with peri-hydroxy quinones.

The subsequent preparation of tri-tertiary butyl borate (loc.cit.), which did not give positive development of colour with benzene solution of peri-hydroxy quinones, indicated that the compound of Anderson could not be tri-tertiary butyl borate.

In view of these results it was decided to investigate the nature of the reaction between alcohols and orthoboric acid in order to determine the following points:-

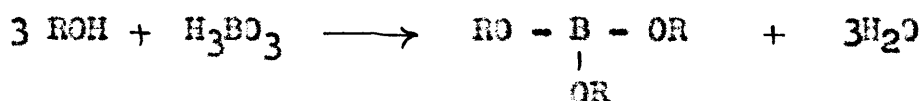
- (1) Is the esterification of orthoboric acid with alcohols a stepwise reaction involving the successive alkylation of each OH group of the boric acid?

(ii) What is the structure and composition of the benzene soluble boron compounds which give positive colour development with peri-hydroxy quinones?

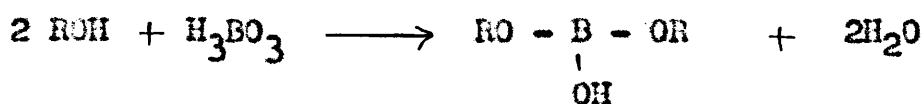
(b) Discussion

Cyclohexanol was chosen as the alcohol for the experiment because of its ready availability.

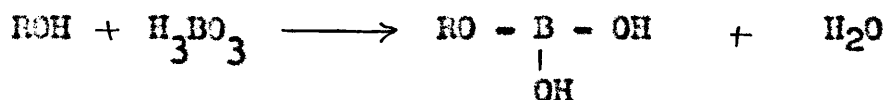
A series of experiments was carried out in an attempt to prepare tri-cyclohexyl borate, di-cyclohexyl borate and mono-cyclohexyl borate, using three, two and one mol of alcohol per mol of orthoboric acid, benzene being used as the azeotroping agent. The reactions were expected to take the following courses.



Tri-alkyl borate



Di-alkyl borate



Mono-alkyl borate.

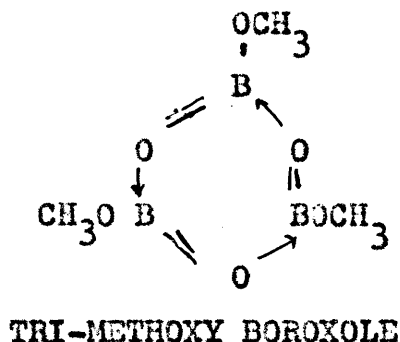
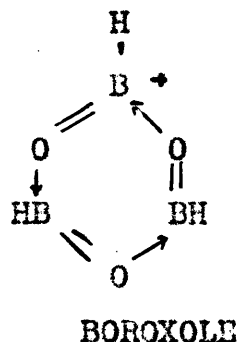
It was found that in the case of three mols of alcohol to one of orthoboric acid a quantitative yield of tri-cyclohexyl borate was obtained, the product being white, crystalline, M.P. 56.4°C, Molecular weight 306, boron content 3.6%. Benzene

solution gave no colour development with quinalizarin.

Where two mols of alcohol reacted with one of orthoboric acid, a mixture of indeterminate composition was obtained as a colourless solid. A benzene solution gave positive development of colour with quinalizarin. However the boron content was not constant and the melting was spread over a range of five degrees. Attempts to purify the product by recrystallisation gave products of variable composition. Distillation under reduced pressure led to complete decomposition. Apparently the reaction products were a mixture whose boron content did not correspond to di-cyclohexyl borate.

The reaction of one mol of alcohol with one mol of orthoboric acid gave a pure white crystalline compound. M.P. 167°C , Molecular Weight 383, Boron Content 8.6% and a benzene solution gave an intense purple colour with quinalizarin.

A search of the literature failed to reveal the existence of any such known compound. However, Goubeau (1951) prepared a compound tri-methoxy boroxole, which he considered was a derivative of a compound, boroxole which has not as yet been isolated.



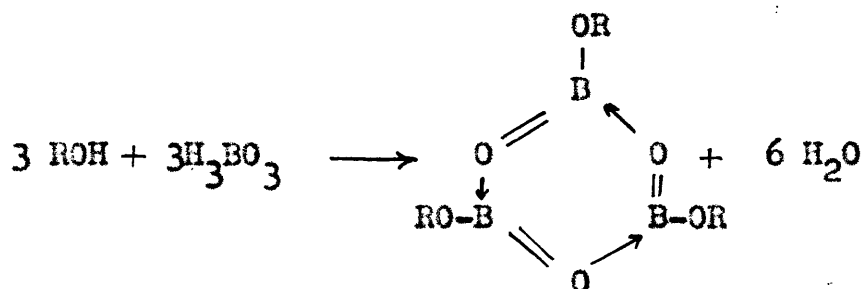
By the substitution of cyclohexyl radicals for methyl radicals, calculations showed that the resultant tri-cyclohexyl boroxole compound had the same empirical composition as found above, i.e. Molecular weight 383 and Boron content of 8.6%.

Tri-cyclohexoxy boroxole was prepared according to the method of Goubeau from boron oxide and tri-cyclohexyl borate. The resultant compound was white crystalline M.P. 167°C which was not depressed on mixing with sample prepared above. The molecular weight and boron content were found to correspond to the previously prepared compound. A benzene solution gave positive development of deep purple colour with quinalizarin. For comparison purposes tri-methoxy boroxole was prepared also by the method of Goubeau and it also gave deep colour development with quinalizarin in benzene solution. To confirm that the structures were the same, a comparison of the infra red spectra of the three compounds was made and it was shown that they all possess strong absorption on the 1340cm^{-1} bands together with absorption at 700 cm^{-1} and 747 cm^{-1} which is characteristic of tri-alkoxy boroxoles (loc. cit). Therefore it was concluded that they possessed similar structures.

From the fact that it was structure of the boroxole type which gave the colour reaction with peri-hydroxy quinones, Anderson's experiment was repeated and the resultant product, which was thick, viscous and rather intractable to handle, was

analysed for boron content and gave results corresponding to tri-tertiary butoxy boroxole, also giving the colour development with the benzene solution of quinalizarin.

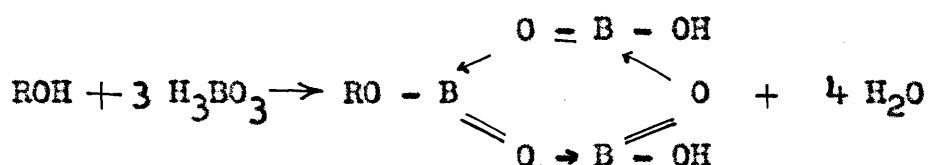
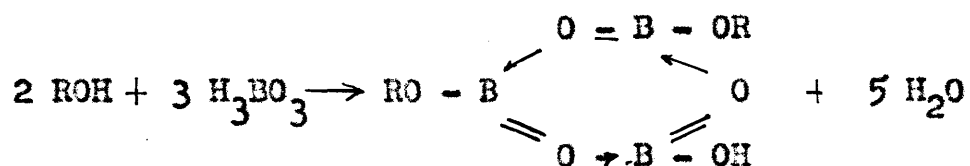
In conclusion, then, it appears that the reaction of one mol of orthoboric acid with one mol of alcohol produces a new type of compound, namely an alkoxy boroxole, rather than the expected mono-alkyl borate, and it is this boroxole structure which is responsible for the development of colour with the benzene solutions of quinalizarin. One may formulate the reaction then in the following manner.



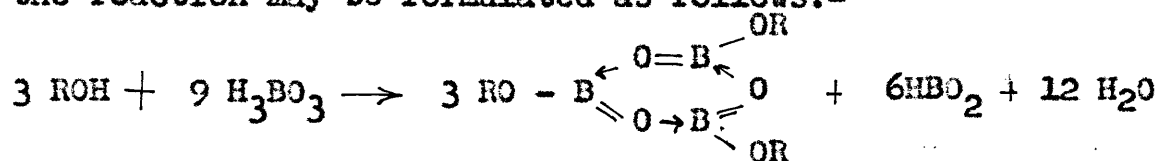
Although it was found impossible under experimental conditions used above to prepare mono- or di- alkyl esters of orthoboric acid, it was decided to investigate the nature of the products obtained by the reaction of two and one mol of alcohol per three mols of orthoboric acid to determine whether it would be possible to prepare di- and mono-cyclohexoxy boroxole. Because a ratio of one mol of alcohol to one of orthoboric acid led to the formation of one mol of tri-cyclohexoxy boroxole it was concluded that a ratio of three mols of alcohol to three of boric acid would lead to the formation

of three mols of tri-cyclohexoxy boroxole hence no further action was taken in this direction.

The reactions were expected to follow the formulation



It was found that irrespective of whether one or two mols of alcohol were used per three mols of orthoboric acid, only two products were obtained in each case, namely tri-cyclohexoxy boroxole and metaboric acid. There was no tendency to form mono- or di-alkoxy boroxole derivatives under the experimental conditions. It appears that the reaction follows the lines of preferential formation of tri-alkoxy boroxole which dissolves in the solvent, and contrary to expectations, the excess boric acid, rather than causing the formation of a high molecular weight polymer, becomes dehydrated by the azeotroping agent to form insoluble metaboric acid which does not react with the tri-alkoxy boroxole. The course of the reaction may be formulated as follows:-

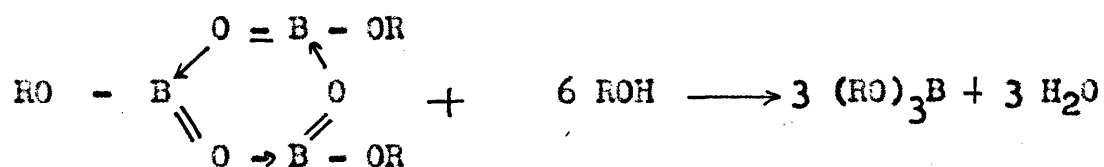
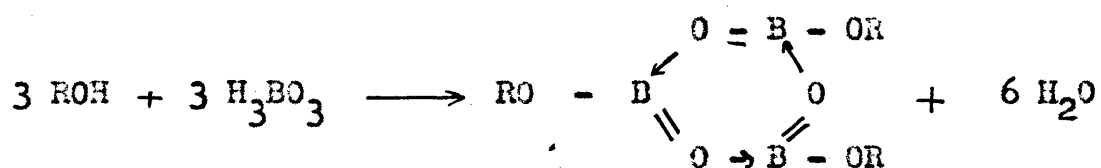


On addition of excess alcohol to the tri-cyclohexyl boroxole and metaboric acid mixture in benzene, the whole was converted to tri-cyclohexyl borate on further refluxing.

From the above results it was considered that, although the esterification of orthoboric acid did not necessarily involve successive esterification of each OH group, it was possible that the intermediate product in the esterification would be tri-alkoxy boroxole.

A series of esterifications was undertaken using excess of alcohol. Samples were withdrawn at irregular intervals and it was found that there was a gradual increase to a maximum intensity on testing reaction of solution with quinalizarin. Sample at this stage failed to give absorption in the $1340 - 10\text{ cm}^{-1}$ and 700 cm^{-1} regions, which are characteristic for boroxoles. The lack of absorption could well be due to the boroxole concentration being too small. As the reaction proceeded further, the intensity of colour with quinalizarin gradually decreased until finally there was no colour change whatsoever, indicative of the complete conversion of the tri-cyclohexoxy boroxole to tri-cyclohexyl borate;

It is considered that the reaction may be formulated as follows:-



The following tri-alkoxy and tri-aryloxy boroxole compounds were prepared:-

Tri-tertiary butoxy boroxole

Tri-cyclohexoxy boroxole

Tri-n-propoxy boroxole

Tri-n-pentoxy boroxole

Tri-n-butoxy boroxole

Tri-n-hexoxy boroxole

Tri - (Imethyl) - n - heptoxy boroxole

Tri - (2-ethyl) - n - hexoxy boroxole

Tri-phenoxy boroxole

Tri - (p - methyl phenoxy) boroxole

EXPERIMENTALSERIES I.

(a) Cyclohexanol (0.6 Mol), boric acid (0.2 Mol) and crystallisable benzene (300 ml) were heated in azeotropic apparatus of Anderson et al (1952). The azeotropic distillate was recycled until there was no apparent further evolution of water. The solvent was removed and the residual ester purified by vacuum distillation. The product, tri-cyclohexyl borate was a white crystalline compound, b.p. 323-6 /760mm. m.p. 56.4°C. Yield 56g.

Analysis for boron content

Calculated for $C_{18}H_{33}O_3B$	3.5%
Found	3.6%

Molecular weight, boiling point elevation of cyclohexane

Calculated for $C_{18}H_{33}O_3B$	307
Found	306

No colour change with quinalizarin.

(b) Cyclohexanol (0.2 mol), boric acid (0.1 mols), benzene (50 ml) were reacted to complete evolution of water. On removal of solvent, white solid residue, m.p. 160-165°C.

Analysis for boron content

Calculated for $C_{12}H_{23}O_3B$	4.8%
Found	9.5%

On repetition of experiment the isolated solid was found to have m.p. 156-160°C with boron content 6.5%.

No colour with benzene solution of quinalizarin.

(c) Cyclohexanol (0.5 mol), boric acid (0.5 mol) benzene (50 ml) were refluxed in small fractionation column to completion of evolution of water. On removal of solvent white crystalline compound obtained. M.P. 166-167°C. Yield 58g.

Analysis for boron content

Calculated for $C_6H_{13}O_3B$	7.6%
$C_{18}H_{33}O_6B_3$	8.6%
Found	8.6%

Molecular weight determination by boiling point elevation of cyclohexane

Calculated for $C_6H_{13}O_3B$	144
$C_{18}H_{33}O_6B_3$	377
Found	383

Solution in benzene gave intense violet colouration with quinalizarin.

Combustion analysis

Calculated for $C_{18}H_{33}O_6B_3$	C, 57.1%; H, 8.7%
Found	C, 57.2%; H, 8.7%

(d) All of sample (c) less sample for mixed melting point, was refluxed with excess cyclohexanol until all the water had azeotroped out. On removal of the solvent, a white crystalline residue of tri-cyclohexyl borate remained. M.P. 56.4°C. Undepressed on mixing with authentic sample of tricyclohexyl borate.

Analysis for boron content

Calculated for $C_{18}H_{33}O_3B$	3.5%
Found	3.6%

Solution in benzene did not give any colour development with quinalizarin.

(e) Tri-cyclohexyl borate (0.05 mols) was heated with freshly prepared boron oxide (0.55 mols) on an oil bath at 170-190°C until all the boron oxide dissolved. On cooling the resultant solid was recrystallised from anhydrous benzene. White crystalline product was obtained, M.P. 167°C undepressed on admixture with sample of authentic tri-cyclohexoxy boroxole, prepared in (c) above.

Analysis for boron content

Calculated for $C_{18}H_{33}O_6B_3$	8.6%
Found	8.6%

Solution in benzene gave deep violet colouration with quinalizarin.

(f) Refluxing of (e) with excess alcohol also yielded the corresponding tri-cyclohexyl borate M.P. 56.4°C.

Analysis for boron content

Calculated for $C_{18}H_{33}O_3B$	3.5%
Found	3.6%

Solution of the compound in benzene did not give any positive colour development with quinalizarin.

(g) Tertiary butyl alcohol (1.5 mols), boric acid (0.5 mols) and benzene (500 ml) were refluxed in the apparatus of Anderson et al (1952) for thirty hours, by which time all the

water had been removed from the reaction. Solvent was then removed under reduced pressure to leave a thick viscous residue, a sample of which decomposed when an attempt was made to purify by distillation under very low pressure (0.001 mm)

Analysis for boron content

Calculated for $C_{12}H_{27}O_3B_3$	4.7%
$C_{12}H_{27}O_6B_3$	10.8%
Found	9.9%

Sample gave positive development of colour with benzene solution of quinalizarin.

SERIES II.

(a) The reaction of three mols of cyclohexanol with three of boric acid is equivalent to one mol alcohol to one of boric acid therefore see series I (c).

(b) Cyclohexanol (0.2 mol) and orthoboric acid (0.3 mols) were refluxed with toluene (100 ml) until the temperature of the distillate rose to that of toluene, i.e. $110^{\circ}C$. A toluene insoluble precipitate was formed which was filtered and analysed for boron content

Analysis for boron content

Calculated for HO_2B	24.2%
H_3O_3B	17%
Found	24.8%

Molecular weight determination by elevation of boiling point of glacial acetic acid

Calculated for HO_2B	43.8
Found	42

On removal of the solvent, a white crystalline product was obtained M.P. 167°C Yield 22g.

Analysis for boron content

Calculated for $\text{C}_{12}\text{H}_{23}\text{O}_6\text{B}$	11%
$\text{C}_{18}\text{H}_{33}\text{O}_6\text{B}_3$	8.6%
Found	8.5%

The melting point was not depressed on admixture with an authentic sample of tri-cyclohexoxy boroxole.

Solution in benzene gave characteristic development of deep violet colour with quinalizarin.

(c) Cyclohexanol (0.1 mol), boric acid (0.3 mol), toluene (100 ml) were refluxed until there was no further evolution of water. The toluene insoluble precipitate was filtered. Yield 9g.

Analysis for boron content

Calculated for $\text{H}_2\text{O}_2\text{B}$	24.2%
Found	24%

EXPERIMENTAL

On removal of solvent, white crystalline compound remained M.P. $166-7^{\circ}\text{C}$. Yield 11g.

Analysis for boron content

Calculated for $\text{C}_6\text{H}_{13}\text{O}_6\text{B}_3$	15.4%
$\text{C}_{18}\text{H}_{33}\text{O}_6\text{B}_6$	8.6%
Found	8.5%

Benzene solution gave violet colouration with quinalizarin.

Melting point undepressed on mixing with authentic sample of tri-cyclohexoxy boroxole.

Tri-n-heptoxy boroxole

n-heptanol (116g, 1.0 mol) and boric acid (62g, 1.0 mol) were heated under fractionation column in the usual manner with toluene (250 ml) until such time as there was no further evolution of water, the temperature of the distillate rising to 110°C, the boiling point of toluene. The solvent was then removed under reduced pressure. It was noticed that the temperature of distillate rose to 208°C/5mm. It was thought that it might be possible to distil the boroxole under reduced pressure, consequently after weighing yield (123g, 87%) an attempt was made to distil 60g at 3 mm. but it was found as in all previous cases the compound decomposed.

Analysis	Calculated for $C_{21}H_{45}O_6B_3$	C, 59.24%; H, 10.58%, B 7.6%
	Found	C, 59.09%; H, 10.65%, B 8%

Tri-n-heptoxy boroxole

Tri-n-heptyl borate (34g 0.1 mol) was heated with boron oxide (6.9g 0.1 mol) until all the latter had dissolved. The resultant yellow liquid was heated with decolourising carbon and filtered hot to give a straw yellow product. This compound gave positive colour with quinalizarin. Yield 40g. (94%)

Analysis	Calculated for $C_{21}H_{45}O_6B_3$	Boron 7.63%
	Found	Boron 8.1%

Tri-methoxy boroxole

Tri-methyl borate (10.4g 0.1 mol) and boron oxide (6.9g 0.1 mol) were heated until all the boron oxide had dissolved. The resultant clear liquid tri-methoxy boroxole was found to give positive development of colour with benzene solution of quinalizarin.

Analysis for boron content	Calculated for $C_3H_9O_6B_3$	Boron 18.6%
	Found	18.7%

Tri-n-propoxy boroxole

Tri-n-propyl borate (18.7g 0.1 mol) and boron oxide (6.9g 0.1 mol) were heated until all the boron oxide dissolved. Resultant clear liquid tri-n-propoxy boroxole gave positive colour development with quinalizarin.

Analysis	Calculated for $C_9H_{21}O_6B_3$	Boron 12.61%
	Found	Boron 12.59%

Tri-n-butoxy boroxole

Tri-n-butyl borate (22.9g 0.1 mol) and boron oxide (6.9g 0.1 mol) were heated to dissolve boron oxide. Resultant clear colourless tri-n-butoxy boroxole was found to give colour with benzene solution of quinalizarin.

Analysis	Calculated for $C_{12}H_{27}O_6B_3$	Boron 10.84
	Found	Boron 10.8

Tri-sec-butoxy boroxole

As for tri-n-butoxy boroxole

Analysis	Calculated for $C_{12}H_{27}O_6B_3$	Boron 10.84
	Found	Boron 10.88

Tri-n-pentoxy boroxole

Tri-n-amyl borate (27.2g 0.1 mol) and boron oxide (6.9g 0.1 mol) were heated until the oxide had dissolved. Resultant colourless liquid which gave positive colour with quinalizarin solution was analysed.

Analysis results	Calculated for $C_{15}H_{33}O_6B_3$	C, 52.78%; H, 9.68%; B, 9.51%
	Found	C, 53.23%; H, 9.79%; B, 9.8%
$n_{21.5}^{21.5}$	1.4223	$d_{21.5}^{21.5}$ 0.970

Tri-2-octoxy boroxole

Tri-2-octyl borate (3.8g, 0.1 mol) and boron oxide (6.9g, 0.1 mol) were heated until all boron oxide dissolved. Resultant thick viscous colourless liquid was analysed for boron content. Positive colour with quinalizarin.

Analysis	Calculated for $C_{24}H_{51}O_6B_3$	C, 61.61%; H, 10.91%; B, 6.96%
	Found	C, 61.24%; H, 11.09%; B, 7.2%
Molecular weight	Calculated 467	Found 440.

Tri-phenoxy boroxole

Tri-phenyl borate (28.9g 0.1 mol) and boron oxide (6.0g 0.1 mol) were heated until all the boron oxide dissolved. On cooling a solid compound was obtained which hydrolysed too rapidly for melting point to be determined. Like the tri-alkoxy boroxoles gave positive colour with tri-quinalizarin.

Analysis	Calculated for $C_{18}H_{15}O_6B_3$	Boron Content	9.0%
	Found		8.8%

Tri-p-cresyl boroxole

Tri cresyl borate (33.2g, 0.1 mol) was heated with boron oxide (6.9g, 0.1 mol) until all the oxide had dissolved. The resultant liquid crystallised on cooling to give a very hygroscopic solid which hydrolysed before melting point could be obtained.

Analysis	Calculated for $C_{21}H_{21}O_6B_3$	Boron content	7.8%
	Found		7.4%

Tri-(2-ethyl)-hexoxy boroxole

Tri-(2-ethyl)-hexyl alcohol (65g, 0.5 mol) was refluxed with boric acid (31g, 0.5 mol) in toluene (100ml) until there was no further evolution of water. The solvent was removed under reduced pressure to give a yellow viscous liquid residue of tri-(2-ethyl)-hexoxy boroxole.

Yield 91%	$n_D^{21.5}$	1.4435	$d_{21.5}^{21.5}$	0.935
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Analysis	Calculated for $C_{24}H_{51}O_6B_3$	C, 61.61%; H, 10.91%; B, 6.95%
	Found	C, 62.55%; H, 11.01%; B, 6.7%

Boron Oxide

Crystallised boric acid was placed in a flask containing an air leak and connected to a reservoir containing phosphorous pentoxide. The flask was heated in an oil bath to 200°C slowly and water removed at about 2mm. pressure. It was important to raise the temperature slowly to 200°C to prevent formation of glassy boron oxide. Average time for complete conversion of boric acid to the anhydride was about 8 hours for 16g sample. Each sample prepared was heated to constant boron content of 32.1%. The boron content of sample was checked from time to time to make sure that there was no hydration occurring. Any sample in which boron content dropped below 32% was discarded and fresh sample prepared for use.

Infra-red spectra of some Boroxoles

While boroxoles and tri-hydroxy boroxoles are unknown, several derivatives have been prepared. The first alkoxy boroxole to be prepared was that described by Goubeau (1951). However no attempt was made to determine the infra-red spectra of such compounds.

From the results obtained in infra-red examination of the tri-alkyl and aryl esters of orthoboric acid, it seemed that a similar examination of a series of alkyl boroxole derivatives as described in previous section should be carried out to determine whether there was present any characteristic absorption bands which would allow ready identification of the boroxole structure.

The samples were submitted to Dr. R. Werner, Senior Lecturer in Physical Chemistry, N.S.W. University of Technology for infra red analysis and interpretation of the spectra.

Conclusions

From a consideration of the spectra it was found that, as with the borate esters there was a very strong absorption band between 1335 and 1367 cm^{-1} which is as intense as that found with the borate esters. Another feature of more interest is the presence of two strong bands between 700 and 747 cm^{-1} in all the compounds except tri-cyclohexoxy boroxole in which the results were somewhat lower.

As described in section 3 (b) this thesis, molecular

weights of the compounds under discussion were determined using an ebullioscopic method in cyclohexane. These determinations clearly showed that the formula is clearly expressed as $B_3O_3(OR)_3$ in agreement with the expected ring structure. It is possible however that the compounds might associate in solution or polymerise on boiling. A comparison of the spectrum of each of three boroxole derivatives as received in a sealed tube and after boiling in cyclohexane, showed no difference whatsoever. Further, the absorption peaks in cyclohexane are only slightly shifted from the values in the pure state. This affords supporting evidence therefore as to the correctness of the formulation of the compounds.

The above conclusions are based on the following discussion and experimental work of Dr. Werner.

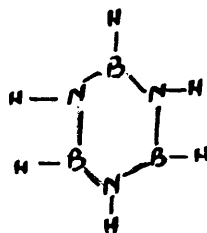
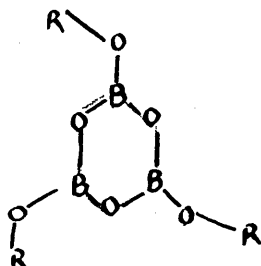
The spectra show some interesting features. In all compounds there is found a very strong band between 1335 cm^{-1} and 1367 cm^{-1} . This band is as intense as the band found in this position in the spectra of the tri-alkyl and tri-aryl borate esters. This suggests that it is associated with a motion involving the asymmetric stretching of the BO bonds in the BO_3 groups. It might therefore indicate that the BO_3 units behave in an essentially independent fashion. On the other hand it may well represent a ring vibration in which the boron and oxygen atoms move in opposition. It would thus be analogous to the infra-red active fundamental of class E'

of the borazole molecule which involves a stretching of the B - N bonds and gives rise to a very intense band at 1465 cm^{-1} . Benzene also gives rise to a strong band in this region of the spectrum (1486 cm^{-1}) which similarly corresponds to a stretching of the c-c bonds (13, class E_{1u} , see Herzberg p. 365). This question cannot be resolved here but could more definitely be decided if the infra-red spectra of other boroxole derivatives were available in which the extranuclear oxygen atoms were replaced with other atoms.

Another feature of interest is the presence of two strong bands between 700 and 740 cm^{-1} in all compounds except tri-cyclohexoxy boroxole, for which compound somewhat lower values were obtained. These two bands have characteristic relative intensity, the higher frequency band being the weaker. It is suggested that they represent modes in which the boron and oxygen atoms move in opposite directions out of the plane of the molecule. In this sense they therefore represent vibrations analagous to the out of plane B-O bending mode of trimethyl borate, which gives rise to an infra-red absorption at 661 cm^{-1} . Again, studies of other classes of boroxole derivatives would be necessary to establish this.

The ring structure for boroxole compounds has been upheld by both Raman and electron diffraction studies and the compounds therefore bear a resemblance to borazole (ii) which has many properties of an aromatic system. In this latter compound the boron atom is in a trigonal state and there are

six π electrons, two from each nitrogen atom. These are shared by the six atoms producing a benzene like structure.

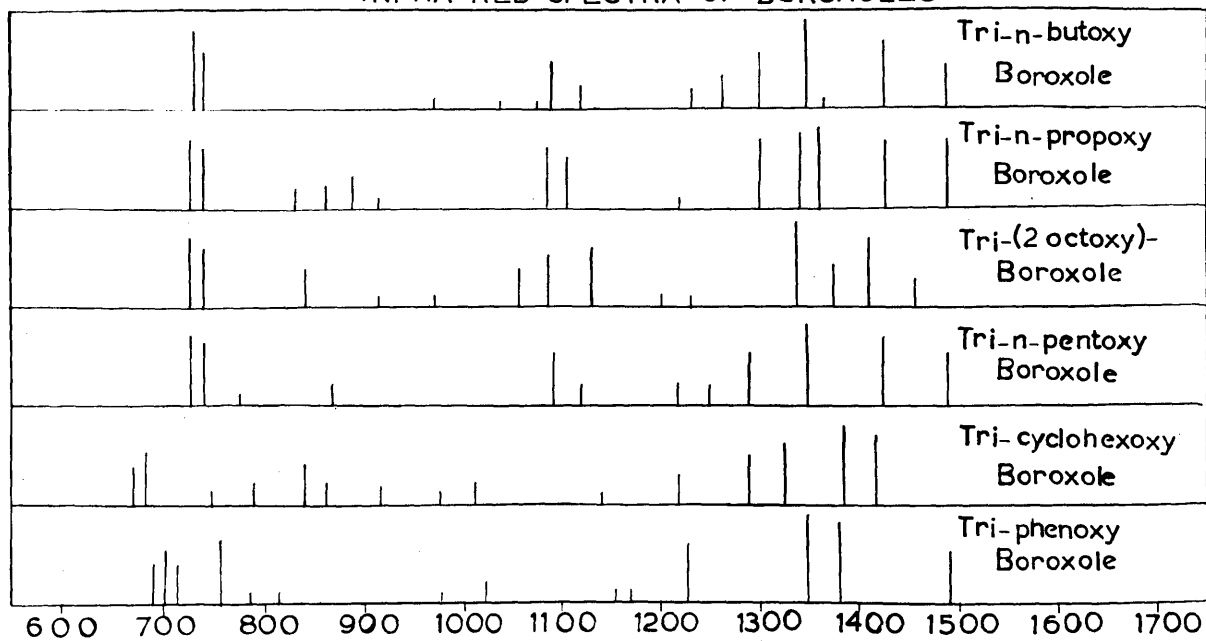


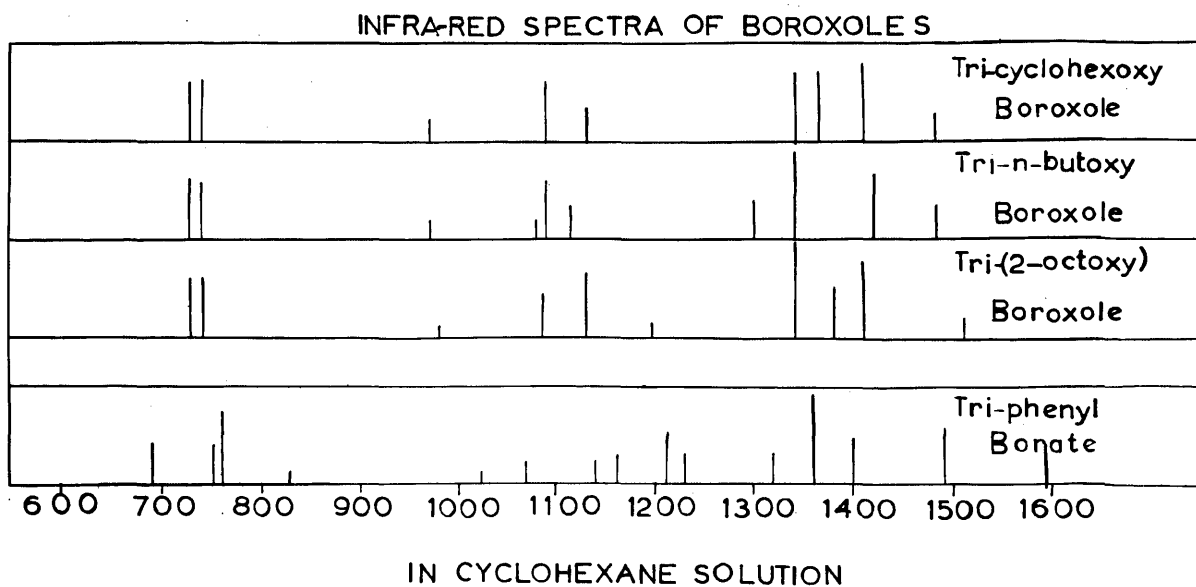
EXPERIMENTAL

The compounds were examined in the region from 1800 cm^{-1} to 670 cm^{-1} as liquid capillaries or paraffin pastes. In addition the region $3600\text{--}3000\text{ cm}^{-1}$ was quickly scanned to check on the presence of hydrolysed products. Small hydroxyl bands were generally found using thick samples, but these indicated that the small amount of decomposition products present would have had a very minor effect on the spectra. All manipulative work was carried out in the dry box. The spectra were recorded with the double beam spectrometer using a sodium prism.

Additionally, tri-n-butoxy boroxole, tri-1-methyl-n-heptoxy boroxole and tri-cyclohexoxy boroxole were examined as 4% w/v solutions in cyclohexane over the range 1600 cm^{-1} to 670 cm^{-1} using sealed cells of thickness 0.05, 0.10 and 0.20 mm.

INFRA-RED SPECTRA OF BOROXOLES





Discussion of the Spectra

The frequencies of the absorption peaks are set out in Table I and the absorption curves are presented in fig. 1.

TABLE I

Tri (Cyclo- hexoxy) Boroxole	Tri (Phenoxy) Boroxole	Tri (p-Methyl Phenoxy) Boroxole	Tri (2-Ethyl n-hexoxy) Boroxole	Assignment
	1594(m) 1492(ms)	1605(w) 1510(m)		phenyl ring phenyl ring
1466(ms) 1434(s)		1415, 1400(m)	1526(mw) 1486(m) 1444(s) 1426(ms)	C-H bending CH bending
1372(ms) 1339(ms)	1384(s) 1344(vs)	1380(ms) 1363(vs)	1379(m) 1367(vs)	B-O stretching
1263(w) 1191(w)	1283(w) 1226(ms) 1196(w) 1164, 1151(w) 1071(m)	1242(w) 1227(ms) 1214(mw) 1173(w) 1106(m)	1333(ms) 1268(m) 1222(w) 1195(w) 1148, 1120(w) 1092(ms) 1074(w)	C-O stretch.
1078(s) 1062(mw) 1028,968, 908(w) 889(m) & 840(w)	1022, 978(w) 854,812, 787(w) 757(s)	1018,977 932(w)	891, 848(w)	phenyl
795(w) 682(ms) 673(m)	714(m) 704(ms) 691(m)	821,813(s) 738(m) 715(m) 705(ms)	736(m)) 725(ms))	Boroxole system mono subst. phenyl

Tri(2-Ethyl n-Hexoxy) Boroxole which is a liquid was run as a capillary between NaCl plates. The remainder were run as mulls in paraffin oil.

TABLE I (Continued)

Tri(n-Propoxy) Boroxole	Tri(n-Butoxy) Boroxole	Tri(n-Pentoxo) Boroxole	Tri(n-Heptoxy) Boroxole	Tri (1-Methyl n-Heptoxy) Boroxole	Assignment
1486(ms)	1485(m)	1483(m)	1526(w)	1511(w)	
1424(s)	1422(s)	1424(s)	1485(m)	1453(mw)	C-H bending
1358(s)			1426(s)	1411(vs)	C-H bending
1337(vs)	1346(vs)	1346(vs)	1345(vs)	1376(m)	CH ₃ bending
1299(ms)	1301(m)	1296(m)	1298(m)	1335(vs)	B-O stretch
1261(m)	1263(mw)	1246(w)			
1216(w)	1233(w)	1217(w)	1221(w)	1228(w)	
				1200(w)	
1105(ms)	1120(m)	1122(m)	1119(m)	1128(s)	
1086(s)	1093(s)	1092(s)	1092(s)	1085(s)	C-O stretch
	1035(w)			1055(m)	
913(w)	970(w)			971, 912(w)	
886(mw)		863(mw)	891(w)		
860(w)		775(w)	848(w)	823(w)	
742(s)	737(ms)	736(ms)	736(ms)	737(ms)) Boroxole
724(s)	725(s)	725(s)	724(s)	726(s)) System

The samples which were all viscous liquids, were run as liquid capillaries between NaCl plates.

THE INFRA RED SPECTRA OF SOME BOROXOLES IN
CYCLOHEXANE SOLUTION

(4% solutions run in cells 0.20; 0.10 and 0.05mm thickness)

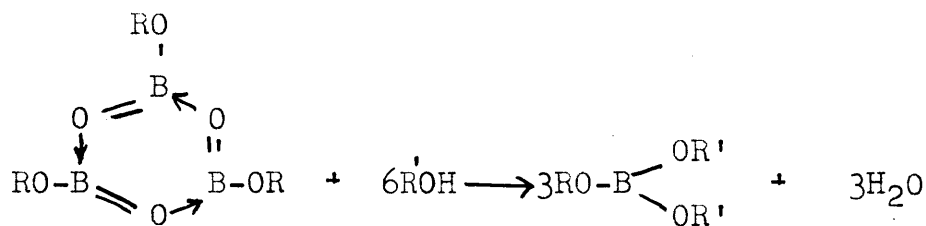
Tri n-But- oxy Boroxole	Tri-2-Oct- oxy Boroxole	Tri-cyclohex- oxy Boroxole	Assignment
1481(mw)	1507(w)		
1419(m)	1407(s)	1408(s)) C-H bending
	1376(m)	1364(ms)	
1341(s)	1336(s)	1336(s)	B-O stretching
1301(mw)	1198(w)		
1118(mw)		1129(mw)	
1092(m)	1129(m)	1085(m)	C-O stretching
1077(w)	1083(m)		
967(w)	980(w)	970(w)	
737(ms)	737(ms)	737(ms)) Boroxole system
726(ms)	726(ms)	726(ms)	

ASYMMETRICAL MIXED ESTERS OF ORTHOBORIC ACID

(a) Discussion

The normal method of preparation of mixed esters of orthoboric acid by the reaction between an alcohol and a tri-alkyl borate ester is subject to inconvenient limitations. The resultant products are invariably a mixture of mixed esters from which it is extremely difficult to obtain a high yield of the required mixed ester. Wuyts and Duquesne (1939) for example, obtained only a very low yield of tri-dimethylbutyl carbinol borate ester on treatment of tri-propyl borate with dimethyl butyl carbinol, together with minor mixed esters. (See also Kaufman (1933) and Schiff (1867)).

Since it had been shown that tri-cyclohexoxy boroxole could be converted into tricyclohexyl borate by reaction with excess cyclohexanol, it was expected that the boroxole compound should react with an alcohol other than cyclohexanol to form a mixed ester thus



By using the technique of azeotropic fractional distillation of the appropriate alcohol with the relevant boroxole compound, the following mixed esters were prepared in yields exceeding 60% of calculated yield.

Di-(2-octyl)-cyclohexyl borate

Di-cyclohexyl-2-octyl borate

Di-phenyl-cyclohexyl borate

Di-cyclohexyl-phenyl borate

Di-(2-octyl)-phenyl borate

Di-phenyl-2-octyl borate

Ethylene glycol n-heptyl borate

Trimethylene glycol n-heptyl borate.

It was found that all the tri alkyl esters gave no development of colour with benzene solutions of quinalizarin, but, in the case of the aryl-alkyl mixed esters the diphenyl alkyl borate gave a weaker colour than tri-phenyl borate and the di-alkyl phenyl compound gave no visible colour change whatsoever.

In the case of alcohols below amyl alcohol in the homologous series it was found that the volatility of the alcohols, their miscibility with water and the volatility of the resultant esters made impossible the production of mixed esters by the method described above.

(b) Experimental detailsMono-(2-octyl)-dicyclohexyl borate

Tri-(2-octyl)-boroxole (23.4g. 0.05 mol) was refluxed with cyclohexanol (66g. 0.6 mol) through a fractionation column until there was no further evolution of water. The distillation was continued until the distillate reached the boiling point of the solvent 79°C.

Excess solvent was removed under reduced pressure. Resultant ester was collected at 178-80°C/4-5mm.

Analysis	Calculated for $C_{20}H_{39}O_3B$	C, 71.2%; H, 11.56%; B, 3.2%
	Found	C, 70.5%; H, 11.38%; B, 3.3%

Molecular weight ebullioscopic in cyclohexane	Calculated	337
	Found	292.

Negative reaction in benzene solution with quinalizarin.

Mono-cyclohexyl-di-(2-octyl) borate

Tri-cyclohexyl borate (19g, 0.05 mol) was refluxed with 2-octyl alcohol (78g, 0.6 mol) until there was no further evolution of water and no further development of colour by a sample with quinalizarin. The solvent was removed under reduced pressure followed by the ester b.p. 188°C at 7 mm. Colourless clear liquid.

Analysis	Calculated for $C_{22}H_{45}O_3B$	C, 71.71%; H, 12.31%; B, 2.9%
	Found	C, 71.93%; H, 12.71%; B, 3.0%

Diphenyl cyclohexyl borate

Tri-cyclohexoxy boroxole (7.7g 0.02 mol) was refluxed with phenol (16.9g 0.18 mol) in toluene (50 ml) until there was

no further evolution of water. Excess phenol and toluene were removed by distillation at atmospheric pressure and the resultant mixed ester distilled at 7 mm.

Yield 12g, 68%; B.P. 211°/7

Analysis

Calculated for $C_{18}H_{21}O_3B$ C, 72.98; H, 7.15, B, 3.67

Found C, 72.28; H, 6.97, B, 3.65

Molecular weight determination ebullioscopic method in cyclohexane

Calculated 295. Found 300.

Dicyclohexyl monophenyl borate

Tri-phenoxy boroxole (14.4g) was refluxed with cyclohexanol under fractionation column in usual manner until there was no further evolution of water. Excess alcohol was removed under reduced pressure followed by the monophenyl dicyclohexyl borate at 8 mm.

Yield 30g. (83%), B.P. 182-4/8mm.

Analysis

Calculated for $C_{18}H_{27}O_3B$ C, 71.53; H, 9.01; B, 3.6%

Found C, 68.85; H, 10.59; B, 3.8%

Molecular weight determination, ebullioscopic method in cyclohexane

Calculated 302. Found 290.

(c) Mono-phenyl-di(2-octyl) borate

Tri-phenoxy boroxole (23g, 0.06 mol) was refluxed

with 2-octyl alcohol (100g, 0.77 mol) for four hours. The water did not appear at the top of the column, but on cooling, it was noticed as globules at the bottom of the flask. The alcoholic solution was carefully decanted free of water, distilled under reduced pressure to remove excess alcohol and the ester distilled at 3-4 mm. B.P. ester 169°C at 3-4 mm. 96% yield 50g.

Analysis Boron content Calculated for $C_{22}H_{39}O_3B$ 3% Found 2.9%

Molecular weight Calculated for $C_{22}H_{39}O_3B$ 361 Found 337

Reaction with quinalizarin negative.

Diphenyl-mono-(2-octyl) borate

Tri-(2-octoxy-) boroxole (7.4g) and phenol (16.8g) were refluxed with benzene (25 ml) until there was no further evolution of water. Excess phenol and water were distilled off at atmospheric pressure followed by the diphenyl-mono-2-octyl borate at 194-8°C at 5mm. Yield 4.0g 83%

Analysis

Boron content Calculated for $C_{20}H_{27}O_3B$ 3.3% Found 3.7%

Elementary Analysis " " $C_{20}H_{27}O_3B$ C, 73.8%; H, 8.3%
Found C, 71.5%; H, 8.77%

Ethylene glycol n-heptyl borate

Ethylene glycol (12.4g, 0.2 mol) and tri-n-heptoxy boroxole (21.3g, 0.05 mol) were refluxed with toluene (50 ml) under a McIntyre reflux ratio head attached direct to the reaction flask. The mixture was refluxed until there was no

further evolution of water. The reaction appeared complete within fifteen minutes. Excess ethylene glycol and toluene were removed by distillation at atmospheric pressure to leave a clear colourless viscous liquid which boiled at 250-253°C at 742 mm. The distillate was colourless, very viscous and readily hydrolysed by water.

Elementary Analysis

Calculated for $C_9H_{19}O_3B$ C, 58.2%; H, 10.2%; B, 5.9%

Found C, 56.9%; H, 9.9%; B, 6.4%.

Trimethyleneglycol n-heptyl borate

Trimethylene glycol, freshly distilled (15.2g 0.2 mols) and tri-n-heptoxy boroxole (21.2g, 0.05 mols) were refluxed with 25 ml. benzene under a McIntyre weir ratio head until there was no further evolution of water. The reaction was complete in fifteen minutes, solvent and excess trimethylene glycol distilled off. The residual ester distilled at 260-300°C 738 mm. as clear colourless very viscous product.

Analysis for boron content

Calculated for $C_{10}H_{20}O_3B$ B, 5.5%

Found B, 6.2%

(c) Infra red spectra of asymmetric esters of orthoboric acid

The mixed esters prepared above were subjected to infra-red examination under the same conditions as used for the symmetrical tri-alkyl and tri-aryl esters of orthoboric acid. (loc cit.)

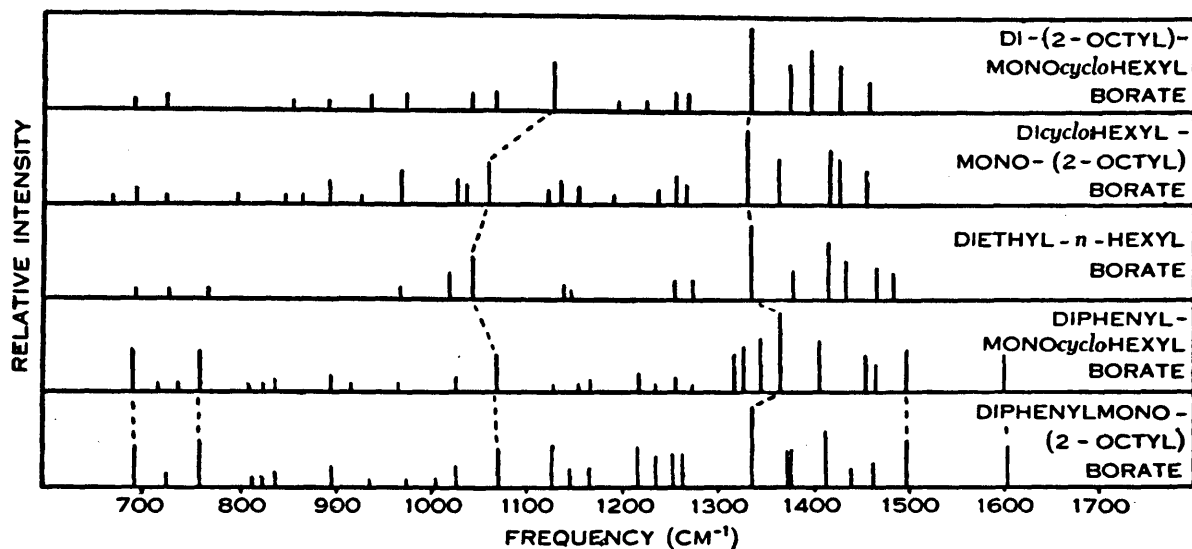
The frequencies of the absorption peaks (in wave numbers) of these compounds are given in table I, and in fig. I the linear relationship of these bands is given.

Comparison of these spectra with those recorded for the symmetrical esters (loc.cit) shows a similar strong band due to the B - O link within the range $1340 \pm 10 \text{ cm}^{-1}$, with the exception of diphenyl-cyclohexyl borate which is somewhat higher at 1363 cm^{-1} .

THE INFRA-RED SPECTRA OF SOME BORATE ESTERS

Samples were run as capillary film

Di-(2-octyl)- mono- cyclohexyl Borate	Dicyclohexyl- mono- (2-octyl) Borate	Diethyl <i>n</i> -Hexyl Borate	Diphenyl- mono- cyclohexyl Borate	Diphenyl- mono- (2-octyl) Borate	Assignment
			1600 (s)	1601 (s)	Phenyl
			1496 (s)	1498 (s)	Phenyl
		1482 (m)	1466 (w)	1460 (m)	} C—H bending
1458 (m)	1452 (m)	1466 (m)	1451 (m)	1440 (m)	
1426 (m)	1428 (ms)	1431 (ms)			
1397 (s)	1416 (s)	1414 (s)	1405 (s)	1411 (s)	
1376 (m)	1361 (ms)	1379 (w)		1376, 1371 (ms)	
1332 (vs)	1330 (vs)	1333 (vs)	1363 (vs)	1336 (vs)	B—O stretching
1268 (w)	1266 (w)		1343 (s)	1262, 1252 (m)	
1254 (w)	1255 (m)		1327, 1318 (ms)	1235 (m)	
1225 (w)	1236 (w)	1271 (w)	1272, 1256 (w)	1216 (ms)	
		1252 (w)	1236 (w)		
1194 (w)	1190 (w)		1216 (m)		C—O stretching
	1152 (mw)	1146 (w)	1165, 1152 (w)	1165, 1145 (w)	
	1133 (m)	1138 (w)	1129 (w)	1127 (m)	
	1120 (mw)				
1129 (ms)	1060 (ms)	1040 (ms)	1069 (ms)	1070 (ms)	
1068 (mw)					
1040 (w)	1035 (w)		1035 (w)		
	1025 (mw)	1019 (w)	1023 (mw)	1023 (m)	
				1003 (w)	
971 (w)	968 (m)	967 (w)	965 (w)	973 (w)	
933 (w)	925 (w)		925, 915 (w)	931 (w)	Phenyl
			895 (mw)	896 (mw)	
890 (w)	891 (m)		836, 821, 810 (w)	835, 821, 811 (w)	
851 (w)	852, 845 (w)		759 (s)	759 (s)	
	797, 785 (w)				
723 (w)	724 (w)	769, 728 (w)	736, 718 (w)	723 (m)	Phenyl
690 (w)	692 (w)	691 (w)	691 (s)	691 (s)	
	670 (w)				



The relation of corresponding bands in the infra-red spectra of some asymmetrical borate esters.

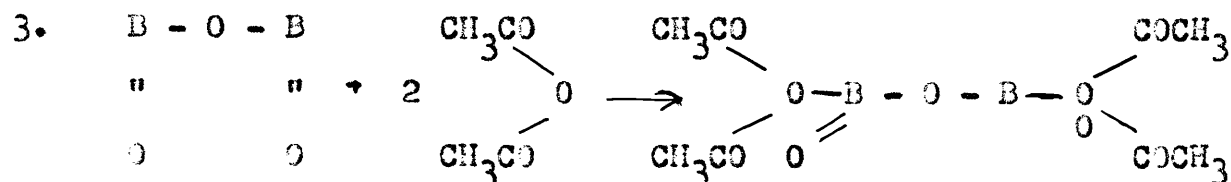
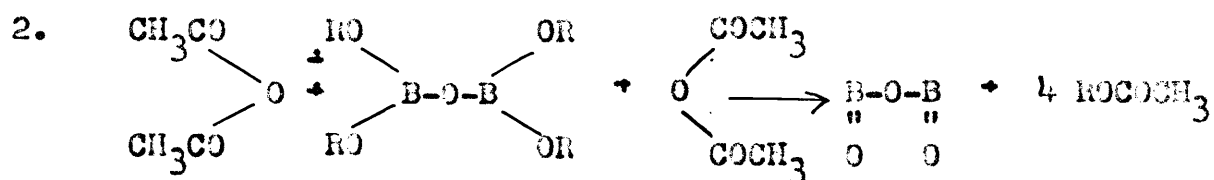
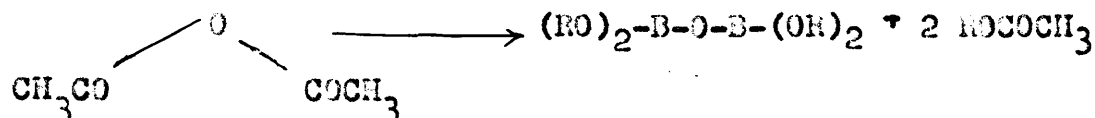
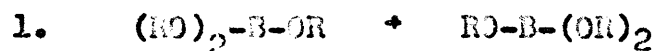
PREPARATION OF ALKYL ACETATES FROM TRI-ALKYL BORATES(a) Discussion of Reaction

Tri-n-amyl borate, tri-cyclohexyl borate, tri-(2-octyl) borate, tri-n-heptyl borate and tri-2-ethyl hexyl borate were refluxed in turn with increasing amounts of acetic anhydride until the initial precipitate formed in each case reached constant composition. At the completion of the reaction the corresponding alkyl acetate was isolated in a pure state.

Samples of the precipitate formed during the reaction were removed and analysed for acetic acid and boron content. It was found that the ratio of acetic acid to boron increased until a constant composition of approximately 80% acetic acid and 20% boron was obtained which corresponds to the composition of pyroboracetic anhydride. The solubility of the precipitate in benzene also increased until complete solubility was obtained. The benzene solution was found to give a distinct colour reaction with guinalizarin, which is a characteristic reaction of pyroboracetic anhydride (loc.cit).

Although boron oxide was not isolated, it is considered that it is formed during the reaction from the decomposition of the tri-alkyl ester and subsequently reacts with the acetic anhydride to form pyroboracetic anhydride. That such a reaction could occur is indicated by the fact that pyroboracetic anhydride may be prepared by the direct reaction between boron oxide and acetic anhydride (loc.cit).

On the basis of the above facts it is postulated that the reaction between tri-alkyl borates and acetic anhydride may be illustrated as follows:-



(c) Experimental detailsn-Amyl Acetate

Tri-n-amyl borate (13.6g 0.05 mol) was refluxed with acetic anhydride (15.3g, 0.15 mol) for one hour. During the reaction the solution gradually turned brown and a fine white precipitate formed which caked the bottom of the flask and gradually charred. At the end of the reflux time the mixture was poured into boiling water to hydrolyse the excess acetic anhydride, washed with saturated sodium bicarbonate solution, then finally with water. After drying over anhydrous magnesium sulphate for four hours the residual oil was distilled at atmospheric pressure.

B.P. 144-146°C Yield 13g, 68% theoretical. n_D^{20} 1.4015,
Literature n_D^{20} 1.4012. for n-amyl acetate.

Reaction was repeated in order to isolate and identify the precipitate. After ten minutes refluxing it was noticed that the white precipitate began to form. The reaction mixture was cooled and a sample of the precipitate removed, washed with ether and dried rapidly on a tile.

On testing the following results were obtained:-

The precipitate was partially soluble in benzene, completely in acetic anhydride.

The benzene solution gave characteristic development of colour with quinalizarin.

The precipitate was analysed for boron in usual manner

for pyroboracetic anhydride (loc.cit) and found to contain the equivalent of 71% acetic acid and 8.1% Boron. Pyroboracetic anhydride theoretically contains 86.5% acetic acid and 7.95% Boron.

0.1 mol acetic anhydride was added and reaction continued for further thirty minutes. Then allowed to cool with resultant formation of precipitate.

n-amyl acetate

A sample of the precipitate was removed, washed with ether and rapidly dried on a tile and analysed for boron content as above taking precautions to work rapidly in order to prevent the decomposition of the pyroboracetic anhydride. From the titration results it was found that the compound contained 85% acetic anhydride and 8% boron which corresponds to theoretical calculated results of acetic anhydride 86.5% and boron 7.9%. The precipitate was completely benzene soluble to give colour development with quinalizarin.

cyclohexyl acetate

Tri-cyclohexyl borate (30.8g, 0.1 mol) was refluxed with acetic anhydride (30.6g, 0.33 mol) for one hour. Again it was noticed that precipitate was formed. At end of reaction time the mixture was treated to isolate the cyclohexyl acetate as in the case on n-amyl acetate.

B.P. 172-174°C, (recorded literature B.P. 175°C) Yield 38g, 89%.

Reaction was repeated using tri-cyclohexyl borate (15.4g, 0.05 mol) and acetic anhydride (30.6g, 0.33 mol). With the increase in ratio of acetic anhydride to borate ester there was no formation of precipitate from the hot solution. However on cooling after one hour a white precipitate was formed which was then sampled. The sample after rapid washing with ether and drying on a tile was found to have following properties.

Soluble in hot acetic anhydride, partially soluble in benzene.

Benzene solution gave positive colour with quinalizarin.

Analysis gave following results. Acetic acid equivalent 70%, Boron 9.1%.

Mixture was then refluxed for further half hour then precipitate removed, washed, dried as above and analysed.

Acetic acid equivalent 81%; Boron 9%.

The precipitate was found to be completely soluble in benzene to give positive purple colour with quinalizarin.

2-Octyl acetate

Tri-(2-octyl) borate (20g, 0.05 mol) was refluxed with acetic anhydride (15.2g, 0.15 mol) for an hour. Again there was a precipitate formed. At end reaction time mixture treated as for n-amyl acetate to yield 2-octyl acetate B.P. 194-6°C. Literature B.P. 197°C.

n-Heptyl acetate

Tri-n-heptyl borate (17.3g, 0.05 mol) was refluxed with acetic anhydride (15.2g, 0.15 mol) for an hour. Formation of precipitate was noticed. The reaction mixture was treated as for n-amyl borate after refluxing for one hour. Yield 16g. (65% of calculated yield) B.P. 190°C, Literature B.P. 191°C.

Tri-(2-ethyl) hexyl acetate

Tri-(2-ethyl)-hexyl borate (40g, 0.1 mol) was refluxed with acetic anhydride (30g, 0.3 mol). After half an hour precipitate was formed. Solution was cooled sample precipitate removed and tested:

Slightly soluble in benzene, completely soluble in hot acetic anhydride.

Benzene solution gave positive purple colour with quinalizarin.

Analysis Acetic acid equivalent 64%, Boron 11.6%.

Mixture refluxed for further half hour then precipitate removed and sample analysed. Acetic acid equivalent 78%, boron content 8.4%.

The precipitate was then further refluxed for half an hour with an additional 0.1 mol acetic anhydride. On isolation of the precipitate it was analysed and following result obtained. Acetic acid equivalent 84.4%, boron content 7.9%.

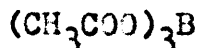
The 2-ethyl-hexyl acetate was not isolated because there was insufficient product left after carrying out above

reactions and also there was no further supplies of 2-ethyl-hexyl alcohol for the preparation of the required tri-alkyl borate.

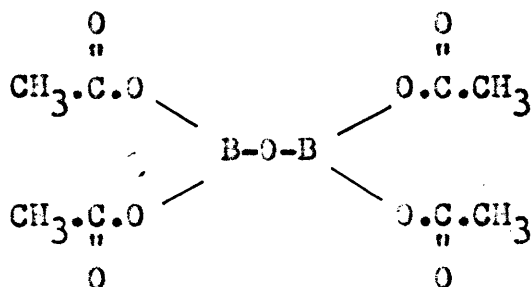
PYROBORACETIC ANHYDRIDE

(a) Discussion of Structure

Pictet and Geleznoff (1903), refluxed acetic anhydride with boric acid and isolated a compound which they described as boron triacetate with the following formula.



Dimroth (1926), on the other hand, repeated the reaction and found that the only compound that he could isolate was a mixed anhydride of boron oxide and acetic anhydride which he called pyroboracetic anhydride and gave the following formula.



Cooke, Ilett, Saunders and Stacey (1950) repeated the work of Pictet and Geleznoff and, without analysis of the resulting compound, claimed to have prepared boron triacetate which they then used for the preparation of esters of boric acid by transesterification.

Because of the contradictory evidence in the literature it was decided to repeat the experiments of the above authors in an attempt to prepare both tri-acetyl borate and pyroboracetic anhydride. It was intended to compare the properties of both

compounds as possible reagents for identification of peri-hydroxy quinones.

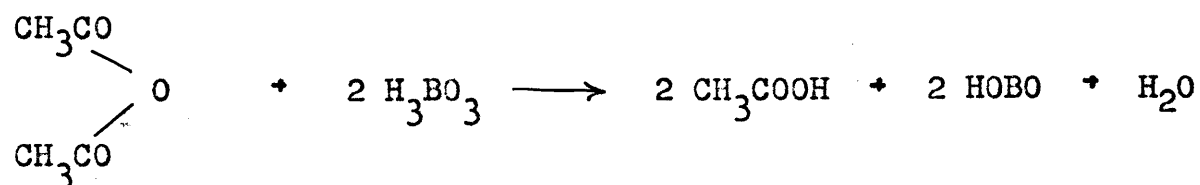
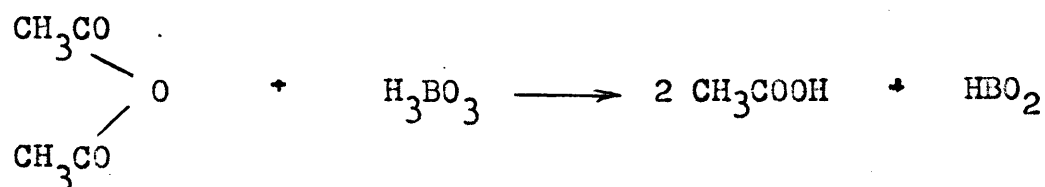
It was found that in all cases, when there was an excess of acetic anhydride a white crystalline compound was obtained with either boron oxide or boric acid. Analysis of this product gave results which were characteristic of pyroboracetic anhydride. Likewise, acetyl chloride reacted with boron oxide to produce pyroboracetic anhydride.

From the above results it was concluded that Dimroth was substantially correct in his criticism of the findings of Pictet and Geleznoff and that the product obtained was pyroboracetic anhydride rather than tri-acetyl borate.

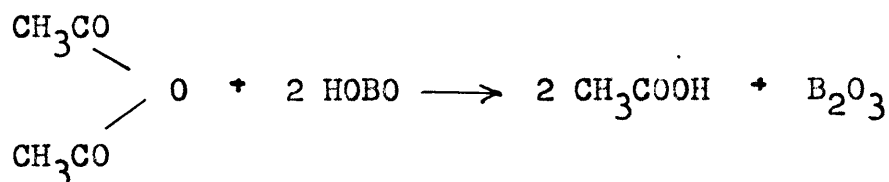
The problem was reopened by Tofael Ahmad and Khundar (1954) who reported that they had obtained a product in which the ratio of acetic acid to boric acid was three to one. On the other hand Gerrard and Wheelans (1954) refuted the possibility with the observation that under the experimental conditions used the products obtained contained acetic acid and boric acid in the ratio of two to one which corresponds to the composition of pyroboracetic anhydride.

A series of experiments were carried out in order to determine the nature of intermediate products formed in the reaction between acetic anhydride and orthoboric acid. It was found that one mol of acetic anhydride reacted with one or two mols of orthoboric acid to give a quantitative recovery of meta-

boric acid, the reactions may be formulated as follows:-



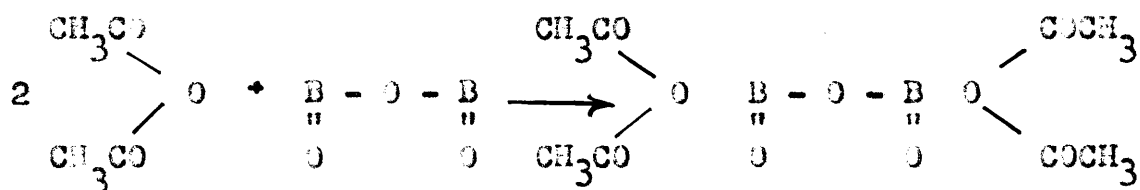
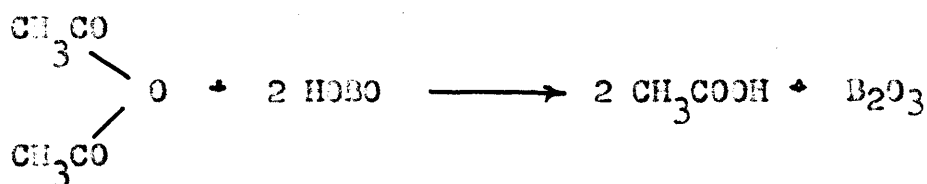
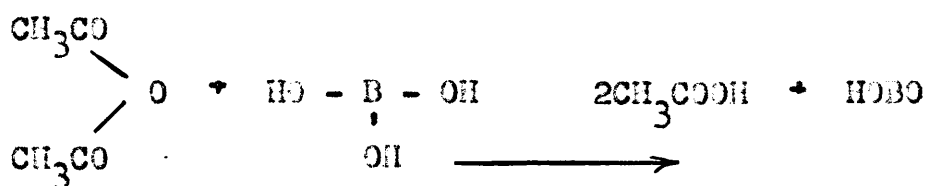
On reacting one mol of acetic anhydride with two mols of metaboric acid it was found that instead of the metaboric acid being further dehydrated to boron oxide according to the following equation



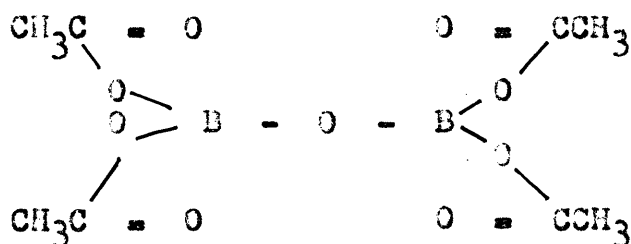
the reaction led to the formation of a small yield of crude pyroboracetic anhydride and large residue of unreacted metaboric acid.

In view of the above results it is considered that the reaction between acetic anhydride and orthoboric acid is one which involves the intermediate formation of metaboric acid and acetic acid from the dehydration of the orthoboric acid followed by the dehydration of the metaboric acid to boron oxide in the presence of large excess acetic anhydride which then co-ordinated with the boron oxide to form pyro-

boracetic anhydride. The reactions may be formulated as follows:-



The structure of pyroboracetic anhydride as designated by Dimroth below



indicates a stable structure in which all the atoms are covalently bonded.

It has been found that the compound is not only rapidly quantitatively decomposed by cold water but is also unstable in the solid state to such an extent that the acetyl content

gradually drops when the compound is allowed to stand on a porous tile in a dry box, washed with anhydrous ether, allowed to stand in a desiccator under continuous evacuation or allowed to dry in an oven at 117°C .

From a consideration of these facts, together with the observation that pyroboracetic anhydride may be prepared by the reaction between boric anhydride and pyroboracetic anhydride it appears that Dimroth's formulation is inadequate. It is proposed that a more correct formulation could be as follows:-



a structure in which the boron is directly bound to the acetic anhydride by a co-ordination bond from the oxygen, a structure which would be relatively unstable because the more stable state of boron is the one in which it is tricovalent.

EXPERIMENTAL

1. Boric oxide (1.4g, 0.02 mol) was heated with acetic anhydride (19.2g, 0.16 mol). An exothermic reaction occurred and all the boric oxide dissolved. The reaction was then considered to be complete. Sulphuric ether was added to the cold solution and a white crystalline compound was precipitated; the precipitate was filtered rapidly on a sintered glass buchner funnel, washed with ether until free of acetic anhydride odour and finally dried in a vacuum desiccator to remove the last traces of ether.

Analysis:- The general method of analysis was to hydrolyse approximately 0.2g in 50 ml. water, titrate to neutral red with N/10 Barium hydroxide for acetic acid content, then add mannitol (4g) a few drops of phenolphthalein indicator and titrate to permanent red with N/10 barium hydroxide for boron content.

Results:-	Calculated for $C_8H_{12}O_9B_2$	75% Acetic anhydride	7.9% Boron
	Found	74% Acetic anhydride	9.1% Boron

It was observed that even though the compound had been washed free of acetic anhydride prior to drying in the desiccator, there was a pronounced odour of acetic anhydride on opening the desiccator.

The determination of the melting point was indefinite since it varied with the time the sample was outside the desiccator, due to the rapidity of hydrolysis.

2. Boric Acid (62g, 1.0 mol) was heated under reflux with acetic anhydride according to the method of Pictet and Geleznoff (1903). After refluxing for an hour after all the boric acid

Analysis:-

Calculated for $C_8H_{12}O_9B_2$	Acetic anhydride 75%	Boron 7.8%
Found	Acetic anhydride 71%	Boron 8.8%

4. Boric acid (2.0g, 0.032 mol) was heated with acetyl chloride (10g, 0.13 mol) and benzene (10ml) until all the boric acid had dissolved. On cooling, the resultant crystalline product was filtered, washed with a little ice cold benzene and dried in a vacuum desiccator.

Analysis:-

Calculated for $C_8H_{12}O_9B_2$	Acetic anhydride 75%	Boron 7.9%
Found	Acetic anhydride 53%	Boron 7.7%

The resultant product was then refluxed with acetyl chloride (10g, 0.13 mol) in benzene solution for an hour then cooled. The crystalline product was filtered, dried and analysed in usual manner.

Analysis:-

Calculated for $C_8H_{12}O_9B_2$	Acetic anhydride 75%	Boron 7.9%
Found	Acetic anhydride 74%	Boron 8.3%

5. Acetic anhydride (10.2g, 0.1 mol) and orthoboric acid (6.2g, 0.1 mol) were gently heated under reflux in an oil bath at 117 - 125°C. A vigorous exothermic reaction occurred and 11.8 ml. acetic acid distilled over at 117°C.

Analysis:-	Calculated for CH_3COOH	100%
	Found	99%

The white insoluble residue in the still pot was washed with

60-80°C petroleum ether and analysed for boron content.

Boron analysis:-

Calculated for HOB(O)_2 B, 24.7%

Found B, 23.2%

6. Acetic anhydride (10.2g, 0.1 mol) and orthoboric acid (12.4g, 0.2 mol) were heated with xylene (100 ml) in a Dean and Starke apparatus until there was no further apparent evolution of xylene immiscible product. The xylene was filtered free of insoluble white residue. The xylene was found to give negative reaction with quinalizarin, indicating the absence of formation of pyroboracetic anhydride. On titration it was found that the acetic acid content of the xylene was 2.7g and the acetic acid content of the distillate 8.4g making a total of 11.1g.

Calculated yield 12.0g.

The insoluble residue was well washed with 60-80°C petroleum ether and analysed for boron content.

Calculated for HOB(O)_2 B, 24.7%

Found B, 23%

Yield 8.4g Calculated 8.8g

Molecular weight determination, ebullioscopic method, glacial acetic acid as solvent.

Calculated for HOB(O)_2 43.8

Found 42.

7. Acetic anhydride (10.2g, 0.1 mol) metaboric acid (8.8g, 0.2 mol) were heated with xylene (100 ml) in a Dean and

Starke apparatus until there was no further evolution of xylene immiscible distillate. Xylene solution was filtered hot and allowed to stand overnight. Yield of xylene insoluble product 7.1g analysis for boron content.

Calculated for B_2O_3	B, 32.1%
HDBO	B, 24.7%
Found	B, 24.8%

White crystalline product from xylene solution was filtered, washed dry with petroleum ether weighed, yield 3g.

Analysis for acetyl and boron content:-

Calculated for $C_8H_{12}O_9B_2$	CH_3COO	86.5%	B, 7.5%
Found	CH_3COO	71.7%	B, 10.3%

8. Spontaneous decomposition of pyroboracetic anhydride.

Sample of pyroboracetic anhydride was analysed then placed in vacuum desiccator and allowed to stand invacuo over sulphuric acid and solid potassium hydroxide. Sample was removed after 24 hours and analysed for acetyl and boron content. This was repeated. One sample was removed after 25 hours and analysed after standing in drying over at $110^\circ C$ for three hours.

Results are as follows:-

Time	Calculated		Found	
	CH_3COO	B	CH_3COO	B
0 hrs.	86.5%	7.5%	85.5%	8%
24 hrs.	76.5%	7.5%	76.8%	9.2%
48 hrs.			73.0%	9.9%
56 hrs.			63.0%	11.0%
80 hrs.			61.0%	12.4%

Sample allowed to stand in oven for three hours.

Calculated	CH_3COO	85.5%	B, 7.5%
Found		12%	24.0%

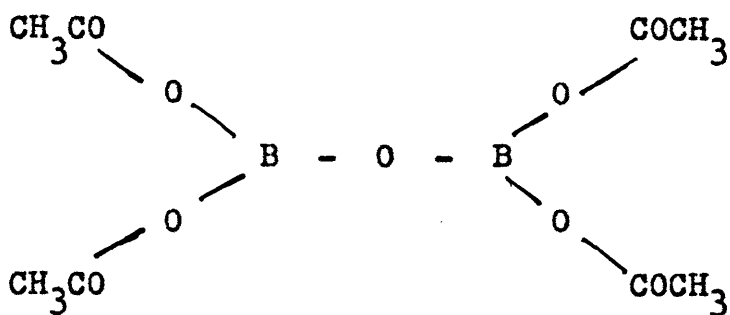
REACTION OF BORON COMPOUNDS WITH HYDROXYQUINONES

A COLOUR TEST OF DIAGNOSTIC VALUE

HISTORICAL INTRODUCTION

The detection of minute traces of boron utilising such reagents as alizarin, purpurin or quinalizarin dissolved in concentrated sulphuric acid to develop intensely coloured products has been known to chemists for a considerable number of years. Dimroth (1921), however, approached the study of such coloured compounds from a novel point of view, i.e. the use of a known organic compound of boron as a means of detecting specifically the presence of peri-hydroxy or peri-amino quinones.

Dimroth (1921) first considered that the reagent used was tri-acetate of boron ($B(OCOCH_3)_3$) since the method of preparation was that of Pictet and Geleznoff (1903). In a later communication Dimroth (1926) concluded that the method of Pictet and Geleznoff led not to the formation of boron triacetate as originally claimed but rather to the formation of pyroboracetic anhydride which was given the following formula.

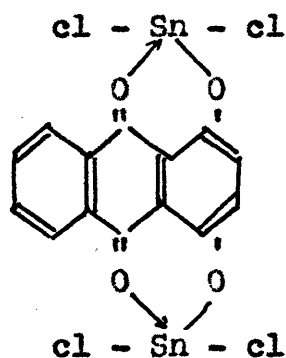


Dimroth (1921, 1926) studied the reaction of pyroboracetic anhydride in acetic anhydride solution with similar solutions of hydroxy and amino quinones. It soon became apparent when the reactants were heated a characteristically intense colour change preceded the formation of a vividly coloured insoluble reaction product whenever the hydroxyl or amino group occupied a peri-position in relation to the quinone group. Working under mild conditions, i.e. below 60°C, he found that the products contained one boron atom and two acetate residues for each peri-hydroxy- or peri-amino- group: on heating in vacuo acetic anhydride was liberated, yielding the corresponding derivatives of metaboric acid. Where there were two hydroxyl or amino groups peri- to the one quinone oxygen, as in 1:8 dihydroxy anthraquinone, then it was found that one of the hydroxyls was acetylated and the other reacted in the usual manner as above. In the case where the hydroxyl or amino group was not peri- to the quinone group, then there was no development of characteristic colour, the group being acetylated in the usual manner.

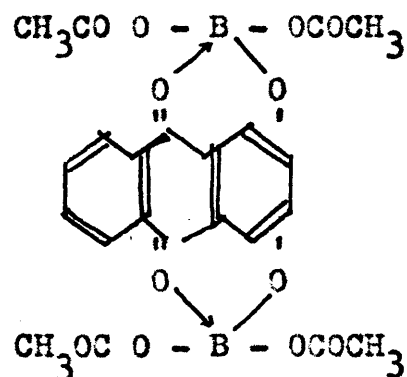
Dimroth also observed that non-quinoid hydroxy carbonyl compounds such as 2:3:4-trihydroxybenzophenone and acetophenols with groups on adjacent carbon atoms reacted similarly although the colours produced were much less intense. Of the heterocyclic compounds, hydroxy xanthenes and 8-hydroxyquinoline were the only ones investigated. Of the former only compounds with

the hydroxyl in the I- or peri-position reacted; 8-hydroxy-quinoline was also positive.

By analogy with Pfeiffer's concept (1927) of the constitution of the co-ordination compounds containing stannic tin and peri-hydroxy-anthraquinones, these reaction products were considered by Dimroth to be chelated compounds in which the carbonyl oxygen is co-ordinated to the boron atom thus:-



Pfeiffer's Structure



Dimroth's Structure

Although quite characteristic for peri-hydroxy and peri-amino quinones, Dimroth's reaction obviously suffers from the disability that relatively large quantities of reagents are necessary which severely limits the scope of the reaction as a research tool. In addition the reactants must be heated for some time in the presence of acetic anhydride and finally very little indication was given as to the degree of sensitivity of the reagent.

A more gentle reagent was described by Wilson (1939) and later studied in greater detail by Wolfram et al (1948)

as a diagnostic test for 5-hydroxy flavones. In this case the reagent consisted of a saturated solution of boric acid in anhydrous acetone and a ten percent solution of anhydrous citric acid also in anhydrous acetone solution. Equal volumes of the two solutions were mixed just prior to use to form the reagent mixture. In this test the formation of a coloured solution was not followed by the precipitation of an intensely coloured precipitate and no attempt was made to isolate the coloured reaction product or to determine their chemical constitution.

Taubbeck (1942), investigated the effect of variation of the acidic component in the Wilson test and found that organic acids such as oxalic, malonic, fumaric, adipic and malic, amongst others could be substituted for citric acid without any apparent detriment to the efficiency of the test.

Wolfram et al (1941) found that methylation of the 5-hydroxyl group in the isoflavone series led to a negative Wilson test, from which they concluded that methylation of the 5-hydroxyl group in the flavone series would likewise lead to negative results as was found by Dimroth on methylation of the peri-hydroxy and peri-amino quinones. These conclusions however, are at variance with the results found by Rangaswami and Seshadri (1942).

In general it appears that the Wilson test is limited in application to the flavones and related compounds and is

not suitable as a general reagent for the specific detection of peri-hydroxy quinone structures.

The Dimroth reagent found some application in the investigation of the structure of some naturally occurring hydroxynaphthoquinones in the hands of Macbeth and Winzor (1935) but little attempt was made to improve the technique of Dimroth.

Anderson (1950) attempted to isolate alkyl esters of boron as very insoluble co-ordination products of peri-hydroxyquinones. Although the required separation was not accomplished, it was noted that very intense colours were developed in benzene solution of the reagents. This observation led to the postulation that a benzene solution of esters of boric acid could replace the acetic anhydride solution of pyroboracetic anhydride as a reagent for detection of presence of peri-hydroxy or peri-amino quinones. To test the thesis, Anderson prepared a series of compounds which, from method of preparation, he presumed were triphenyl-, tri-n-butyl-, tri-tertiary-butyl-, mono-n-butyl-, di-tertiary-butyl-borates and tetra-n-butyl-boric oxide. Each of these compounds in benzene solution gave intense colours with benzene solutions of peri-hydroxy quinones. A few compounds such as 8-hydroxy quinoline, 2-hydroxy 3-naphthoic acid, 2:4:6-trimethoxyacetophenone and some acridones were tested and it was found that although colour development occurred it was of too faint a

nature to be of diagnostic value. Some of the compounds were tested by Wilson's method for comparison and results of Dimroth's tests were also noted.

From the results obtained Anderson concluded that the esters of boric acid in benzene solution were apparently satisfactory reagents for the detection of the presence of peri-hydroxy and peri-aminoquinones. The fact that the flavones reacted showed that the reaction was not confined to fully aromatic structures, but nevertheless a fundamental requirement was that a double bond be conjugated with a carbonyl group. As with the Dimroth test, methylation of the aromatic perihydroxy group completely inhibited colour formation but in the case of the flavones methylation of the I-hydroxyl group did not produce such an inhibiting effect.

DISCUSSION

REACTION OF BORON COMPOUNDS WITH PERI-HYDROXY

QUINONES AND RELATED COMPOUNDS

INTRODUCTION

From a survey of the literature it was found that there were two principle approaches to the question of the development of a suitable reagent for the identification - of peri-hydroxy quinones, (i) the use of pyroboracetic anhydride in acetic anhydride solution (Dimroth 1921, 1926) and (ii) the use of triphenyl borate and tri alkyl esters of boric acid respectively in benzene solutions (Anderson 1950).

The Dimroth technique suffers from the limitations that it involves the use of macro quantities, it is necessary to heat the reaction mixture which would make it useless for testing heat sensitive substances, more so since the reaction is carried out in acetic anhydride solution which could lead to the acetylation of the hydroxyl groups in positions other than peri- to the quinoid oxygen. In the case of compounds which may be available only in small quantities such acetylation would probably be undesirable, since the original compound could not be recovered on hydrolysis with water. Another weakness in the method is that no attempt was made to determine the sensitivity of the reaction, a fact which prohibits its

application as a spot test reagent for the peri-hydroxy quinones.

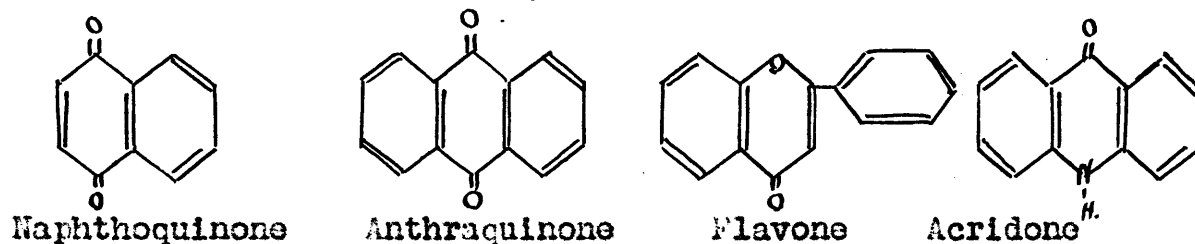
The work of Anderson was a slight improvement on that of Dimroth in that it was found that tri-phenyl borate could be used in the cold in benzene solution as a reagent which was specific for peri-hydroxy quinones. However, again very little attempt was made to determine the sensitivity of the reagent. A careful examination of the work of Anderson showed that there were no analytical figures to show that the compounds he prepared and used in situ in benzene solution were actually in fact those which he claimed to have prepared. In view of these facts then, it was decided to carry out careful preparation and isolation of appropriate esters in order to check their efficiency as reagents. The preparation and properties of such compounds has been previously described (loc. cit sections 3, 4 and 7 this thesis).

Because the work of Anderson indicated that there was a possibility that saturated benzene solution of tri-phenyl borate in benzene may be a reagent of diagnostic value, it was decided to determine whether a saturated benzene solution of pyroboracetic anhydride in benzene would be as satisfactory. Simultaneously tri-alkyl esters and tri-alkoxy boroxoles were tested for suitability as reagents.

It was envisaged that the reagents would possibly find

use as spot test reagents, consequently the solutions of compounds tested were of known strength and were successively diluted until there was no further possibility of detecting any colour change by eye. In this way it was proposed to compare the relative sensitivities of the reagents used, i.e. saturated benzene solutions of pyroboracetic anhydride, tri-phenyl borate and tri-alkyl esters of orthoboric acid respectively. Because of the difficulty in preparation of the boroxoles at the time of carrying out the sensitivity tests, they were only used on typical members of different classes of compounds examined for the sake of record.

The skeleton structures of the compounds tested were as follows:-



Other miscellaneous structures were tested which possessed related structures, in order to determine the specificity of the reagents.

RESULTS AND GENERAL DISCUSSION

The Dimroth (1921, 1926) technique, as originally described, used excess acetic anhydride as a solvent and required heating under reflux for up to one hour. In addition comparatively large amounts of material were required.

It has been found that the colour reaction may be carried out in the cold using only small quantities of material. However, a considerable improvement both in sensitivity and convenience was obtained by using a cold saturated solution of pyroboracetic anhydride in benzene rather than in acetic anhydride. This has been termed the modified Dimroth reagent. As judged by the rate and depth of colour development, the reaction appeared to be complete in a minute or two and warming made no appreciable difference in the velocity or degree of completion of the reaction.

The coloured solutions initially formed, (probably colloidal) were unstable and intensely coloured precipitates formed on standing. However, at the low concentrations of the compounds tested the solutions were stable for at least fifteen minutes if the test tubes were stoppered, and there was no difficulty in determining whether the colour reaction were positive or negative.

Attempts were made to develop a satisfactory technique for colourimetric method of estimating amounts of peri-hydroxy quinones but it was found that at low concentrations the colour quickly faded due to atmospheric moisture and at higher concentrations precipitation occurred after coagulation. It was considered that complicated technique required to carry out such quantitative colourimetric estimations would be unsatisfactory and the problem was not further investigated.

Quantitative tests were run simultaneously with benzene solutions of tri-phenylborate and pyroboracetic anhydride and also the Wilson reagent. A few Dimroth tests were also carried out but, due to the disagreeable nature of the acetic anhydride solvent, these tests were confined to representative compounds from the various groups.

In all the cases tested it was found that the sensitivity of the tri-phenyl borate and the modified Dimroth reagent were of the same order, covering a range of concentration from 1 to 10 ug of the compounds tested. Where the sensitivity was very low, such as in the acridones and aromatic carbonyl compounds, the reagents were not very satisfactory because there was very little difference in colour between peri-hydroxy compounds and those with hydroxyl groups in other positions. However, these two reagents were very definite in their reaction specifically with peri-hydroxy compounds belonging to naphthoquinone, anthraquinone, flavone series. None of these compounds showed negative result when there was a hydroxyl group present in the peri-position and all were negative when the hydroxyl group was in any other position. Methylation of the peri-hydroxyl group completely inhibited the reaction except in the case of the flavone series where there was a slight increase in sensitivity. In the case of the acridones, methylation or acetylation of the peri-hydroxyl group does not affect the reaction. The

substituent may be either in the 1 or 4 position to give positive reaction. Therefore a compound with a hydroxyl group peri- to a nitrogen atom in an aromatic ring is as effective as a peri-hydroxy quinone in giving a positive reaction, cf. 8-hydroxy quinoline, but the colours are usually yellow quite distinct in shade from the yellow orange of the naphthoquinones, anthraquinones and flavones. The reagents are incapable of differentiating between hydroxyl groups peri- to either quinoid oxygen or the nitrogen in the ring.

The Wilson test was found to give negative results for all compounds except the 5-hydroxy flavones. Reactions with the acridones were weaker than those recorded for the modified Dimroth and tri-phenyl borate reagents and to all intents and purposes may be considered as negative and inapplicable. It is to be noted that the Wilson test was very sensitive even though the 5-hydroxyl group in the flavones had been methylated. There has been some conflict in the literature regarding the behaviour of methoxy flavones to the Wilson reagent. Wolfram et al (1941) found that in the iso-flavone series methylation of the 5-hydroxyl group led to a negative test. They concluded that this methylation of the 5-hydroxyl group would lead to a negative test in the flavone series also. This conclusion is at variance with the results recorded above and also with those recorded by Rangaswami and

Seshadri (1942). Thus we see that the Wilson test is given by 5-hydroxy flavones 5-hydroxy flavonols and 2-hydroxy chalcones (Wolfram et al 1941) and by the methyl derivatives of these compounds. However, 5-acetoxy flavones do not appear to react (Rangaswami and Seshadri 1942). An outstanding difference between the Wilson reagent and the others is that only the Wilson test is positive with 2-hydroxy chalcones and flavones or flavonols.

The usefulness of the original Dimroth test as a diagnostic test for peri-hydroxy quinones was considerably reduced because positive reactions were reported for a considerable number of miscellaneous compounds, viz. o-nitro phenol, 1-aminoanthraquinone, o-hydroxyacetophenone, o-hydroxysalicylaldehyde, 1-acetyl-2-naphthol, salicylic acid, 2-hydroxy-3-naphthoic acid, and 8-hydroxyquinoline. By the use of the modified Dimroth reagent or tri-phenyl borate the interference of ortho-nitrophenols, peri-aminianthraquinones and salicylic acid is eliminated. Moreover, since ortho-hydroxy aromatic ketones and aldehydes give only very pale colours and the tests are relatively insensitive, the interference of this class of compound is not important.

Tri-alkyl esters of orthoboric acid were found to give negative results with all compounds tested. On the other hand it was found that tri-alkoxy boroxoles were capable of developing positive colours with peri-hydroxy naphthoquinones

and anthraquinones but negative colours with 2-hydroxy naphthoquinone and 2-hydroxy anthraquinone. Because of the difficulty of preparation and the fact that compounds for testing as used for modified Dimroth reagent etc. were no longer available, exhaustive tests were not carried out with the boroxoles to determine their relative sensitivity as reagents.

CONCLUSIONS

A saturated solution of either pyroboracetic anhydride or tri-phenyl borate in benzene constitutes a reagent which may be used to determine specifically whether the free hydroxyl group in naphthoquinones, anthraquinones or flavones occupies the peri- position in relation to the quinone structure or not. Either reagent is more specific and sensitive than either the original Dimroth reagent or the Wilson reagent, thus enabling the use of minute quantities of the compound to be tested.

Tri-alkyl borates are unsuitable as reagents whereas alkoxy boroxoles and tri-aryl borates, on the other hand, may possibly be substituted for modified Dimroth reagent should the occasion arise.

EXPERIMENTAL

(I) The Compounds Tested

Many of these were comparatively rare substances and were donated by workers in the appropriate fields. Where the donors guaranteed the purity, the substances were used without further purification. Where the purity was unknown or doubtful, the materials were suitably purified to the correct melting points.

(II) The Reagents

The reagent referred to hereafter as Dimroth's reagent was a solution of pyroboracetic anhydride in acetic anhydride saturated at room temperature. The composition of the pyroboracetic anhydride was checked by analysis (loc.cit this thesis) When used hot, this reagent approximates to the conditions originally used on a larger scale by Dimroth.

The modified Dimroth reagent was a solution of pyroboracetic anhydride in crystallizable thiophene free benzene, saturated at room temperature.

The Wilson reagent was made up freshly for use from equal volumes of solutions in anhydrous acetone of boric acid (saturated) and anhydrous citric acid (10%), conforming to the original technique of Wilson.

The tri-alkyl and tri-aryl borates were prepared and analysed as described in section 3 of this thesis; like-

wise with the substituted boroxoles.

All reagents were kept in tightly stoppered bottles and were periodically checked for purity. Average period of stability was approximately six weeks.

(iii) Experimental Technique

A solution of the test substance was prepared in acetic anhydride (1 mg. per ml.) for use with the Dimroth reagent and in crystallizable thiophene free benzene for all other reagents except for the Wilson test when anhydrous acetone was employed. Substances which were not sufficiently soluble in benzene (i.e. glycosides) were dissolved in benzene containing up to 20% dioxane. Further dilutions to establish the limit of sensitivity were prepared from these stock solutions. The colour reactions were carried out by adding 2 ml. of the reagent to 1 ml. of the solution in a small test tube which was corked immediately and compared against a white background with a blank of the same concentration.

Since the modified Dimroth reagent was so much more convenient to use than the Dimroth reagent, tests with the latter were only carried out for comparative purposes on substances typical of each group. The Dimroth test was most unpleasant and inconvenient to use owing to the disagreeable nature of the solvent.

It is to be noted that in the case of the tri-alkyl borates and substituted boroxoles no attempt was made to

determine the sensitivity of such compounds as gave positive colour with perihydroxy quinones because it was considered that triphenyl borate and pyroboracetic anhydride were the most suitable reagents because of ease of preparation and manipulation. These compounds were included in order to show that trialkyl borates do not give any colour development with peri-hydroxy quinones whereas substituted boroxoles, on the other hand, produce intensely coloured solutions.

RESULTS

The results of the tests are recorded in Tables I to IX inclusive.

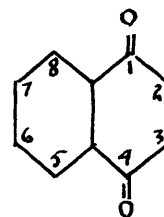


TABLE I

REACTIONS OF NAPHTHOQUINONES

2	Positions 3	5	8	Triphenyl Borate	Modified Dimroth
-	-	-OH	-	1ug. Orange	1ug. Orange
-	-	-OMe	-	-ve.	-ve.
-OH	-	-	-	-ve.	-ve.
-OMe	-	-	-	-ve.	-ve.
-	-Me	-OH	-	2ug. Orange	2ug. Orange
OH	-	-OH	-	2ug. Orange	2ug. Orange
-OH	-	-OMe	-	-ve.	-ve.
-OH	-OH	-	-	-ve.	-ve.
-Me	-	-OH	-OH	2ug. Mauve	2ug. Mauve
-	-	-OAc	-OAc	-ve.	-ve.
-	-	-OH	-OH	2ug. Mauve	2ug. Mauve
-OH	-	-OH	-OH	3ug. Mauve	3ug. Mauve

In all these tables these figures represent the concentration limit per ml. for the test. Due mainly to variation between observers they are accurate within a factor of two.

The Wilson test was negative in all cases.

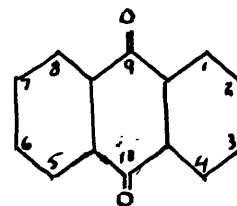
The Dimroth reagent gave with 5-hydroxynaphthoquinone a positive reaction of concentration limit 25ug.

(a) Naphthoquinones (Table I)

In all cases the Wilson test was negative. Naphthoquinones having at least one hydroxyl group peri- to a carbonyl group gave positive reaction with the Dimroth reagent, the modified Dimroth and triphenyl borate reagents. Both 2:3 dihydroxy and 2-hydroxy-1:4 naphthoquinone gave negative results showing that a hydroxyl group ortho to a carbonyl group is not sufficient for a positive reaction. Methylation or acetylation of the peri-hydroxyl group completely inhibits the reaction.

(b) Anthraquinones (Table II)

TABLE II
REACTIONS OF ANTHRAQUINONES



1	Positions		5	8	Triphenyl Borate	Modified Dimroth
	2	4				
-OH	-	-	-	-	3ug. Yellow	2ug. Yellow
-	-OH	-	-	-	-ve.	-ve.
-OH	-OH	-	-	-	lug. Yellow	lug. Yellow
-OH	-OH	-OH	-	-	lug. Mauve	lug. Mauve
-OH	-OH	-	-OH	-OH	lug. Purple	lug. Purple
-OAc	-	-	-	-	-ve.	-ve.
-OH	-	-	-OH	-	lug. Purple	lug. Purple
-OH	-	-OH	-	-	lug. Mauve	lug. Mauve

The Wilson reagent was in all cases negative.

The Dimroth reagent gave with I-hydroxyanthraquinone a positive reaction of concentration limit 25ug.

The reactions of the anthraquinones closely parallel those of the naphthoquinones. Reference to Tables I and II will show that in both the naphthoquinones and anthraquinones compounds with one peri-hydroxyl group give colours yellow to orange but those with two peri-hydroxyl groups give colours mauve to purple. Although hydroxyl or methoxyl groups situated in other positions have small effect on the colour, their presence or absence does not vitiate this broad division. Hence it is clear that within the scope of the compounds tested,

the shade of colour may be used to indicate the number of peri-hydroxy groups present in the molecule.

(c) Flavones and related compounds (Table III)

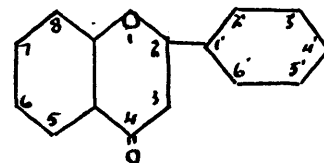


TABLE III

REACTIONS OF FLAVONES AND RELATED COMPOUNDS

Positions							Common Name	Triphenyl Borate, Modified Dimroth, Wilson *
1	2	6	7	8	3'	4'		
-OMe	-OMe	-	-OMe	-	-OMe	-OMe	Pentamethyl quercetin	1ug. Yellow
-OMe	-OMe	O-CH ₂ -O	-	-	O-CH ₂ -O	-		1ug. Yellow
-OMe	-OH	-	-OMe	-	O-CH ₂ -O	-		1ug. Yellow
-OMe	-OMe	-	-OMe	-	O-CH ₂ -O	-		3ug. Yellow
-OMe	-OH	-	-OMe	-	-OMe	-OMe	Tetramethyl quercetin	3ug. Yellow
-OMe	-OMe	-	-OMe	-OMe	O-CH ₂ -O	-		5ug. Yellow
-OMe	-OH	-	-OMe	-	-OH	-OMe		5ug. Yellow
-OMe	-OH	O-CH ₂ -O	-	-	O-CH ₂ -O	-		5ug. Yellow
-OMe	-OH	-	-OH	-	O-CH ₂ -O	-		10ug. Yellow
-OMe	-OH	-OMe	-OMe	-	O-CH ₂ -O	-		10ug. Yellow
-OMe	-OMe	-OH	-OMe	-	O-CH ₂ -O	-		10ug. Yellow
-OH	-OH	-	-OH	-	-OH	-OH	Quercetin	10ug. Yellow
-OMe	-OMe	-OMe	-OMe	-	-OMe	-OMe	Hexamethyl quercetin	10ug. Yellow
-	-OH	-	-OMe	-	-	-	Tectochrysin	50ug. Yellow
-OSugar	-OH	-	-OH	-	-OH	-OH	Rutin	50ug. Yellow
-OSugar	-OH	-	-OSugar	-	-	-OH	Robinin	100ug. Yellow

TABLE III (Contd.)

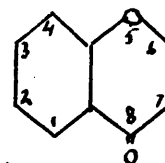
1	2	6	7	8	3'	4'	Common Name	Triphenyl Borate, Modified Dimroth, Wilson *
-OSugar	-OH	-	-OH	-	-OH	-OH	Quercetin	100ug. Yellow
-	-OSugar	-	-OSugar	-	-OH	-OH	Nariginin	-ve.
-	-OH	-	-OH	-	-	-	Hesperetin	-ve.
-	-OH	-	-OSugar	-	-	-	Hesperidin	-ve.
-	-	-	-OSugar	-	O-CH ₂ -O		Psuedobaptisin	-ve.
-	-OH	-C ₅ H ₉	O-CH ₇ = CH-		-OH		Osajin	30ug. Yellow
-	-C ₉ H ₉	O-CH ₇ = CH-			-OH	-OH	Pomiferin	30ug. Yellow

* The three reagents have identical results.

The Dimroth reagent gave with pentamethylquercetin a positive reaction of concentration limit 25ug.

The 5-substituted flavones and related compounds were found to give positive reactions with the Dimroth, Modified Dimroth, triphenyl borate and Wilson reagents, the sensitivities to all reagents being identical. Glycoside formation, not involving the 5-hydroxyl group, does not inhibit the reaction since both robinin and rutin give positive reactions.

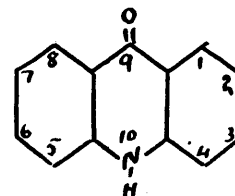
A compound of this class unsubstituted in the 5-position does not react (psuedobaptisin). Reduction of the 2:3 double bond leads to a negative reaction (hesperetin and nariginin). The isoflavones osajin and pomiferin give positive reactions. Unfortunately, insufficient of these were available to permit the preparation and examination of their methyl derivatives.

(d) Xanthenes (Table IV)TABLE IVREACTIONS OF XANTHONES

1	Positions		Triphenyl Borate
		4	Modified Dimroth Wilson *
-OH	-	-	5 ug. Deep Yellow
-OMe	-	-	100 ug. Yellow
-	-OH	-	-ve.

* These reagents gave identical results.

From Table IV it will be seen that a positive reaction for all reagents is given when there is a hydroxyl group in the peri- position to a carbonyl group. Methylation reduces the sensitivity considerably, but the reaction is still positive. When the hydroxyl group is similarly situated with respect to the cyclic oxygen, then the reaction is negative.

(e) Acridones (Table V)TABLE VREACTIONS OF ACRIDONES

Positions					Triphenyl Borate Modified Dimroth	Wilson
1	2	3	4	10		
-OMe	-	-	-	-H	3ug. Deep Yellow	50ug. Yellow
-OMe	-	-OMe	-	-H	5ug. Yellow	50ug. Yellow
-OMe	-OMe	-OMe	-	-H	5ug. Yellow	50ug. Yellow
-OMe	-OMe	-	-OMe	-H	3ug. Deep Yellow	50ug. Yellow
-OMe	-	-	-	-Me	Yellow	Yellow
-	-	-	-OMe	-Me	Yellow	Yellow
-	-	-	-OH	-Me	3ug. Deep Yellow	50ug. Yellow
-	O-CH ₂ -O 		-OH	-Me	Yellow	Yellow
-	O-CH ₂ -O 		-OAc	-Me	Yellow	Yellow
-	O-CH ₂ -O 		-OMe	-Me	Yellow	Yellow
-OH	-	-	-	-Me	Yellow	Yellow

The Dimroth reagent gave with 4-hydroxy-10-methylacridone a positive reaction of concentration limit 50ug.

It is evident that methylation of the peri-hydroxyl group does not effect the reaction. The substituent may either be in the 1 or 4 position to give a positive reaction. Therefore a compound with a hydroxyl group peri- to a nitrogen atom in an aromatic ring is as effective as a peri-hydroxy quinone in giving the positive reaction (cf. 8-hydroxyquinoline).

The Wilson reagent is far less sensitive than the triphenyl borate or modified Dimroth reagent.

(f) Aromatic Ketones (Table VI)TABLE VIREACTIONS OF AROMATIC CARBONYL COMPOUNDS

1	2	4	Triphenyl Borate	Modified Dimroth	Cold	Dimroth* Boiling
-COMe	-	-	-ve.	-ve.	-ve.	-ve.
-COMe	-	-OH	-ve.	-ve.	-ve.	-ve.
-COMe	-OH	-	1 mg. Pale Yellow	1 mg. Pale Yellow	-ve.	-ve.
-COMe	-OMe	-	10mg. Pale Yellow	10mg. Pale Yellow		
-COMe	-OH	-OH	1 mg. Pale Yellow	1 mg. Pale Yellow		
-CHO	-OH	-	10mg. very Pale Yellow	10mg. very Pale Yellow		

The Wilson reagent was in all cases negative.

★ Although these tests were negative, Dimroth originally obtained positive reactions with the ortho-hydroxy compounds by working in high concentrations and after longer reactions.

From Table VI it will be seen that any aromatic ketone or aldehyde which has either a hydroxyl or methoxy group in the ortho-position gives a positive reaction with all except the Wilson reagent which is in every case negative. This class of compound is however distinguished by being much less sensitive than peri-hydroxy compounds and the colours produced are very much more intense.

(g) Miscellaneous Compounds (Table VII)TABLE VIIREACTIONS OF MISCELLANEOUS COMPOUNDS

Substance	Triphenyl Borate	Modified Dimroth	Wilson
Salicylic acid	-ve.	-ve.	-ve.
Benzoin	-ve.	-ve.	-ve.
Benzil	-ve.	-ve.	-ve.
o-Nitrophenol	-ve.	-ve.	-ve.
2-hydroxy-3-naphthoic acid	100ug. Yellow	100ug. Yellow	-ve.
o-nitrobenzene-azo- resorcinol	-ve.	-ve.	-ve.
8-hydroxyquinoline	500ug. Pale Yellow	500ug. Pale Yellow	500ug. Pale Yellow
Tumeric	100ug. Pale Yellow	100ug. Pale Yellow	Pink
1-aminoanthraquinone	-ve.	-ve.	-ve.
Partially methylated hesperetin chalkone	-ve.	-ve.	Yellow
Dimedone, diosphenol, Angustione, Acetylacetone, Cyclohexanel:4dione-2:5 dicarboxylic acid.		-ve.	-ve.

The original Dimroth reaction was reported as positive with salicylic acid, 8-hydroxy quinoline, 1-aminoanthraquinone, o-nitrophenol, and 2-hydroxy-3-naphthoic acid.

(g) Miscellaneous Compounds (Table VII Contd.)

Noteworthy amongst these are the enolisable compounds dimedone, di²phenol, angustion², cyclohexane-1:4-dione-2:5-dicarboxylic acid, and acetylacetone, all of which gave negative reactions with all reagents. The partially methylated hesperetin chalkone consisted of a mixture of 2:4:6-trimethoxy-3':4'-dimethoxy chalkone and 2-hydroxy-4:6-dimethoxy-3':4'-dimethoxy chalkone obtained from hesperetin by methylation in alkaline solution. The fact that this gives a negative reaction with modified Dimroth and triphenyl borate reagents shows that neither 2-hydroxy nor 2-methoxy chalkones give positive reactions with these reagents. 8-hydroxyquinoline gives a positive reaction with all reagents and 2-hydroxy-3-naphthoic acid gives a positive reaction with all except the Wilson reagent.

(h) Trialkyl esters (Table VIII)

TABLE VIII
REACTIONS OF TRIALKYL BORATES

Ester	Quinalizarin	Alizarin	Naphthoquinone
Tri-n-butyl borate	-ve.	-ve.	-ve.
tri-secondary-butyl borate	-ve.	-ve.	-ve.
tri-tertiary-butyl borate	-ve.	-ve.	-ve.
tri-cyclohexyl borate	-ve.	-ve.	-ve.
tri-(2-octyl) borate	-ve.	-ve.	-ve.
tri-methyl borate	-ve.	-ve.	-ve.
tri-n-propyl borate	-ve.	-ve.	-ve.
tri-(2-ethyl)-hexyl borate	-ve.	-ve.	-ve.
tri-n-amyl borate	-ve.	-ve.	-ve.
tri-n-hexyl borate	-ve.	-ve.	-ve.
tri-n-heptyl borate	-ve.	-ve.	-ve.

It is quite definitely seen here that tri-alkyl borates are incapable of producing coloured reaction products with peri-hydroxy quinones under conditions of the experiment.

(1) Reactions of substituted Boroxoles (Table IX)

TABLE IX
REACTIONS OF SUBSTITUTED BOROXOLES

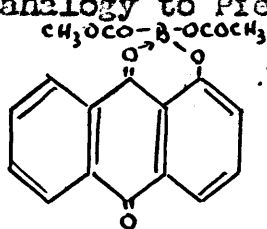
Compound	Quinalizarin	Alizarin	Naphthoquinone
Tri-methoxy boroxole	+ve.	+ve.	+ve.
Tri-n-propoxy boroxole	+ve.	+ve.	+ve.
Tri-n-butoxy boroxole	+ve.	+ve.	+ve.
tri-sec-butoxy boroxole	+ve.	+ve.	+ve.
tri-tert-butoxy boroxole	+ve.	+ve.	+ve.
tri-(2-Octoxy)-boroxole	+ve.	+ve.	+ve.
tri-cyclohexoxy boroxole	+ve.	+ve.	+ve.
tri-n-pentoxy boroxole	+ve.	+ve.	+ve.
tri-n-heptoxy boroxole	+ve.	+ve.	+ve.
tri-(2-ethyl)hexoxy boroxole	+ve.	+ve.	+ve.
tri-n-heptoxy boroxole	+ve.	+ve.	+ve.

From these results it would appear that the property of forming coloured reaction products with peri-hydroxy quinones is not confined to tri-phenyl borate and pyroboracetic anhydride but is also a property of alkoxy substituted boroxoles.

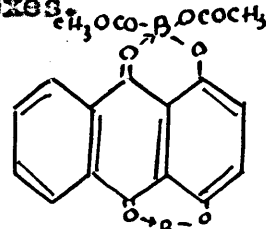
THE CHEMICAL CONSTITUTION OF SOME BORON COMPOUNDS
OF PERI-HYDROXY QUINONES

INTRODUCTION

Dimroth (1921, 1926) reacted pyroboracetic anhydride with 1-hydroxy anthraquinone, 1:2 dihydroxy anthraquinone (alizarin), 1:4 dihydroxy anthraquinone (quinizarin) and 1:2:4 trihydroxy anthraquinone (purpurin) with acetic anhydride as solvent and found that compounds were obtained to which he gave the following structures on basis of his analysis and from analogy to Pfeiffer's tin complexes.



1-hydroxy anthraquinone
pyroboracetate



1:4 di-hydroxy anthraquinone
pyroboracetate

Since the colours of the precipitates formed and their general solubility were shown in previous sections of this thesis to be slightly different from those of Dimroth it was decided to investigate their composition in order to determine whether they were identical with those obtained by Dimroth. In addition the compounds obtained from tri-phenyl borate were included to see whether they fitted into the general pattern.

DISCUSSION OF RESULTS

Compound II was prepared and analysed according to the method of Dimroth and it was found that the ratio of acetic anhydride to hydroxy anthraquinone to boron was 4:1:2 as recorded by Dimroth. On these grounds it was concluded that the method of analysis, with slight variations, could be applied to the tri-phenyl borate complexes prepared in benzene solution.

1-hydroxy anthraquinone, alizarin and quinizarin were then reacted with pyroboracetic anhydride in benzene solution to give intensely coloured products which were filtered, dried in vacuo and analysed. During handling the products were not allowed to stand in the air in order to avoid decomposition by atmospheric moisture. Analysis gave the following results:-

Hydroxy Quinone	Ratio of	
	Acetic Anhydride : Found	Hydroxy Quinone : Boron Calculated
1-hydroxy anthraquinone	1 : 1 : 12 0.6 : 1 : 5	1 : 1 : 1
alizarin	1 : 1 : 5	1 : 1 : 1
Quinizarin	0.5 : 1 : 3	2 : 1 : 2

It can be seen that in all cases the ratio of acetic anhydride to hydroxy quinone to boron is such that the acetic anhydride content is much lower and the boron content much higher than would be expected if the resultant compounds were identical with those prepared by Dimroth.

Likewise it was found that the sum total weight of acetic anhydride hydroxy quinone and boron was always less than the weight taken for analysis. It is considered that this difference can be accounted for to some extent if it is surmised that the boron is present as a variable polymer of boron oxide which must be attached to the hydroxy quinones at the quinoid and peri-hydroxy groups. These two groups must be present or else there is no colour formation. In addition acetic anhydride is attached to the boron oxide polymer in some indeterminate manner.

Because benzene solution of pyroboracetic anhydride apparently gave products which differed in composition from those obtained in acetic anhydride solution, it was decided to examine a few compounds prepared by the reaction between benzene solution of tri-phenyl borate and selected peri-hydroxy quinones. The intensely coloured reaction products were filtered, dried in vacuo and analysed. As with the compounds obtained by reaction with pyro-boracetic anhydride it was found that the ratio of phenol to hydroxy quinone to boron was entirely different from that expected, except in the case of quinizarin. The analytical results are summarised as follows:-

Hydroxy Quinone	Ratio of		
	Phenol Found	Hydroxy Quinone Calculated	Boron
Alizarin	0.1 : 1 : 0.6	2 : 1 : 1	
Purpurin	3 : 1 : 3	4 : 1 : 2	
Quinizarin	4 : 1 : 2	4 : 1 : 2	
Quinalizarin	0.5 : 1 : 3	4 : 1 : 2	

Here again it is seen that in general the ratio of boron to the phenol and hydroxy quinone is higher than expected, but differs from the previous compounds in that the ratio of boron is not as high. However, no conclusion could be drawn as to the manner in which the three components were linked together in these coloured compounds.

It was found impossible to determine the molecular weights of the compounds isolated because they were either insoluble or decomposed by solvents used for molecular weight determinations. It was thought that dioxane would be a suitable solvent, however it was found that this solvent co-ordinated with boric oxide on warming (loc.cit) and so was not used.

CONCLUSIONS

The compounds obtained by the reaction of benzene solutions of pyroboracetic anhydride and tri-phenyl borate respectively with peri-hydroxy quinones appear to differ in composition from what would be expected by comparison to those obtained by Dimroth by reaction with an acetic anhydride solution of pyroboracetic anhydride.

EXPERIMENTALTHE CHEMICAL CONSTITUTION OF SOME BORON COMPOUNDS OF
PERI-HYDROXY QUINONES.

1. Quinizarin (1.5g), pyroboracetic anhydride (2.0g) were dissolved in acetic anhydride (20ml) on gentle warming. The resultant purple solution was allowed to stand over night in the refrigerator and then filtered. The deep red coloured precipitate was washed with anhydrous benzene and then dried in a vacuum desiccator. At no stage was the precipitate allowed to dry out sufficiently in the air to cause hydrolysis, as indicated by change in colour to dark ochre.

The precipitate was analysed according to the technique of Dimroth, i.e. hydrolyse a weighed sample with warm water, filter off and weigh the insoluble hydroxy quinone, titrate the filtrate with N/10 barium hydroxide solution to neutral red for acetic acid, then add mannitol and titrate to phenolphthalein for boron.

Analysis results.

Weight of sample	0.3133g	0.2767g.
Wt. quinizarin found	0.1343g	0.1159g
Wt. Acetic anhydride	0.1564g	0.1370g
Wt. Boron as B.	0.0113g	0.0159g
Total	0.3020g	0.2688g

Ratio of quinizarin : boron : acetic anhydride 1 : 2 : 2 mols

Calculated ratio for $C_{22}H_{18}O_{12}B_2$ 1 : 2 : 2 mols.

2. Quinizarin (1.5g), pyroboracetic anhydride (2.0g) were dissolved in dioxane (40 and 20 ml respectively). The solutions were mixed cold, 50 ml benzene added and the whole allowed to stand overnight in the refrigerator. These conditions approximate to those existing in the tests for peri-hydroxy quinones as carried out in section I of this thesis.

The resultant purple precipitate was filtered, washed with benzene and analysed after drying in vacuum desiccator.

Weight of sample	0.1694g	0.1156g
Wt. quinizarin found	0.0881g	0.0869g
Wt. acetic anhydride	0.0102g	0.0102g
Wt. boron as B.	0.0128g	0.0121
Total weight	0.1111g	0.1089g

Ratio of quinizarin : boron : acetic anhydride = 1 : 3 : 0.5 mols

Calculated for $C_{22}H_{18}O_{12}B_2$ 1 : 2 : 2

3. Alizarin (1.5g) was treated with pyroboracetic anhydride (2.0g) as for quinizarin and the resultant red product analysed to give following results:-

Weight of Sample	0.1476g	0.1113g
Weight of Alizarin found	0.0620g	0.0466g
Weight acetic anhydride	0.0136g	0.0118g
Weight of boron as B.	0.0147g	0.0104g
Total weight	0.0903g	0.0688g

Ratio of Alizarin - boron - acetic anhydride 1 : 5 : 1

Calculated for $C_{18}H_{13}O_8B_2$ 1 : 2 : 1

4. 1:Hydroxy anthraquinone (0.44g) was treated with pyroboracetic anhydride (0.72g) in dioxane solution as above and the resultant yellow precipitate separated, dried in vacuum and analysed.

Weight of sample	0.0518g	0.0405g
Wt. 1-Hydroxy anthraquinone found	0.0122g	0.0894g
Wt. acetic anhydride	0.0041g	0.0030g
Wt. boron as B.	0.0075g	0.0056g
Total weight	0.0238	0.0180g

Ratio of 1:Hydroxy anthraquinone : acetic anhydride : boron
1 : 1 : 12

Calculated for $C_{18}H_{13}O_7B$ 1 : 1 : 1

Weight of sample	0.0397g	0.0438g
Wt. 1-Hydroxy anthraquinone	0.0190g	0.0170g
Wt. acetic anhydride	0.0035g	0.0029g
Wt. boron as B.	0.0049g	0.0053g
Total Weight	0.0274g	0.0252g

Ratio of :-Hydroxy anthraquinone : acetic anhydride : boron
1 : 0.6 : 5

5. Quinizarin (1.5g) and tri-phenyl borate (2.0g) were dissolved in dioxane (40 and 10ml respectively), benzene (50ml) was then added and the solution allowed to stand overnight in the refrigerator. The resultant red precipitate was filtered vacuum dried and analysed.

Weighed sample (0.2g) was hydrolysed with warm water (50ml), cooled and the precipitated peri-hydroxy quinone filtered through tared sintered glass crucible, dried at 100°C and weighed. The filtrate was made up to 100ml. and divided into two portions. 25 ml. were titrated with N/10 barium hydroxide solution to neutral red, followed by addition of mannitol and final titration to phenolphthalein for boron determination. To determine the phenol content, 25 ml. of the filtrate was treated with 30 ml. N/10 bromide bromate solution in an iodine flask; 5 ml. hydrochloric acid were added and the stoppered flask shaken at irregular intervals over a period of half an hour and then allowed to stand for fifteen minutes. 5 ml. of 20% aqueous potassium iodide solution was then added and the mixture titrated with sodium thiosulphate using soluble starch indicator. 1 ml. Bromide/bromate solution equivalent to 0.001596g phenol. Simultaneously a blank determination was carried out and the difference in titration gave equivalents of bromide bromate solution.

Results of analysis

Weight of sample	0.2238g	0.2013g
Wt. quinizarin	0.0711g	0.0644g
Wt. phenol	0.1036g	0.0986
Wt. boron	0.0744g	0.0584
Total weight	0.2591	0.2204

Calculated for $C_{38}H_{26}O_8B_2$ quinizarin : phenol : boron = 1 : 4 : 2
 Found 1 : 4 : 2

6. Alizarin (1.2g) and tri-phenyl borate (2.9g) were treated in dioxane as for quinizarin above and the resultant red precipitate analysed under same conditions to give following results:-

Weight of sample	0.2826g
Weight of alizarin	0.2532g
Weight of phenol	0.0075g
Weight of boron	0.0065g
Total weight	0.2672g

Ratio of alizarin : phenol : boron 1 : 0.1 : 0.6

Calculated for $C_{26}H_{17}O_6B$ 1 : 2 : 1

7. Purpurin (1.28g) and triphenyl borate (5.8g) were treated in dioxane and resultant red purple precipitate dried and analysed as above.

Weight of sample	0.2712g
Wt. purpurin	0.0835g
Wt. phenol	0.0941g
Wt. boron	0.0110g
Total weight	0.1886g

Ratio of purpurin : phenol : boron 1 : 3 : 3

Calculated for $C_{38}H_{26}O_9B_2$ 1 : 4 : 2.

8. Quinalizarin (1.36g) and tri-phenyl borate (5.8g) were dissolved in dioxane and the resultant purple precipitate isolated and analysed as above.

Weight of sample 0.2379g

Weight of quinalizarin 0.1201g

Weight of phenol 0.0213g

Weight of boron 0.0139g

Total weight 0.1553g

Ratio of quinalizarin : phenol : boron 1 : 0.5 : 3

Calculated for $C_{38}H_{26}O_{10}B_2$ 1 : 4 : 2.

METABORIC ACID

Discussion

From the reaction between one mol of an alcohol and one of orthoboric acid, using benzene as solvent, it was found possible to isolate alkoxy boroxoles. Where the ratio of boric acid to alcohol was greater than one to one it was found that metaboric acid was formed from the excess orthoboric acid. Under the conditions of the experiment, all the alcohol would have been used in the reaction, therefore the only dehydrating agent present would be the hydrocarbon solvent. To show that benzene, toluene, and xylene were able to dehydrate orthoboric acid, a sample of the acid was refluxed with each solvent and it was found that the resultant product was metaboric acid.

Although the orthoboric acid was heated at 124°C in boiling xylene, it was found impossible to take the dehydration further than the formation of the metaboric acid.

Although the dehydration of orthoboric acid was found to occur readily with benzene as the azeotroping agent, and the ease of dehydration increased with the increase in boiling point of the azeotropic solvent, however, it was found that heating at 124°C in xylene failed to lead to the formation of boron oxide.

In view of the following facts:-

- (i) Orthoboric acid is readily dehydrated to metaboric acid.

(loc.cit)

(ii) Tri-alkoxy boroxoles are intermediates in the formation of tri-alkyl borates. (loc.cit).

(iii) Metaboric acid may be prepared by dehydration of orthoboric acid with acetic anhydride (loc.cit),

it is proposed that the reactions of orthoboric acid are rather those of a hydrate of metaboric acid. In each of the reactions quoted above, the reaction is not that of orthoboric acid but rather that of its dehydration product, metaboric acid, which is formed initially in the reaction.

EXPERIMENTAL

1. Orthoboric acid was dried in an oven at 110°C for two hours and then analysed for boron content.

Calculated for H_3BO_3	B, 17.5%
--	----------

HOB(O)_2	B, 24.7%
-------------------	----------

Found	B, 24.1%
-------	----------

The sample was pulverised and replaced in oven for further twelve hours, then removed and analysed for boron content.

Found	B, 27%
-------	--------

2. Orthoboric acid (5g) was heated with toluene (50ml) in an apparatus containing a McIntyre weir reflux ratio head until there was no further evolution of water. The residue in the flask was filtered free of solvent, washed with anhydrous petroleum ether and analysed for boron content.

Calculated for H_3BO_3	17.5%
--	-------

HOB(O)_2	24.7%
-------------------	-------

Found	24.7%
-------	-------

Sample was replaced in flask and refluxed for further three hours. There was no further evolution of water and on removal, drying and analysis the following results were obtained:-

Found	B, 24.7%
-------	----------

Sample was recrystallised from glacial acetic acid and washed with anhydrous petroleum ether and molecular weight determined in boiling acetic acid.

Molecular weight.

Calculated for H_3BO_3	61.8
$\text{H}_3\text{O}_6\text{B}_3$	141.5
HOB0	43.8
Found	44.8

The experiment was repeated using benzene and then xylene as azeotroping agents, in each case it was found that orthoboric acid was dehydrated to metaboric acid as above.

BIBLIOGRAPHY

- Ananthrakrishnan K. (1936) Proc. Indian Acad. Sci. A4 74
- Anderson J, O'Brien K, and Reuter F. (1952) J. Applied Chem. 2; 241
- Anderson J.R. (1950) B.Sc. Thesis, N.I.T. University of Technology.
- Bannister W.J. (1928) U.S. Patent 1,668,797
(1928) Chem. Abstracts 22; 2172
- Bauer S.H. and Beach J.Y. (1941) J. Amer. Chem. Soc. 63; 1396
- Bethell D.E. and Sheppard H. (1955) Trans. Faraday Soc. 51; 9
- Colthup W.B. (1950) J. Opt. Soc. Amer. 40; 397
- Cohn G. (1911) Pharm. Centr. 52; 479
- Cook H.G., Ilett J.D, Saunders B.C. and Stacey G.J. (1950) J. Chem. Soc. 1950: 3125.
- Copaux H. (1898) Compt. rendu. 127; 719
- Counciler C. (1878a) Ber. dtsh.Chem. Ges. 9; 485
- Counciler C. (1878b) Ber. dtsh.Chem. Ges. 10; 1655
- Counciler C. (1878c) Ber. dtsh.Chem. Ges. 11; 1106
- Counciler C. (1871) J. fur prakt Chem. 18; 371
- Dennis and Johnson (1923) J. Am. Chem. Soc. 45; 1380

- | | | | |
|-------------------------------|--------|---|------------|
| Dixon | (1949) | J. Soc. Chem. and Ind. | 68; 88 |
| Dimroth O. | (1921) | Ber. dtisch. Chem. Ges. | 54; 3020 |
| Dimroth O. | (1926) | Ann. | 446 106 |
| Edelman and Bouquet | (1846) | Ann. | 60 251 |
| Edridge J.J. and Judgen S. | (1928) | J. Chem. Soc. | 1928; 989 |
| Frankland G. | (1862) | Ann. | 124 132 |
| Gerrard W. and Lappert M.F. | (1951) | J. Chem. Soc. | 1951 1020 |
| Gerrard W. and Lappert M.F. | (1952) | Chemistry and Industry | 1952 53 |
| Gerrard W. and Wheelans M.A. | (1954) | Chemistry and Industry | 1954 758 |
| Gosselin V. | (1894) | Ann. Chem. Phys. | VIII 3; 46 |
| Goubeau J. and Keller H. | (1951) | Z. anorg. u. allgem. Chem. | 267; 1 |
| Herzberg | | | |
| Joglekar M.S. and Thatte V.H. | (1936) | Z. Phys. | 98; 692 |
| Johnson and Dupine | (1936) | Compt. rendu. | 202 2086 |
| Johnson J. and Tompkins S. | (1950) | Organic Synthesis is
Collective Vol II.
p. 107. H.H. Blatt
John Wiley & Sons, N.Y. | |
| Kahovec L. | (1938) | Z. Phys. Chem. | B.40; 135 |
| Kahovec L. | (1939) | Z. Phys. Chem. | B.43; 109 |
| Kaufman A. | (1933) | German patent | 582,917 |

- Khotinsky M. and Pupjo S.L. (1929) Ukrain. Chem. J.
4; 13
- MacBeth R and Winzor (1935) J. Chem. Soc.
1935; 334
- Laubengayer A.W. and Corey R.B. (1926) J. Phys. Chem.
30; 1943
- McIntyre R. (1933) J. Chem. and Ind.
1933; 578
- Milone H. (1936) R. Accad. Sci. Torino
71; 14
- Naves Y.H. (1949) Helv. Chim. Acta
31; 414
- O'Johnner G.L. and Mace H.H. (1955) J. Am. Chem. Soc.
77; 1578
- Oetjen R.A, Kao C.L. and Randall H (1942) Rev. Sci. Instrum.
13; 515
- Pictet A. and Geleznoff A. (1913) Ber. dtsh. Chem. Ges.
33; 2221
- Pictet A and Karl G (1908) Bull. soc. chim. France
(4)3; 1123
- Pfeiffer (1927) Organische Molekulverb-
indung; Ferdinand Lake;
Stuttgart.
- Rangaswami S. and Veshadri T.H. (1942) Proc. Indian Acad. Sci.
16A; 231
- Rose H. (1856) J. Chem. Soc.
1856; 574
- Saunders and Stacey (1948) J. Chem. Soc.
1948; 1773
- Scattergood A, Miller W.H. and
Gannon J. (1945) J. Am. Chem. Soc.
67; 2150
- Schiff H. (1867) Ann. Suppl.
5; 158
- Schmidt (1928) Chem. Zeit
52; 898

- | | |
|---|---|
| Sheffield | (1936) U.S. Patents
2,050,671 |
| Snyder H.R., Kuck J.A. and
Johnson J.R. | (1938) J. Am. Chem. Soc.
60; 195. |
| Stock and Priess | (1914) Ber. Dtsch. chem. Ges.
47; 3109 |
| Sutherland H. | (1950) Private comm. |
| Taubock | (1950) Naturwiss
30; 439 |
| Thomas L.H. | (1946) J. Chem. Soc.
1946; 823 |
| Webster S.H. and Dennis L.M. | (1933) J. Am. Chem. Soc.
55; 3233 |
| Wiberg E. and Sutterlin W. | (1931) Z. Anorg.u.allgem. Chem.
202 |
| Wilson G.H. | (1939) J. Am. Chem. Soc.
61; 2303 |
| Wuyts H. and Duquesne A. | (1939) Bull. soc. chim. Belg.
48; 77 |
| Wolfrom H.L, Mahan W.W, Morgan
P.W, and Johnson G.F. | (1941) J. Am. Chem. Soc.
63; 1248 |

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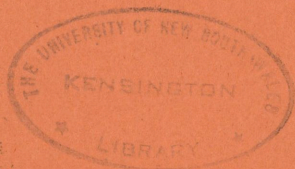
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**THE ESSENTIAL OIL OF *MYOPORUM CRASSIFOLIUM*
FORST.**

By K. G. O'BRIEN, A. R. PENFOLD, and R. L. WERNER



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By K. G. O'BRIEN, A. R. PENFOLD, and R. L. WERNER

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By K. G. O'BRIEN,* A. R. PENFOLD,† and R. L. WERNER*

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Summary

The essential oil of *Myoporum crassifolium* Forst., a shrub endemic to New Caledonia, is shown to consist principally of a tertiary sesquiterpene alcohol which is either identical with or isomeric with synthetic bisabolol.

I. INTRODUCTION

The essential oil of *Myoporum crassifolium* Forst. was first examined by Messrs. Plaimar Ltd. (1930), purely in relation to its possible application to the perfumery and essential oil industry. No indication was given as to the nature of the chemical constituents.

In 1941, a sample of the wood was received at the Museum of Applied Arts and Sciences, Sydney, from New Caledonia, where it is known as Anime or Anyne wood, from which the essential oil was obtained by steam distillation. A preliminary investigation indicated that the principal constituent of the oil was probably a sesquiterpene alcohol of high laevorotation.

Further examination of the oil was deferred until 1947 when the investigation was reopened in order to establish the chemical identity of the principal constituent.

Examination of the fractions obtained after repeated fractionation under reduced pressure showed that the majority possessed similar constants, the density, optical rotation, refractive index, and solubility in alcohol (80 per cent.) being notably high in each. The fractions of similar physical properties were mixed. Elementary analysis and molecular weight estimations showed the molecular formula to be $C_{15}H_{26}O$.

Dehydrogenation with platinum/carbon catalyst or sulphur gave hydrocarbons which failed to give picrate derivatives, indicating the possible absence of bi- or tricyclic hydrocarbon skeletons.

On hydrogenation under the conditions of Ruzicka and van Veen (1929) it was found that the equivalent of three molecules of hydrogen was absorbed. Such a phenomenon could not be due to the presence of three double bonds in the alcohol since such a compound would not be capable of forming bisabolene trihydrochloride or trihydrobromide and can conceivably only be due to hydrogenolysis occurring during the hydrogenation. The absorption of three molecules of hydrogen by the hydrocarbon recovered from the trihydrochloride confirms these results and excludes the possibility of the presence of a cyclopropane ring.

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The ease with which the alcohol was dehydrated on treatment with formic acid (100 per cent.) or on azeotropic distillation with benzene in the presence of a little concentrated sulphuric acid, indicated that the hydroxyl group was most likely in the tertiary position. This would account for the lack of derivative formation with the usual alcohol reagents.

The phenylazophenylurethane formed orange needles, m.p. 103–103.5 °C.

The alcohol gave a positive test for unsaturation when treated with bromine in carbon tetrachloride and potassium permanganate in acetone respectively.

On treatment of the alcohol with hydrogen chloride, an optically-inactive crystalline derivative of molecular composition $C_{15}H_{27}Cl_3$, m.p. 79–80 °C., was formed, apparently identical with bisabolene trihydrochloride prepared by

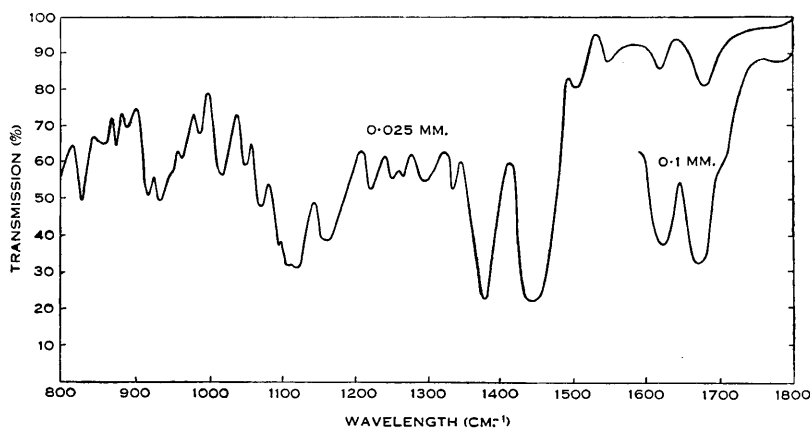


Fig. 1.—The infra-red spectrum of the tertiary alcohol from *M. crassifolium*.

Ruzicka and Liguori (1931), and undepressed in m.p. on mixing with an authentic sample. On treatment of this trihydrochloride with sodium acetate in glacial acetic acid, a hydrocarbon was obtained with physical properties similar to those of bisabolene (cf. Ruzicka and Capato 1925). On treatment of this hydrocarbon with hydrogen chloride, a trihydrochloride was obtained with m.p. 79–80 °C., which was not depressed on mixing with the original trihydrochloride. The hydrocarbon on treatment with hydrogen bromide formed a crystalline trihydrobromide, m.p. 84 °C., identical with that recorded for bisabolene trihydrobromide. It was concluded from these results that the alcohol was a tertiary sesquiterpene alcohol containing two double bonds.

It has previously been demonstrated that *isopropylidene* and *isopropenyl* groups give unique infra-red absorption bands which may be used to detect their presence (Thompson and Torkington 1945; Rasmussen and Brattain 1947; Barnard *et al.* (1950). Thus an *isopropylidene* group gives rise to two characteristic bands, one about 1670 cm^{-1} , due to the stretching of the $C=C$ linkage and the other in the region from 820–840 cm^{-1} due to the out-of-plane vibration of the hydrogen atom. Due to the symmetrical nature of the group it is found that both of these bands are of only medium intensity. On the other hand the *isopropenyl* group gives rise to strong bands at about 1640 and 890 cm^{-1} ,

The intensity of the isopropenyl band near 890 cm.^{-1} is in fact so high that as little as 1 per cent. of a typical compound containing an *isopropenyl* group can be detected in a mixture using a cell thickness of only 0.025 mm. (Werner and Sutherland 1952).

The alcohol (Fig. 1) has a band of medium intensity at 828 cm.^{-1} , using a cell of thickness 0.025 mm. This suggests the presence of an *isopropylidene*-type group $R_1R_2C=CR_3H$, which is confirmed by the presence of a second band at 1674 cm.^{-1} , also of medium intensity. The actual values found are close to those recorded by Barnard *et al.* (*loc. cit.*) for other terpenes containing *isopropylidene* groups.

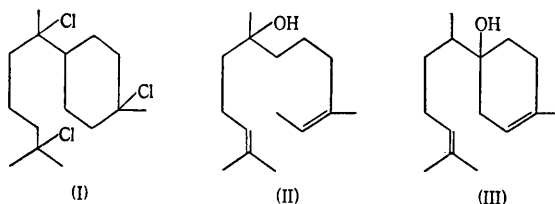
On the other hand, a careful examination of the spectrum in the region close to 890 cm.^{-1} reveals only weak bands, although at the cell thickness used, an *isopropenyl*-type group $R_1R_2C=CH_2$ would have been expected to give a strong band. There is, in the 6μ -region, a band of medium intensity only at 1619 cm.^{-1} , but this is lower than would be expected for an *isopropenyl* group (normally about 1645 cm.^{-1}) and is in any case too weak. Similar cases in which overtone and combination bands occur in this region are cited by Barnard *et al.* (*loc. cit.*).

It should be noted that the infra-red spectra disposes of any possibility of conjugation of double bonds for such would have lowered the $C=C$ stretching frequencies to about 1600 cm.^{-1} .

In proposing a formula for the alcohol we must therefore take into account the following points:

- (i) The facile conversion of the alcohol into bisabolene trihydrochloride (I).
- (ii) The optical activity of the alcohol in contrast to the inactivity of the bisabolene trihydrochloride.
- (iii) The nature of the unsaturation in the alcohol as indicated by infra-red spectra, which excludes conjugation and indicates two *isopropylidene*-type groups.

Only two formulae (II and III) will satisfy these conditions of which II



is the accepted formula for bisabolol.

II. EXPERIMENTAL

(a) *Distillation*.—The Anyme wood oil (250 ml.), on fractionation at 12 mm. through a 30 cm. Vigreux column, gave the fractions presented in Table 1.

Fractions 8–14 were mixed and used in the following experiments unless otherwise stated.

(b) *Preliminary Examination*.—(i) *Unsaturation*. Solutions of bromine tetrachloride and potassium permanganate in acetone were immediately decolourized.

(ii) *Test for Alcohols.* On treatment of the oil (1 ml.) with a small pellet of sodium only a slight evolution of hydrogen was obtained in the cold. Probably a secondary or tertiary alcohol. On treatment of the oil (1 ml.) with an equal volume of formic acid (100%) the oil was initially immiscible, but on warming a purple coloured homogeneous solution was formed, which soon separated into two layers—a reaction indicative of tertiary alcohols.

TABLE 1

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}	α_D^{20}
1	4	140–142	1.4934	–42
2	6	144–148	1.4940	–45
3	7	148–151	1.4944	–47
4	12	151–154	1.4964	–49
5	11	154–156	1.4964	–51
6	14	155–156	1.4975	–53
7	7	156–157	1.4977	–54
8	9	157	1.4977	–57
9	17	157	1.4976	–60
10	23	157	1.4976	–60
11	35	157	1.4976	–61
12	32	157	1.4976	–63
13	32	157	1.4976	–62
14	35	157	1.4976	–61
15	6	157	1.4976	—

(c) *Derivatives.*—(i) The alcohol did not react when heated with phthalic anhydride, either alone for 2 hr., or in benzene and pyridine respectively for 8 hr. No derivatives were formed on heating the alcohol with xenylcarbimide or on treatment with naphthylisocyanate, phenyl isocyanate, or benzoyl chloride under standard conditions.

(ii) *Dehydrogenation.* Treatment of the oil with either sulphur or platinum/carbon dehydrogenation catalyst gave products which failed to form picrate derivatives.

(iii) *Trihydrochloride Formation.* The oil (5 g.) was dissolved in anhydrous ether (5 ml.) and hydrogen chloride gas passed into the solution cooled to -15 – -20 °C. until the reaction mixture set to a solid red crystalline mass. The crystals were drained on a tile and recrystallized from ethyl acetate in the presence of carbon to give white crystalline flakes, m.p. 79.5 – 80 °C. Mixed m.p. with an authentic sample of bisabolene trihydrochloride showed no depression (Found: C, 57.55; H, 8.44; Cl, 33.72%. Calc. for $C_{15}H_2Cl_3$: C, 57.41; H, 8.61; Cl, 33.90%).

(iv) *Conversion of Trihydrochloride to Hydrocarbon.* The hydrochloride (15 g.) prepared as above was heated with anhydrous sodium acetate (45 g.) and glacial acetic acid (150 ml.) for 8 hr. on a steam-bath. The resultant oil was poured into water, extracted with ether, the extract washed with sodium carbonate solution, and finally with water. After drying over anhydrous sodium sulphate and removal of the solvent, the resultant oil (8 g., n_D^{20} 1.4875) was fractionated at 12 mm. to give the data of Table 2.

On treatment of fraction 1 (1 ml.) with hydrogen chloride, the trihydrochloride was reformed (m.p. 79 – 80 °C.) with the mixed m.p. unchanged.

(v) *Dehydration.* The oil (22 g.) was refluxed for 3 hr. in a Dean and Stark apparatus with benzene (100 ml.) containing concentrated sulphuric acid (0.5 ml.) until there was no further evolution of water (1.7 ml.). The benzene solution was washed first with sodium carbonate

solution and finally with water, dried over sodium sulphate, and the solvent removed. The residual oil (22 ml.) was fractionated at 12 mm. The results are presented in Table 3.

(vi) *Residue*. Fraction 3 formed the trihydrochloride with mixed m.p. undepressed.

(d) *Final Distillation and Examination*.—In the course of this investigation two efficient fractionation columns, namely the Lecky and Ewell (1940) type and the Bower and Cooke (1942) pattern, were acquired.

TABLE 2

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}	d_{15}^{15}
1	5	to 136	1.4915	0.8755
2	—	136–138	1.4915	0.8755
3	2	138	1.4860	—

Advantage was taken of their introduction to collect all the fractions and any remaining original Anyme wood oil, and to fractionate the mixture further through the Lecky and Ewell column, and finally through the Bower and Cooke column, in an endeavour to obtain increased purity of the alcohol fraction. The results of the final distillation are given in Table 4.

In view of the similarity in physical properties fractions 9–15 inclusive were mixed and used in the following examination, unless otherwise stated.

Molecular weight, determined by cryoscopic method, using benzene solvent (Found : 226, 219, 229. Calc. for $C_{15}H_{26}O$: 222). Combustion analysis (Found C, 80.94; H, 11.52%. Calc. for $C_{15}H_{26}O$: C, 81.02; H, 11.78%).

TABLE 3

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}
1	5.5	to 132	1.4962
2	8.5	132–134	1.4962
3	4.0	134–137	1.4962

(i) *Trihydromide*. The oil (5 ml.) was dissolved in anhydrous ether (5 ml.) and hydrogen bromide passed into the solution cooled to -20°C . A red solid crystalline mass formed after approximately half an hour. On repeated recrystallization from ethyl acetate and a little carbon, white crystalline flakes were obtained with constant melting point of 84°C . (corresponds to that recorded for bisabolene trihydrobromide).

(ii) *Dehydration with Formic Acid*. The oil (30 ml.) was refluxed for 3 hr. with formic acid (150 ml. of 98–100%). The reaction product was poured into water, extracted with ether, and washed with sodium carbonate solution and water. The dried ethereal extract yielded an oily residue which was distilled at 12 mm.

A mixture of 1.0 ml. each of fractions 1 and 4 (Table 5) gave the trihydrochloride, m.p. $79-80^{\circ}\text{C}$., undepressed on mixing with an authentic sample.

(iii) The oil (0.5 g.) was treated with excess *p*-phenylazophenylisocyanate in the presence of excess pyridine at 0 °C. for several hours and then at room temperature for 2 days.

TABLE 4

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{25}	α_D^{20}	d_4^{25}
1	4	to 125	1.4970	-36	0.0000
2	1	125	1.4985	-15	0.9703
3	4	150	1.5042	-33	0.9600
4	2	150-155	1.5013	-41	0.9888
5	7	155	1.5010	-44	0.9754
6	10	155	1.4975	-64	0.9537
7	11	155	1.4969	-66	0.9426
8	10	155	1.4970	-66.5	0.9404
9	10	155	1.4966	-67	0.9385
10	10	155	1.4970	-66.8	0.9376
11	10	155	1.4970	-67.1	0.9376
12	10	155	1.4972	-67.6	0.9377
13	10	155	1.4970	-67.6	0.9377
14	10	155	1.4970	-67.6	0.9376
15	10	155	1.4972	-67.6	0.9376

The reaction mixture was taken up in light petroleum, washed with water, filtered free of the insoluble urea, and then the aminoazobenzene removed by washing with dilute hydrochloric acid. The light petroleum solution was dried over anhydrous sodium sulphate and then allowed to evaporate leaving an orange-red oil which crystallized in the refrigerator.

TABLE 5

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}
1	1	to 118	1.4976
2	5	118-122	1.4984
3	10	122-124	1.4951
4	7	124	1.5020

The orange-red oil was crystallized from light petroleum (b.p. 30-40 °C.) as orange crystals, m.p. 100-102 °C. Recrystallization from light petroleum (b.p. 60-80 °C.) yielded rosettes of orange needles of maximum m.p. 103-103.5 °C. Combustion analysis (Found: C, 74.8; H, 7.8%. Calc. for $C_{28}H_{35}O_3N_3$: C, 75.4; H, 7.92%).

(iv) *Hydrogenation of the Alcohol.* Approximately 0.2 g. of the alcohol was dissolved in 10 ml. of the solvent in the presence of 0.05 g. of Adam's catalyst and the whole shaken at room temperature and pressure until the absorption of hydrogen was complete (Found: 0.1810 g. in 10 ml. cyclohexane absorbed 54 ml. hydrogen at N.T.P. Calc. for $C_{15}H_{26}O$ containing two

double bonds 36.5 ml. hydrogen at N.T.P. Found: 0.2006 g. in 10 ml. acetic acid absorbed 68 ml. hydrogen at N.T.P. Calc. 61.8 ml. hydrogen at N.T.P.).

(v) *Hydrogenation of Hydrocarbon Regenerated from Trihydrochloride.* Approximately 0.2 g. of the hydrocarbon fraction 2 regenerated from the trihydrochloride was hydrogenated in 10 ml. of solvent, using cyclohexane in the first instance and glacial acetic acid in the second case, with 0.05 g. of Adam's catalyst (Found: 0.1511 g. hydrocarbon absorbed 47 ml. hydrogen at N.T.P. Calc. for $C_{15}H_{24}$ containing three double bonds 51.7 ml. hydrogen at N.T.P. Found: 0.2800 g. hydrocarbon absorbed 88 ml. hydrogen at N.T.P. Calc. 92.3 ml. hydrogen absorbed at N.T.P.).

(e) *Infra-red Spectrum Analysis.*—The infra-red spectrum of the alcohol was recorded using a Perkin-Elmer model 12C single beam instrument with sodium chloride optics. This instrument was calibrated against bands of water vapour in the 6μ -region and ammonia in the 10 – 12μ -region (Oetjen, Kao, and Randall 1942). Comparison with the spectra used for the calibration indicated that the instrument resolved 6 cm.^{-1} at 1700 cm.^{-1} and 3 cm.^{-1} at 1000 cm.^{-1} . The material which was examined in demountable cells with rock-salt windows, was purified by vacuum distillation immediately prior to running the spectrum.

III. ACKNOWLEDGMENTS

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IV. REFERENCES

- BARNARD, D., BATEMAN, L., HARDING, A. J., KOCH, H. P., SHEPPARD, N., and SUTHERLAND, G. B. B. M. (1950).—*J. Chem. Soc.* **1950**: 915.
BOWER, J. R., and COOKE, L. M. (1942).—*Industr. Engng. Chem. (Anal.)* **15**: 290.
LECKY, H. S., and EWELL, R. H. (1940).—*Industr. Engng. Chem. (Anal.)* **12**: 544.
MESSRS. PLAIMAR PTY. LTD. (1930).—*Perfum. Essent. Oil Rec.* **21**: 238.
OETJEN, R. A., KAO, C. L., and RANDALL, H. M. (1942).—*Rev. Sci. Instrum.* **13**: 515.
RASMUSSEN, R. S., and BRATTAIN, R. R. (1947).—*J. Chem. Phys.* **15**: 120, 131, 135.
RUZICKA, L., and CAPATO, E. (1925).—*Helv. Chim. Acta* **8**: 263.
RUZICKA, L., and LIGUORI, M. (1931).—*Helv. Chim. Acta* **15**: 3.
RUZICKA, L., and VAN VEEN, A. (1929).—*Liebigs Ann.* **468**: 133.
THOMPSON, H. W., and TORKINGTON, P. (1945).—*Trans. Faraday Soc.* **41**: 246.
WERNER, R. L., and SUTHERLAND, M. (1952).—*J. Amer. Chem. Soc.* **74**: 2688.

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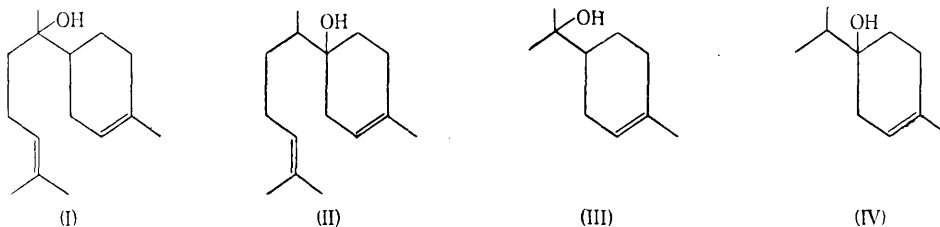
[Manuscript received April 8, 1954]

Summary

The principal sesquiterpene alcohol (anymol) of the wood oil of *Myoporum crassifolium* Forst. is a stereoisomer of bisabolol. A convenient method of detecting methyl groups attached to the hydroxyl-bearing carbon of tertiary alcohols involves the infra-red examination of the pyrolysate of the phenylazophenylurethane for bands due to $=CH_2$.

I. INTRODUCTION

A decision between formulae I and II put forward by O'Brien, Penfold, and Werner (1953) for the principal sesquiterpene alcohol (here called anymol) from the essential oil of the wood of *Myoporum crassifolium* Forst. was prevented by exhaustion of the original supply of oil and the apparent impossibility of



obtaining a further quantity. This difficulty has now been overcome by making use of the only crystalline derivative of anymol that had been obtained, namely, the phenylazophenylurethane, to determine the location of the hydroxyl thus leading to formula I for anymol.

α -Terpineol (III) and terpinen-4-ol (IV) may be regarded as model substances corresponding to the two possibilities (I and II) for the structure of anymol. The phenylazophenylurethanes ("azourethanes") (Davenport and Sutherland 1950) of III and IV decompose with vigorous gas evolution above 170 °C yielding a distillate of terpenes and a residue which is principally aminoazobenzene. This reaction is analogous to the pyrolysis of methyl xanthates (O'Connor and Nace 1952) and may well proceed by a similar mechanism with the resultant advantage of freedom from rearrangements. The advantage of phenylisocyanate as a dehydrating agent in this respect has been noted (Bacon and Farmer 1937).

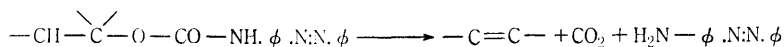
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An alternative manner of decomposition is exhibited by phenylurethanes derived from phenols (Leuckart 1890; Hoshino, Mukaiyama, and Hoshino 1952) or primary alcohols (Schweitzer 1947). In the compounds under consideration, this reaction, which would lead to the regeneration of the alcohol and phenylazophenylisocyanate, occurs to a negligible extent, since the pyrolysate shows very weak absorption in the OH stretching region by infra-red examination.

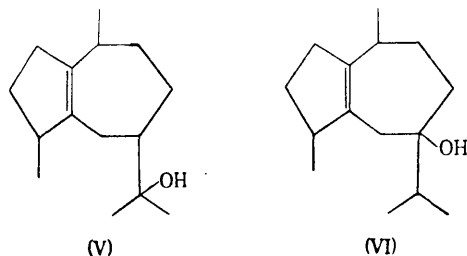


By pyrolysing about 50 mg of azourethane under reduced pressure at 200–210 °C in close proximity to a water cooled finger condenser, a yellow oily condensate is obtained which on cooling deposits crystals of aminoazobenzene but yields sufficient hydrocarbon for infra-red examination. The pyrolysate of the azourethane of III showed bands at 1644 and 887 cm^{-1} , positions expected for $\text{R}_2\text{C}=\text{CH}_2$ absorption (for references see O'Brien, Penfold, and Werner 1953). Also observed were bands at 836 cm^{-1} and another stronger band at 797 cm^{-1} (Werner and Lark 1954) presumably due to out-of-plane bending of the hydrogen attached to the double bond in the ring. On the other hand, the pyrolysate from the azourethane of IV showed the 1660 and 825 cm^{-1} bands derived from $\text{R}_2\text{C}=\text{CRH}$ and no absorption due to the $\text{R}_2\text{C}=\text{CH}_2$ arrangement. The technique thus appears suitable for discriminating between I and II. The pyrolysate from the azourethane of anymol showed distinct bands at 1640 and 888 cm^{-1} which indicates clearly the presence of $\text{R}_2\text{C}=\text{CH}_2$ in the hydrocarbons and establishes the α -terpineol-like structure I for anymol.

The data recorded in Table 4 of the earlier paper shows that the anyme oil fractionated in an effective type of still yielded six consecutive fractions of the sesquiterpene alcohol of almost constant boiling point, refractive index, density, and optical rotation. It is probable, therefore, that this alcohol is only one of the two diastereoisomers represented by formula I, whereas the bisabolols of Ruzicka and Liguori (1932) and Ruzicka and Capato (1925) must be regarded as mixtures of diastereoisomers which were neither separated nor characterized. Naves has shown the presence of a bisabolol in aqueous layer from neroli oil (Naves 1934) and in cabreuva oil (Naves 1947) by isolating bisabolene trihydrochloride in each case. Similarly Seidel, Müller, and Schinz (1944) have obtained evidence for a bisabolol in French lavender oil. Only in the present instance has an apparently pure compound been isolated and the name anymol is thus appropriate to the particular diastereoisomer isolated from anyme oil and characterized by physical constants and the phenylazophenylurethane of m.p. 103–103.5 °C.

The technique described for detecting the grouping $\text{CH}_3-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{OH}$ has been applied also to the sesquiterpene alcohol guaiol and bands at 1643 and 887 cm^{-1} were observed in the pyrolysate. This supports V proposed by Plattner and Lemay (1940).

Structure VI, which accommodates more satisfactorily the products of ozonolysis and of chromic acid oxidation (Plattner and Magyar 1942) of crude dihydroguaiene, is excluded.



II. EXPERIMENTAL

(a) *Pyrolysis*.—Terpinen-4-ol phenylazophenylurethane (50.7 mg) was placed in a side-arm test tube fitted with a water cooled finger condenser reaching to within 1 cm of the sample. The pyrolysis was carried out under a pressure of 100 mm by immersing the bottom of the test tube in an oil-bath at 200–210 °C. Bubbling ceased after about 2 min and the apparatus was then withdrawn from the oil-bath. When the crystallization of the aminoazobenzene on the condenser appeared to be complete, the drop of yellow oil hanging from the tip of the condenser was collected and sealed into a capillary tube. The yield of aminoazobenzene saturated hydrocarbons was 10.5 mg, 57% of the theoretical yield, not allowing for dissolved aminoazobenzene.

α -Terpineol phenylazophenylurethane (87.2 mg) similarly pyrolysed for 4 min yielded 8.5 mg of yellow oil.

Guaiol phenylazophenylurethane (56 mg) (G. Lahey and M. D. Sutherland, unpublished data) pyrolysed under 50 mm pressure at 200–220 °C for 5 min gave an oily sludge from which sufficient oil for infra-red examination was obtained by touching with a capillary.

The phenylazophenylurethane (m.p. 100–102 °C; 55 mg) of the sesquiterpene alcohol from *M. crassifolium* similarly treated gave an oily sludge from which the oil could not be drawn off into the capillary. The difficulty was overcome by washing the oil from the sludge with about 2 ml of light petroleum (b.p. <40 °C) into a clean side-arm test tube. After removal of the solvent, the residue was partially distilled at 170 °C and 50 mm pressure onto a clean finger condenser as a drop of clear yellow oil.

(b) *Infra-red Spectrum Analysis*.—The infra-red spectrum was obtained on a Perkin Elmer model 12C spectrometer equipped with 13 cycles amplifier and NaCl optics. Calibration was effected in the usual manner against the data for water vapour and ammonia tabulated by Oetjen, Kao, and Randall (1942).

III. REFERENCES

- BACON, R. S. R., and FARMER, S. H. (1937).—*J. Chem. Soc.* **1937**: 1071.
 DAVENPORT, J. B., and SUTHERLAND, M. D. (1950).—Pap. Dep. Chem. Univ. Qd., Vol. 1, No. 39.
 HOSHINO, T., MUKAIYAMA, T., and HOSHINO, H. (1952).—*Bull. Chem. Soc. Japan* **25**: 396.
 LEUCKART, R. (1890).—*J. Prakt. Chem.* **41**: 318.
 NAVES, Y-R. (1934).—*Parfums de Fr.* **12**: 61.
 NAVES, Y-R. (1947).—*Helv. Chim. Acta* **30**: 278.
 O'BRIEN, K. G., PENFOLD, A. R., and WERNER, R. L. (1953).—*Aust. J. Chem.* **6**: 166.
 O'CONNOR, S. L., and NACE, H. R. (1952).—*J. Amer. Chem. Soc.* **74**: 5454.
 OETJEN, R. A., KAO, C. L., and RANDALL, H. M. (1942).—*Rev. Sci. Instrum.* **13**: 515.
 PLATTNER, PL. A., and LEMAY, L. (1940).—*Helv. Chim. Acta* **23**: 897.
 PLATTNER, PL. A., and MAGYAR, G. (1942).—*Helv. Chim. Acta* **25**: 581.
 RUZICKA, L., and CAPATO, E. (1925).—*Helv. Chim. Acta* **8**: 259.
 RUZICKA, L., and LIGUORI, M. (1932).—*Helv. Chim. Acta* **15**: 3.
 SCHWEITZER, C. S. (1946).—U.S. Pat. 2,409,712 (Oct. 22). (*Chem. Abstr.* **41**: 1239 (1947).)
 SEIDEL, C. R., MÜLLER, P. H., and SCHINZ, H. (1944).—*Helv. Chim. Acta* **27**: 738.
 WERNER, R. L., and LARK, P. D. (1954).—*J. Chem. Soc.* **1954**: 1152.

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There appears to be little doubt that the Diels-Alder reaction does not take place with aromatic rings having a high degree of "aromatic character" except in the special cases where a double bond is conjugated with the ring. The polycyclic aromatic hydrocarbons which undergo the reaction—sometimes with unfavourable equilibria—contain either activated *meso* positions as in anthracene or a relatively fixed and sterically favourable system of double bonds as in perylene. The simple aromatics which react normally are limited to a few highly substituted thiophenes and furan and its derivatives, in which case again the reaction is markedly reversible.

On this view it seemed advisable to investigate a statement by Norton (1942) in a review of the Diels-Alder reaction that a benzene ring of 9, 10-anthraquinone can act as a diene in the reaction and can undergo 1, 4-addition of maleic anhydride. Such a reaction seems unlikely, particularly in view of the similar electron-deficient nature of the benzene rings of anthraquinone and the double bond of maleic anhydride. Norton quotes as authority a paper by Diels and Alder (1929) to which is attributed also an unlikely proof of the structure of the adduct. Perusal of this paper, however, fails to reveal any mention of adduct formation with anthraquinone, and as far as we can discover the subject is not mentioned in any of the works of Diels and Alder. Norton refers also to an observation by Morrell and Samuels (1932), who, in an account of an unrelated investigation, briefly mention that no reaction takes place between maleic anhydride and anthraquinone. These authors make no reference to any previous work on the subject.

In view of the theoretical interest of such a reaction, the following experiments were undertaken in an attempt to isolate an adduct. A range of temperatures was employed since equilibria in adduct formation are considerably affected by temperature. (Bachmann and Kloetzel, 1938.)

- (1) A solution of anthraquinone (2 g.) and maleic anhydride (10 g., molar ratio 10 : 1) in benzene was refluxed for eight hours.
- (2) A solution of anthraquinone (2 g.) and maleic anhydride (10 g.) in nitrobenzene was refluxed for two hours.
- (3) A melt of anthraquinone (2 g.) and maleic anhydride (10 g.) was held at 200 for two hours.

In all cases both the anthraquinone and the maleic anhydride (as maleic acid) were recovered almost quantitatively and no indications of adduct formation could be found. It is concluded, therefore, that anthraquinone does not react with maleic anhydride in the Diels-Alder reaction.

REFERENCES.

- Bachmann and Kloetzel, 1938. *J. Amer. chem. Soc.*, **60**, 481.
Diels and Alder, 1929. *Ber. dtsh. chem. Ges.*, **62**, 2337.
Morrell and Samuels, 1932. *J. chem. Soc.*, 1932, 2251.
Norton, 1942. *Chemical Reviews*, **31**, 458.
Gascoigne and O'Brien, 1940. *THIS JOURNAL*, **74**, 353, 359.

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