The PREPARATION, ROTATION, and DECOMPOSITION of MENTHYL and BORNYL ESTERS of BENZENESULPHONIC, NAPHTHALENE-α-SULPHONIC, and NAPHTHALENE-β-SULPHONIC ACIDS.

A Thesis

for the Degree of Ph.D.,

by

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I N D E X.

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PART I.

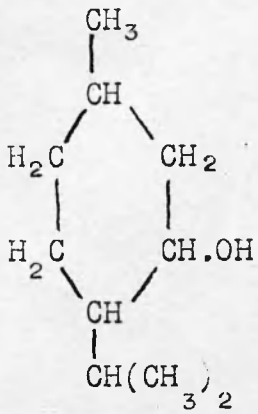
PREPARATION AND DECOMPOSITION OF MENTHYL AND BORNYL ESTERS OF BENZENESULPHONIC, NAPHTHALENE-α-SULPHONIC AND NAPHTHALENE-β-SULPHONIC ACIDS.

INTRODUCTION.

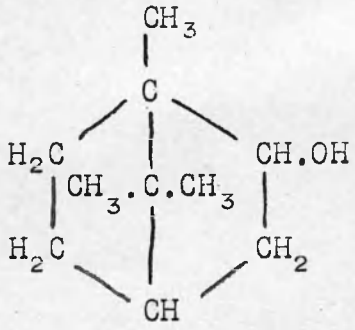
This work arose from the discovery by Patterson and Frew (J., 1906, 89, 332), while engaged in the examination of the optical rotation of menthyl benzenesulphonate and menthyl naphthalene-β-sulphonate, that these esters decompose in the homogeneous state at temperatures just above their melting points, that is, at about 84° and 120° respectively, with the separation of a dark coloured solid, the other product, or products, being liquid. They also noticed that the naphthalene-β-sulphonic ester decomposed in nitrobenzene solution some degrees below its melting point (at 100°). This was unexpected since many other menthyl esters are much more stable, and can be distilled at considerably higher temperatures without decomposition. Examples of such esters are those of the homologous series of acids from formic to octoic (Tschugaeff, 1898, A., (ii), 275), of halogen substituted acetic and propionic acids (Cohen, 1911, T., 1058), of benzoic, o-, m-, and p-toluic, phenyl acetic, and phenyl propionic acids (Tschugaeff, 1898, A., (ii), 495), of the isomeric chloro and dichloro benzoic acids (Cohen and Briggs, 1903, T., 1213). All of these boil at temperatures considerably above 100°, under reduced pressure, many being above 200° at 12 mm. In

the case of three of the isomeric dichlorobenzoic esters, namely the 2:3, 2:5, and the 3:4 esters, slight decomposition into acid was observed at the beginning of the distillation, but the ester was obtained pure after filtering off the solid. Apart from this, the only other menthyl ester showing similar behaviour that can be traced in the literature is menthyl methyl xanthogenate (Tschugaeff, J. Russ. Phys. Chem. Soc., 1903, 35, 1116 - 1179), of structure $C_{10}H_{19}.O.CS_2.Me$: that is to say, another compound containing sulphur in the acid grouping. It therefore seemed of interest to investigate the nature of the decomposition and the varied conditions under which it may be carried out.

Seeing that there is some similarity in the structures of menthol and borneol, the main difference being the linking up of one carbon atom through the propyl group attached to it with the carbon atom in the para position, to give a dicyclic terpene,



Menthol



Borneol

it seemed likely that the corresponding sulphonic esters of this terpenic alcohol would show similar behaviour to that found for the menthyl esters. This seemed the more possible since bornyl methyl xanthogenate decomposes in the same manner as menthyl methyl xanthogenate (Tschugaeff, J. Russ. Phys. Chem. Soc., 1904, 36, 988 - 1052), while the other bornyl esters which do not contain sulphur in the acid group can be distilled at high temperatures in vacuo without any decomposition being observed, and thus behave like the corresponding menthyl esters. Such are those of the homologous series from formic to valeric acid (Tschugaeff, 1898, A., (ii), 495), of halogen substituted acetic and butyric acids (Minguin and de Bollement, C. r., 1902, 134, 608), of benzoic and of salicylic acids (Chemische Fabrik von Heyden (D. R. P., 175097), A., 1907, (i), 429).

PREPARATION OF THE ESTERS.

The same general method was used in the case of all these compounds, both menthyl and bornyl, namely the action of the acid chloride on the terpenic alcohol in cold pyridine solution according to the equation

$$C_{10}H_x\,OH + Cl.SO_2.R \longrightarrow C_{10}H_x.O\cdot SO_2\cdot R + HCl$$

(where x is either 17 or 19, and R is the benzene or naphthalene nucleus). Only slight modifications were necessary, and these will be described in connection with the individual esters.

Preparation of l-Menthyl Benzenesulphonate.

18·7 gms. of pure l-menthol were dissolved in 60 gms. of pure pyridine, and the whole cooled in a freezing mixture to 0°. 21·1 gms. of benzenesulphonic chloride were then added very slowly with constant stirring, considerable rise of temperature being avoided. After some time crystals appeared and became very numerous on stirring. The whole was allowed to stand for three or four hours, and then a large quantity of water was added. The oil which separated solidified immediately, and was filtered and dried.

The crude product thus obtained crystallised readily from methyl or ethyl alcohol in stellate masses

of needle crystals. Even when the solution was moderately dilute the whole set to a solid mass on cooling, from which the solvent had to be removed by draining and pressing at the pump, and finally on porous plate in a vacuum desiccator over sulphuric acid. Two or three crystallisations were sufficient to remove all uncombined menthol. The pure ester then melted at 79°, and had rotation in benzene solution at c = 3 of $[\alpha]^{17.5}_{5461} = -74.06$. The yield was 10·5 gms., or 30% (calculated in the amount of menthol used).

Preparation of l-Menthyl Naphthalene-β-sulphonate.

18·7 gms. of menthol were dissolved in 90 gms. of pure pyridine and cooled as before to 0°. 27·2 gms. of naphthalene-β-sulphonic chloride were added slowly with stirring, the temperature not being allowed to rise considerably. This dissolved in the pyridine and after some time crystals appeared and became more numerous on stirring. The whole was then allowed to stand in the freezing mixture for five hours, and a large quantity of water added as before. The oil separated and solidified immediately and was filtered and dried.

The crude product crystallised well from

ethyl alcohol in which it is fairly insoluble in the cold, and separation from the uncombined menthol was practically complete in one crystallisation. The pure ester formed fine white crystals melting at 114° and showing a rotation in benzene solution at c = 1 of $[\alpha]_{5461}^{17.5} = -59.3$. The yield was 30 gms., or 75% (calculated on menthol used).

Preparation of l-Menthyl Naphthalene-α-sulphonate.

This ester had not been prepared previously but was prepared in exactly the same way as that described for the naphthalene-β-sulphonate, using the same quantities of the reacting materials. The crude ester also crystallised from ethyl alcohol in which it is a little more soluble than the β-ester. Two crystallisations, however, sufficed to free it from uncombined menthol, when it was obtained as fine white crystals slightly elongated, but not needle-shaped, melting with decomposition at 116·5, and had rotation in benzene solution at c = 1 of $[\alpha]_{5461}^{17.5} = -93.25$. The yield was about 11·5 gms., or 29%.

Estimation of Sulphur. (Fusion Method).

0·4182 gms. of compound gave 0·2795 gms. of $BaSO_4$. i.e., S = 9·18%.

0·4120 gms. of compound gave 0·2836 gms. of $BaSO_4$. i.e., S = 9·18%.

$C_{20}H_{26}SO_3$ requires S = 9·26%.

Preparation of l-Bornyl Benzenesulphonate.

Pure l-borneol (18·5 gms.), recrystallised from petroleum ether (M.P. 203°, and rotation in benzene solution at c = 5·25 of $[\alpha]^{17}_{5461}$ = -42·81), was dissolved in pyridine (60 gms.) and cooled in an efficient freezing mixture to 0°. Benzenesulphonic chloride (21·1 gms.) was then added very slowly with constant stirring, care being taken to prevent the temperature rising above 3°. After a little time crystals began to separate and on continued stirring became very abundant. The whole was then allowed to stand for three to four hours in the freezing mixture and then a large quantity of water was added and the whole allowed to stand till the oil which first separated solidified. This should occur in about an hour. It was then filtered and dried. In several preparations the oil could not be made to solidify in contact with the water. It was then extracted with ether or benzene, the extract dried with $CaCl_2$, the solvent partially removed by evaporation in air, and finally in a vacuum desiccator over H_2SO_4, when the residue solidified to a pale yellow crystalline mass.

l-bornyl benzenesulphonate is very soluble in all common organic solvents, but may be freed from uncombined borneol by crystallising from light petroleum ether, when it forms fine white crystals similar in form to those of the menthyl naphthalenesulphonates, melting at 52°, and showing a rotation in benzene solution at c = 2·5 of $[\alpha]^{19^\circ}_{5461} = -22{\cdot}40$, and in alcohol at the same concentration of $[\alpha]^{17{\cdot}5}_{5461} = -22{\cdot}00$. Several crystallisations were necessary to obtain the substance free from borneol, the yield of pure product being about 25% (calculated on the borneol used).

Estimation of Sulphur. (Fusion Method).

0.4170 gms. of compound gave 0·3240 gms. of $BaSO_4$. i.e., S = 10·67%.

0·4176 gms. of compound gave 0·3252 gms. of $BaSO_4$. i.e., S = 10·69%.

$C_{16}H_{22}SO_3$ requires S = 10·95%.

Preparation of l-Bornyl Naphthalene-β-sulphonate.

Pure l-borneol (18·50 gms.) was dissolved in pure pyridine (90 gms.) and cooled in a freezing mixture to 0°. Naphthalene-β-sulphonic chloride (27·2 gms.) was then added gradually with stirring, considerable rise

in the temperature being avoided, when it dissolved in the pyridine. After standing for some time crystals separated. The whole was allowed to stand for five hours and a large quantity of water added. The oil which separated solidified after a short time (usually about half-an-hour), and was filtered and dried. In no case was it found impossible to solidify the oil while in contact with the water.

This ester is soluble in all the common solvents, but may be recrystallised from methyl or ethyl alcohol, and from petroleum ether. Crystallisation from either of the alcohols caused it to separate in stellate masses of glistening crystals from which the solvent had to be removed by draining and pressing at the pump. Three crystallisations freed this ester completely from uncombined borneol. The pure ester melted at 76°C., and showed a rotation in benzene solution at c = 3·0 of $[\alpha]^{18^\circ}_{5461} = -16{\cdot}50$, and in alcohol at c = 2·5 of $[\alpha]^{17^\circ}_{5461} = -16{\cdot}00$. Yield of pure product was 60% (calculated on the amount of borneol used).

Estimation of Sulphur. (Fusion Method).

0·4275 gms. of compound gave 0·2850 gms. of $BaSO_4$. i.e., S = 9·15%.

0·4091 gms. of compound gave 0·2750 gms. of $BaSO_4$. i.e., S = 9·23%.

$C_{20}H_{24}SO_3$ requires S = 9·27%.

Preparation of 1-Bornyl Naphthalene-α-sulphonate.

The preparation of this ester was carried out in the same manner as that already described for the β-ester, using similar quantities of the reagents. It is, however, essential that the freezing mixture be efficient, and that the naphthalene-α-sulphonic chloride be added at such a rate that the temperature never rises above 3°C. If the conditions have been carefully observed, the oil which separates on the addition of the water should solidify in a few hours. In several cases this did not happen. The oil had then to be extracted with ether or benzene, the extract dried with $CaCl_2$, and the solvent partially removed by distillation, and finally in a vacuum desiccator over H_2SO_4, when the residue solidified to a pale yellow mass.

The solid was very difficult to free from uncombined borneol owing to its great solubility in all common solvents. After several crystallisations from petroleum ether (three to six) the ester was obtained as fine white crystals (like those of the benzenesulphonic

ester) with M.P. 90°C., and rotation in benzene solution at c = 2·5 of $[\alpha]_{5461}^{17\cdot5}$ = -23·20, and in alcohol solution at the same concentration of $[\alpha]_{5461}^{17\cdot0}$ = -26·40. The yield was about 20%.

Estimation of Sulphur. (Fusion Method).

0·4136 gms. of compound gave 0·2753 gms. of $BaSO_4$. i.e., S = 9·14%.

0·5060 gms. of compound gave 0·3394 gms. of $BaSO_4$. i.e., S = 9·19%.

$C_{20}H_{24}SO_3$ requires S = 9·27%.

While the bornyl esters are not as readily prepared as the corresponding menthyl esters, nor in such good yields, yet they are not difficult to obtain in quantity, especially the naphthalene-β-sulphonate. Therefore if it were possible, starting from crude d-borneol, containing l-isoborneol, to obtain the d-esters of these sulphonic acids of rotation equal numerically to that of the l-esters, and to hydrolyse these, a more simple method would be available for purifying crude d-borneol than that of Pickard and Littlebury (1907, T., 1973) at present in use, which consists in heating the alcohol with fused zinc chloride to remove most of the isoborneol. After the borneol is recovered by distillation it is converted into the hydrogen phthalate

and this ester purified and hydrolysed, when the borneol is found to be pure and free from l-isoborneol. The preparation of the d-sulphonic esters was therefore carried out with the following results.

Preparation of d-Bornyl Benzenesulphonate.

This ester was prepared in exactly the same way as the corresponding l-ester, and crystallised from the same medium. Its melting point was 52°, but its rotation when prepared from the crude borneol was lower than that of the pure l-compound ($[\alpha]_{5461}^{17.5} = +21.30$ in benzene solution at c = 2·5) and could not be raised by recrystallisation. This ester is therefore useless for the purpose in view.

Preparation of d-Bornyl Naphthalene-β-sulphonate.

This was also carried out in exactly the same manner as for the l-ester using crude d-borneol. Crystallisation from methyl or ethyl alcohol or from petroleum ether gave the constants, M.P. 76°, and rotation in benzene solution at c = 3·0 of $[\alpha]_{5461}^{17.5} = +15.80$: that is, the same melting point but a lower rotation numerically than that of the l-ester. By crystallising the substance from a mixture of methyl alcohol and petroleum

ether, this rotation was raised till it equalled that of the isomer, making it seem possible that the contaminating l-isoborneol had been removed in the process of formation and purification of the ester. Many attempts were now made to hydrolyse the ester, but no borneol was isolated under any of the conditions used, the decomposition having gone further. This will be dealt with in detail under the decomposition of these esters.

Preparation of d-Bornyl Naphthalene-α-sulphonate.

This was also carried out as described for the corresponding l-ester using the crude d-borneol, but it was impossible to purify the crude ester by crystallisation from any solvent, presumably owing to the impurity present, namely the l-isoborneol. Distillation cannot be used as a means of purification since it causes decomposition.

It is thus impossible to purify crude d-borneol by the formation of these esters.

DECOMPOSITION OF THE ESTERS:-

The decomposition of all these esters was effected in four different ways, namely:-

A. In the homogeneous state in sealed tubes.

B. By direct distillation in vacuo.

C. By heating in solution in various solvents.

D. By hydrolytic methods.

In the case of the menthyl esters the main investigation of each method of decomposition was carried out on the benzenesulphonate, but with the bornyl esters the naphthalene-β-sulphonic ester was used since it was the only one which could be obtained with ease in large quantities in satisfactory yields.

A. HEATING IN SEALED TUBES.

Menthyl Benzenesulphonate.

When menthyl benzenesulphonate was heated in sealed tubes in a water or steam bath to 85° - 90° for six hours, complete separation into two layers took place, but no pressure was developed. On cooling the lower layer solidified to a brown deliquescent solid. The upper layer in the crude state had a slight positive rotation and on distillation in vacuo separated into a low fraction boiling at 72° - 75° at 4 mm., and a high fraction boiling at 150° - 240° at the same pressure. The low fraction was a clear, colourless, refractive liquid, distilling under ordinary conditions at 167° -

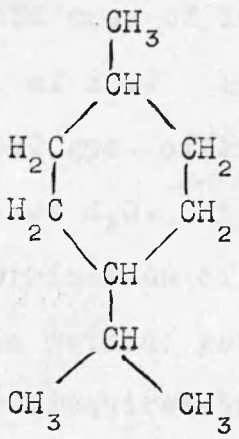
169°. Analysis gave the following results:-

0·1496 gms. of liquid gave 0·4700 gms. CO_2, and 0·1922 gms. H_2O. i.e. C = 85·67% and H = 14·37%.

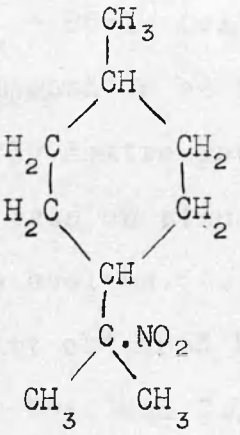
0·1524 gms. of liquid gave 0·4782 gms. CO_2, and 0·1916 gms. H_2O. i.e. C = 85·61% and H = 14·39%.

Determination of the molecular weight in benzene by the cryoscopic method gave the value 142. These results agree with the formula $C_{10}H_{20}$ which requires C = 85·71, H = 14·29, and M = 140.

The liquid had density 0·7965, molecular refractivity 46·35 (calculated on $C_{10}H_{20}R_L$ = 46·18), showing that the substance was completely saturated and was optically inactive. Testing with bromine water confirmed the saturated nature of the compound since it was not decolourised at all. On nitration with HNO_3 of Sp. Gr. 1·075, a yellow nitro derivative was obtained which boiled at 135° - 137° under 25 mm., and which had refractive index μ_D = 1·46241. These data correspond closely with those given by Konowaloff (J. Russ. Phys. Chem. Soc., 1904, 36, 237) for p-menthane hexahydrocymene, proving this to be the same compound of formula



This gives a tertiary nitro compound of formula



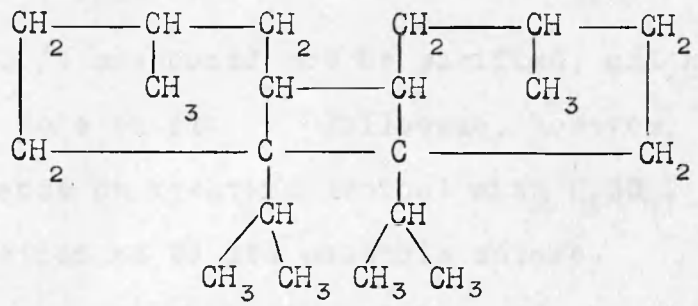
The higher fraction on repeated fractionation in vacuo separated into two fractions, the lower one being a viscous oily liquid boiling at 174° under 4 mm., and the higher one a gelatinous mass boiling at 240° - 270° under the same pressure. Analysis of the viscous liquid gave the following figures:-

0·1532 gms. of liquid gave 0·4878 gms. CO_2, and 0·1804 gms. of H_2O. i.e. C = 86·81, and H = 13·18%.

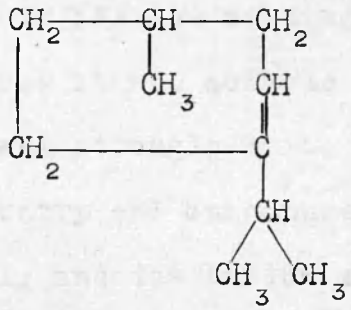
0·1500 gms. of liquid gave 0·4773 gms. CO_2, and 0·1762 gms. of H_2O. i.e. C = 86·78, and H = 13·15%.

Determination of the molecular weight in benzene (cryoscopic method) gave M - 273·1. These values agree with those required by the formula $C_{20}H_{36}$, the correct results being C = 86·87, H = 13·13, and M = 276.

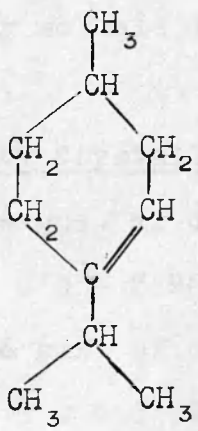
This liquid had $D_{4^\circ}^{17^\circ}$ = 0·8845, and molecular refractivity R_L = 88·14 (calculated on $C_{20}H_{36}R_L$ = 87·96) showing the compound to be completely saturated. It was very slightly dextro rotatory, did not decolourise $KMnO_4$ solution even on standing, but on treatment with bromine HBr was evolved. This compound corresponds closely with that obtained by Tolloczko (J. Russ. Phys. Chem. Soc., 29, 39; and C., 1898, (i), 105) along with menthane (or hexahydrocymene on treatment of menthol with H_2SO_4, the only difference being the complete optical inactivity of the compound obtained in this manner. The determination of the constitution of this dimenthene by physical means, and the fact that it can be obtained from menthene, led I. I. Kannonikow (C., 1899, (2), 860) to give it the constitutional formula:



menthene being:



or, as more commonly represented:



This formula for dimenthene would indicate the possibility of optical activity.

The gelatinous substance boiling at 240 -

270 /4 mm. could not be purified, and no work could therefore be done on it. Tolloczko, however, obtained the same substance on treating menthol with H_2SO_4, but hazards no suggestion as to its possible nature.

An attempt was made to crystallise the solid directly from various solvents, but this was found to be impossible owing to its low melting point and deliquescent nature. Since it was soluble in water and the solution thus obtained was strongly acid, its aqueous solution was purified from tarry and carbonaceous matter by boiling with animal charcoal, and the barium salt formed by neutralisation of the solution with barium carbonate. On recrystallisation of this salt from hot water it formed characteristic glassy crystals, sparingly soluble in cold water, which gave the following analysis:

(a) Water of Crystallisation.

0·3336 gms. of dry salt lost 0·0131 gms. on heating. i.e. H O = 3·92%.

0·4946 gms. of dry salt lost 0·0193 gms. on heating. i.e. H O = 3·89%.

(b) Barium.

This was estimated by dissolving the salt in hot water and precipitating the BaSO with hot dilute H_2SO_4

in presence of HCl.

0·5134 gms. of salt gave 0·2533 gms. of $BaSO_4$. i.e. Ba = 29·03%.

0·5306 gms. of salt gave 0·2618 gms. of $BaSO_4$. i.e. Ba = 29·02%.

$Ba(C_6H_5.SO_2.O)_2H_2O$ requires Ba = 29·27, and H_2O = 3·82, proving that the solid decomposition product was benzenesulphonic acid.

Menthyl Naphthalene-β-sulphonate.

When this ester was heated in a sealed tube to 120 , complete decomposition with separation into two layers again took place. The liquid layer had a low positive rotation as before, and on distillation in vacuo separated into three fractions.

The low boiling fraction was optically inactive and boiled at 167° - 169° under ordinary conditions. Its analysis was as follows:-

0·1616 gms. of liquid gave 0·5076 gms. CO_2, and 0·2051 gms. H_2O. i.e. C = 85·65% and H = 14·20%.

0.1564 gms. of liquid gave 0·4907 gms. CO_2, and 0·2008 gms. H_2O. i.e. C = 85·56% and H = 14·34%. These figures correspond to the formula $C_{10}H_{20}$, proving the liquid to be again hexahydrocymene.

The middle fraction was a viscous liquid boiling at 174° under 4 mm. pressure. It showed a very slight positive rotation, and gave the following analysis:

0·1566 gms. of liquid gave 0·4986 gms. CO_2, and 0·1828 gms. H_2O. i.e. C = 86·82% and H = 13·07%.

0·1583 gms. of liquid gave 0·5035 gms. CO_2, and 0·1861 gms. H_2O. i.e. C = 86·74% and H = 13·16%, corresponding to the formula $C_{20}H_{36}$, and it was therefore the dimenthene already obtained from the benzenesulphonic ester.

Some of the gelatinous substance boiling at 240° - 270° at 4 mm. was also obtained.

The solid in this case crystallised with difficulty from chloroform and melted at 80°. It could not, however, be obtained sufficiently pure for analysis, and its constitution was therefore determined by preparing its barium salt in the same manner as before. It crystallised in flat characteristic glistening plates.

Water of Crystallisation.

0·5050 gms. of dry salt lost 0·0160 gms. on heating. i.e. H_2O = 3·170%.

0·5162 gms. of dry salt lost 0·0164 gms. on heating. i.e. H_2O = 3·176%.

Barium.

0·5542 gms. of salt gave 0·2265 gms. $BaSO_4$, i.e. Ba = 24·07%.

0·5227 gms. of salt gave 0·2133 gms. $BaSO_4$, i.e. Ba = 24·02%.

$(C_{10}H_7SO_3)_2Ba,H_2O$ requires Ba = 24·13, and H_2O = 3·162. Therefore the original product of decomposition was naphthalene-β-sulphonic acid.

Menthyl Naphthalene-α-sulphonate.

This ester was also decomposed in sealed tubes, decomposition taking place fairly rapidly at 120°, when two layers again formed. The liquid layer on distillation and analysis was found to consist of the same three liquids, namely hexahydrocymene (B.P. 167° - 169° and C = 85·58%; H = 14·37%), dimenthene (B.P. 174° at 4 mm.; and C = 86·60; H = 13·08%), and a gelatinous mass boiling at 240° - 270 /4 mm.

The naphthalene-α-sulphonic acid was characterised by the formation of its barium salt which crystallises from water with one molecule of water of crystallisation, and gave the following analysis for barium:

0·5122 gms. of salt gave 0·2106 gms. $BaSO_4$, i.e. Ba = 24·18%.

0·5262 gms. of salt gave 0·2153 gms. $BaSO_4$, i.e. Ba = 24·08%;

the correct result being Ba = 24.13%.

Thus the decomposition of these esters by prolonged heating in sealed tubes results in the splitting off of the sulphonic acid, and the combination of the residues to form dimenthene. No menthene could be found at all. Secondary reactions also take place with the formation of hexahydrocymene, carbonaceous matter, and tarry products.

Decomposition of Bornyl Naphthalene-β-sulphonate.

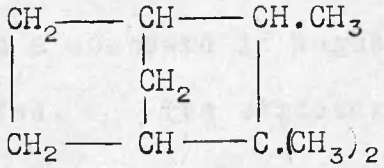
When bornyl naphthalene-β-sulphonate was heated in a sealed tube at ordinary pressure to 80° - 90° for two to three hours, complete separation into two layers took place, no pressure being developed. On cooling the bottom layer solidified to a brown solid. The upper layer in the crude state had a viscous appearance, and, on distilling in vacuo, separated into two fractions, the low one boiling at 60° - 65° at 4 mm., and the high one at 140° - 240° at the same pressure.

The low fraction is a clear, colourless, refractive liquid, of ethereal odour, boiling at 157° - 160° under ordinary conditions, and solidifying only with great difficulty to a white solid melting at 85°. Analysis gave the following results:

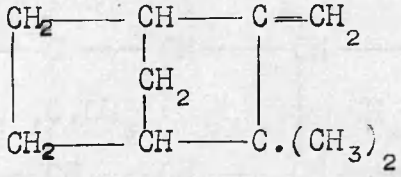
0·1642 gms. of terpene gave 0·5221 gms. CO_2, and 0·1938 gms. H_2O. i.e. C = 86·74% and H = 13·22%.

0·1722 gms. of terpene gave 0·5475 gms. CO_2, and 0·2036 gms. H_2O. i.e. C = 86·71% and H = 13·24%. Determination of the molecular weight in benzene by the cryoscopic method gave the value 136·8. These correspond with the formula $C_{10}H_{18}$ which requires C = 86·87%, H = 13·13%, and M = 138.

Testing with bromine proved this substance to be saturated. No derivative of this compound can be found in the literature to confirm its density with dihydrocamphene, but the data given above corresponds with that given for this substance by Vavon (C. r., 1907, 149, 997) and by Henderson and Pollock (J.C.S., 1910, T., 1620) and it may therefore be presumed to have the formula



if we assume Wagner's formula for camphene, namely the formula



The higher fraction on repeated fractionation in vacuo, separated into two fractions, the lower one boiling at 168° under 4 mm., and the higher one a

gelatinous mass boiling at 240° - 270° at the same pressure.

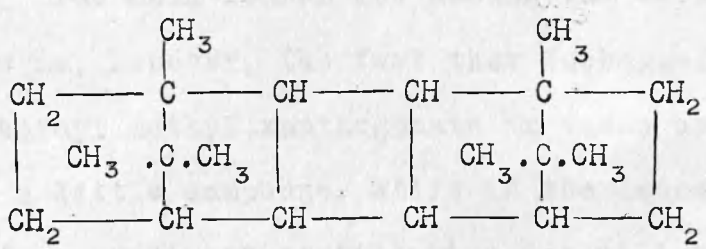
The lower boiling liquid is colourless and viscous and gave the following analysis:

0·1655 gms. of liquid gave 0·5352 gms. CO_2, and 0·1746 gms. H_2O. i.e. C = 88·2%, and H = 11·81%.

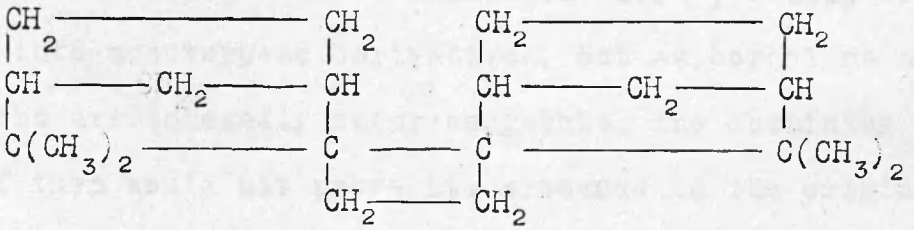
0·1752 gms. of liquid gave 0·5667 gms. CO_2, and 0·1848 gms. H_2O. i.e. C = 88·21% and H = 11·81%.

Molecular weight determination by the cryoscopic method in benzene gave M = 268·7. These data correspond to the formula $C_{20}H_{32}$ which requires C = 88·24%, H = 11·76%, and M = 272.

This compound cannot be traced in the literature either, but is suspected to be a dibornylene (of dimenthene) though it is also possible that camphene might form such a compound if Wagner's formula for camphene is accepted. The structures of the diterpenes would then be:



Dibornylene



Dicamphene.

It seems likely that the four membered ring in dicamphene which contains two methylene groups would, on Ingold's modification of Baeyer's Strain Theory, be less stable than the one in dibornylene where the carbon atoms have only one hydrogen atom attached. On the other hand, however, the dicamphene four membered ring contains two quaternary carbon atoms which might stabilise it, but the whole structure seems less symmetrical and balanced than that of the dibornylene complex. Neither of them, however, contain such a stable grouping as that found in dimenthene where the four membered ring contains two quaternary carbon atoms and no methylene groups.

The main reason for naming the substance dibornylene is, however, the fact that Tschugaeff by distilling bornyl methyl xanthogenate in vacuo obtained bornylene and a little camphene, while in the decomposition of these esters by direct distillation, as will be shown presently (page 36), a little camphene and this terpene are formed, no bornylene being obtained. Little is known

about these diterpenes. Oxidation would probably break it up into monoterpene derivatives, but as bornylene and camphene are so easily interchangeable, the obtaining of one of them would not prove its presence in the original molecule. It had been hoped to prepare bornylene by the xanthogenate method, purify it by the method of Henderson and Caw, and then attempt to obtain the di-compound from it; no method for the latter could, however, be obtained and this idea had therefore to be abandoned.

The gelatinous substance could not be purified, and hence no further work could be done on it.

The solid does not crystallise readily from any solvent, but its aqueous solution is strongly acid. It was therefore purified by boiling with animal charcoal, and the barium salt precipitated with $BaCl_2$; this was analysed after recrystallisation from water and gave the following:

0·5015 gms. of salt gave 0·2037 gms. $BaSO_4$, i.e. Ba = 24·03%.

0·5203 gms. of salt gave 0·2143 gms. $BaSO_4$, i.e. Ba = 24·15%.

$Ba(SO_3C_{10}H_7)_2,H_2O$ requires Ba = 24·12%, proving the acid to be naphthalene-β-sulphonic acid.

Bornyl Benzenesulphonate.

When bornyl benzenesulphonate was subjected to decomposition in the same manner, it decomposed equally readily at the temperature of the water bath, giving two layers. The liquid layer on distillation in vacuo separated into three fractions.

The low fraction boiled at 157° , and on analysis gave the following results:

0·1588 gms. of liquid gave 0·5054 gms. CO_2, and 0·1873 gms. H_2O. i.e. C = 86·78% and H = 13·20%.

0·1638 gms. of liquid gave 0·5215 gms. CO_2, and 0·1925 gms. H_2O. i.e. C = 86·82% and H = 13·20%.

These figures correspond to the formula $C_{10}H_{18}$, proving the liquid to be the same as that obtained in the previous case, namely dihydrocamphene, which only solidifies with difficulty.

The middle fraction was a viscous liquid boiling at 168°/4 mm., and on analysis gave results as below.

0·1753 gms. of liquid gave 0·5663 gms. CO_2, and 0·1854 gms. H_2O. i.e. C = 88·11% and H = 11·84%.

0·1674 gms. of liquid gave 0·5412 gms. CO_2, and 0·1766 gms. H_2O. i.e. C = 88·17% and H = 11·82%.

These figures correspond with the formula $C_{20}H_{32}$ indicating that this compound also is the same as that obtained from the previous ester.

Some of the gelatinous substance was again obtained but could not be further investigated.

The solid in this case was deliquescent, dissolved in water giving an acid reaction, and formed a well-defined barium salt, which gave the following analysis for barium:-

0·6142 gms. of salt gave 0·3989 gms. $BaSO_4$. i.e. Ba = 29·13%.

0·6504 gms. of salt gave 0·3222 gms. $BaSO_4$. i.e. Ba = 29·16%.

$Ba(SO_3C_6H_5)_2,H_2O$ requires Ba = 29·27%, proving the acid to be benzenesulphonic acid.

Bornyl Naphthalene-α-sulphonate.

When bornyl naphthalene-α-sulphonate was decomposed in the same way, two layers were again formed. The liquid layer on distillation and analysis was found to consist of the same three liquids, namely, dihydrocamphene (B.P. 160°, and C = 86·80%; H = 13·17%), dibornylene (B.P. 168°/4 mm., and C = 88·18%; H = 11·83%), and a gelatinous mass boiling at 240° - 270° at the same pressure.

The solid layer was characterised as before by means of the barium salt, and proved by analysis to be naphthalene-α-sulphonic acid, the figures being:-

0·5560 gms. of salt gave 0·2284 gms. of $BaSO_4$, i.e. Ba =24·18%.

0·6050 gms. of salt gave 0·2487 gms. of $BaSO_4$, i.e. Ba = 24·20%.

Therefore the decomposition of these esters by prolonged heating in sealed tubes results in the splitting off of the acid, and the combination of the residue to form a diterpene, and also a small quantity of what is presumably a polyterpene. Secondary reactions again take place with the formation of the saturated terpene dihydrocamphene, carbonaceous matter, and tarry products. There is thus a very close similarity between these two decompositions, the only difference being in the ready interconvertibility of the bornylene and camphene molecules.

B. DECOMPOSITION OF THE ESTERS BY DIRECT DISTILLATION IN VACUO.

Menthyl Benzenesulphonate.

When menthyl benzenesulphonate was subjected to rapid distillation in vacuo, a clear liquid distilled over almost immediately after the solid had melted, the temperature registered on the thermometer being 68°/18 mm., while a brown solid remained in the flask which charred completely on raising the temperature much further.

The liquid did not solidify on cooling, but on

redistillation boiled at 165° under ordinary conditions. It was optically active giving $[\alpha]_{5461}^{17\cdot5} = 9\cdot5$, and on analysis gave the following:-

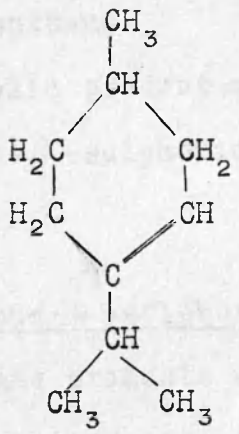
0·1600 gms. of liquid gave 0·5092 gms. CO_2, and 0·1871 gms. H_2O. i.e. C = 86·80% and H = 13·15%.

0·1474 gms. of liquid gave 0·4692 gms. CO_2, and 0·1734 gms. H_2O. i.e. C = 86·82% and H = 13·17%.

Determination of the molecular weight by the cryoscopic method in benzene gave M = 138·4. These data correspond to the formula $C_{10}H_{18}$ which requires C = 86·87% and H = 13·13% and M = 138.

The density of this liquid at 17° was found to be 0·8130, and its molecular refractivity R_L = 45·72. Calculated on $C_{10}H_{18}$ + I ethylene linkage this value should be 45·71. Therefore this compound is unsaturated. This is confirmed by the decolourisation of bromine water. By treatment with amyl nitrite and HCl a well-crystallised, greenish white, nitrosochloride is obtained melting at 117°. The original liquid is thus the menthene obtained by Zelikoff (Ber., 1904, 37, 1374) when testing the dehydrating action of various dibasic acids such as tartaric, succinic, citric, phthalic, and terephthalic acids on menthol at high temperatures, and by Tschugaeff (Ber., 1899, 32, 3332) by distilling menthyl methyl xanthogenate in vacuo, the only difference being that in the present case the

rotation is considerably lower, the menthene from these last named sources having rotation 114° - 116·5° . Tschugaeff, however, points out that other methods of preparation of this compound result in the formation of products having rotation varying from 0° - 60°. The formula of this compound is:



The brown solid was deliquescent, dissolved in water giving the solution a strongly acid reaction, and gave the barium salt characteristic of benzenesulphonic acid. This was confirmed by the analysis of the salt giving Ba = 29·15%. It was noticed that there was a small quantity of the viscous liquid entrapped among the solid, but this was not further investigated since menthene was obviously the main product of the reaction.

Menthyl Naphthalene-β-sulphonate.

On rapid distillation of this substance in vacuo, a liquid boiling at 68°/18 mm. distilled over, and a yellow

solid residue remained in the flask. The liquid boiled at 165° under ordinary pressure, showed practically the same rotation ($[\alpha]^{17.5}_{5461}$ = 9·46) and on analysis gave C = 86·78, 86·81, and H = 13·15 and 13·16: that is, values corresponding to the formula $C_{10}H_{18}$, proving this liquid to be the same as that obtained from the benzenesulphonic ester, namely, menthene.

The solid product was proved in the usual way to be naphthalene-β-sulphonic acid, the barium salt being characteristic.

Menthyl Naphthalene-α-sulphonate.

The same products were also obtained by distilling this ester in vacuo, this being proved in the usual way, namely, menthene (B.P. 165 , and C = 86·79%, H = 13·18%) and naphthalene-α-sulphonic acid (Ba salt gave Ba = 24·05%).

Thus in the decomposition of these esters by direct distillation the sulphonic acid is again split off, and menthene is formed as practically the only product, there being sometimes traces of the diterpene, depending on the rapidity of the distillation, but this quantity never at any time being large.

Decomposition of Bornyl Naphthalene-β-sulphonate.

When bornyl naphthalene-β-sulphonate was distilled from an oil bath as rapidly as possible under a

pressure of 18 mm., a clear liquid distilled over at a temperature of 60° to 65°. The quantity however was not large, probably not more than 15 - 20% of that possible. On redistilling the liquid at ordinary pressure it boiled at 155° - 158°C., and finally solidified to a white solid melting at 51°. When this was analysed the results obtained were:

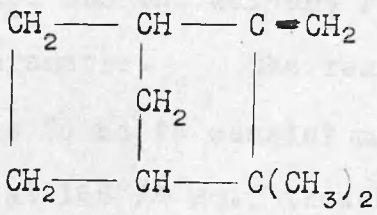
0·1500 gms. of terpene gave 0·4850 gms. CO_2, and 0·1588 gms. H_2O. i.e. C = 88·16% and H = 11·85%.

0·1622 gms. of terpene gave 0·5243 gms. CO_2, and 0·1713 gms. H_2O. i.e. C = 88·14% and H = 11·82%.

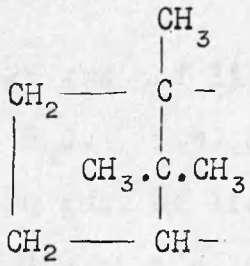
Molecular weight determination (cryoscopic in benzene) gave M = 137·0. These data correspond with the formula $C_{10}H_{16}$ which requires C = 88·24%, H = 11.76% and M = 136.

Testing this substance with bromine water proved it to be unsaturated. Some of the substance was dissolved in ether and the solution saturated with dry HCl gas. A white solid was precipitated, filtered and recrystallised from alcoholic HCl, when it melted at 125° - 127°, and on qualitative analysis was found to contain chlorine. This substance was not stable, but evolved HCl on standing in the air. Water also decomposed it. These data correspond with that given in the literature for camphene hydrochloride (Chemische Fabrik

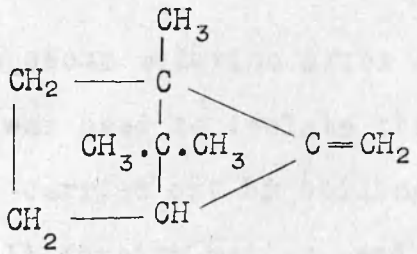
auf Aktien vorm. E. Schering, 1922, A., (I), 943), proving that the original substance was camphene itself, of structure



if one accepts Wagner's formula for it. Henderson and Heilbron (1911, T., 1899), from work on derivatives of camphene and bornylene, consider that both of these terpenes have the same residue, namely:-



and therefore prefer Semmler's formula for camphene, which is



The residue in the flask after distillation was allowed to cool and it was found to separate into two layers, the lower of which solidified. This separation was not,

however, complete, and to do this effectually it was found necessary to dissolve the whole in warm water, and to extract with benzene or toluene. The extract was then dried with $CaCl_2$, and the solvent removed by distillation under reduced pressure. The remainder was then distilled in vacuo and was found to consist mainly of a viscous liquid boiling at 168°/4 mm., though there was also present some of the gelatinous material of indefinite boiling point which could not be purified. The quantity of the viscous liquid obtained in this manner was far in excess of the yield of camphene. On analysis this liquid gave the figures

0·1524 gms. of liquid gave 0·4923 gms. CO_2, and 0·1612 gms. H_2O. i.e. C = 88·13% and H = 11·84%.

0·1600 gms. of liquid gave 0·5175 gms. CO_2, and 0·1691 gms. H_2O. i.e. C = 88·21% and H = 11·83%, corresponding to the formula $C_{20}H_{32}$. It must therefore be dibornylene.

The aqueous solution after extraction with benzene or toluene was used to isolate the barium salt of the acid, this being carried out by boiling with animal charcoal to remove all foreign matter, and neutralising with $BaCO_3$ as before. The salt gave the following analysis

0·5013 gms. of salt gave 0·2050 gms. $BaSO_4$.

i.e. Ba = 24·08%.

0·5162 gms. of salt gave 0·2118 gms. $BaSO_4$.

i.e. Ba = 24·15%,

proving the original solid to be naphthalene-β-sulphonic acid.

Bornyl Benzenesulphonate.

When bornyl benzenesulphonate was distilled rapidly in vacuo in the same way as for the previous ester, a small quantity of a clear liquid distilled over at 68° under 18 mm. On purification by distillation it boiled at 155° and solidified to a white solid, M.P. 51°. Analysis gave C = 88·15 and 88·17%, H = 11·77 and 11·80%, showing that the substance is camphene.

On cooling the residue in the flask there was only very partial separation into two layers. Solution in water and extraction with toluene, however, effected complete separation. The residue after removal of the toluene was mainly the viscous liquid boiling at 168°/4 mm., though there was, as usual, some of the gelatinous material of indefinite boiling point. Analysis of the liquid gave C = 88·16 and 88.18% and H = 11·80 and 11·79%. This liquid is thus the same diterpene as that already obtained.

The barium salt was isolated from the aqueous solution in the usual manner and from crystalline form and

analysis of barium content (Ba = 29·18%) was identified as barium benzenesulphonate, the original solid being benzenesulphonic acid.

Bornyl Naphthalene-α-sulphonate.

This ester was decomposed in the same manner and the products isolated also as described for the previous esters, when camphene (B.P. 155°, and C = 88·21%, H = 11·77%), dibornylene (B.P. 168°/4 mm., and C = 88·18, H = 11·80%), gelatinous mass of indefinite boiling point, and naphthalene-α-sulphonic acid, were the products, the terpenes being formed in the same proportions as before.

Thus in the decomposition of these esters the sulphonic acid splits off as before, and the residues mainly combine in pairs to give the diterpene, a small portion of them, however, undergoing molecular transformation into camphene. No bornylene is obtained. This is quite different from the reaction found by Tschugaeff in the distillation of the bornyl xanthogenates. In this case the chief product was bornylene of high rotation, but nevertheless slightly contaminated with camphene. The decomposition of the sulphonic esters also differs from that undergone by the menthyl sulphonic esters, and menthyl methyl xanthogenate. In both cases the main product is menthene. In the former reaction small quantities of dimenthene were sometimes found, but in the latter case

Tschugaeff makes no mention of finding this compound, but only of menthene of high rotation.

C. DECOMPOSITION OF THE ESTERS IN SOLUTION.

Menthyl Benzenesulphonate.

When menthyl benzenesulphonate was heated to boiling in benzene solution (c = 10) under reflux condenser for six hours, and the rotation of the solution examined before and after heating, there was found to be a very slight decrease in rotation, but further heating did not cause any further change in the rotation, nor in the colour of the solution, the latter remaining colourless. Decomposition cannot therefore be effected in this solvent.

When, however, toluene was substituted for benzene and the solution heated to 110° on an oil bath, decomposition was complete in six hours, and on cooling a brownish solid separated out. This was proved by the usual means to be benzenesulphonic acid. The toluene solution had now a slight positive rotation. It was thoroughly washed with sodium carbonate solution to remove the last traces of the acid, dried with $CaCl_2$, and distilled. The liquid which remained after removal of the toluene distilled under ordinary and reduced pressure and had boiling point 174°/4 mm. It was thus seen to be

dimenthene, and analysis confirmed this (C = 86·81, and H = 13·14%).

Menthyl Naphthalene-β-sulphonate.

When menthyl naphthalene-β-sulphonate was heated in xylene solution to 120° for two to three hours decomposition was again complete, and a solid separated on cooling. This may be identified in the usual way as the sulphonic acid. Distillation of the xylene solution after washing with sodium carbonate solution, and drying gave as residue, after removal of the solvent, dimenthene, boiling at 174°/4 mm.

Heating of this ester in nitrobenzene solution at 100 for about the same time caused the solution to darken and on cooling a solid again separated, which could be made to crystallise from chloroform, when it melted at 80°, but was much more easily identified by means of its barium salt. No attempt was made to isolate the liquid from this solution, it being almost certain that it would be dimenthene.

Menthyl Naphthalene-α-sulphonate.

The decomposition of this ester took place equally readily in xylene solution at the same temperature, with the formation of dimenthene and naphthalene-α-sulphonic acid.

Thus decomposition of the menthyl sulphonic esters in solution results in the formation of dimenthene only, - there being no trace of the low boiling menthene, - the other product being the corresponding sulphonic acid.

Decomposition of Bornyl Naphthalene-β-sulphonate in Solution.

When bornyl naphthalene-β-sulphonate was heated in 10% benzene solution for six hours on the water bath, there was no change in the rotation of the solution, that is, no decomposition took place. When, however, toluene was used as the solvent, and the solution heated to 110° decomposition was complete in one-and-a-half to two hours, the solution being now very dark in colour. On cooling a solid separated out. This was acid and gave a characteristic barium salt which proved, on analysis, to be barium naphthalene-β-sulphonate (Ba = 24·09%).

The filtrate was washed with Na_2CO_3 solution till the last traces of acid had been removed, dried with $CaCl_2$, and the solvent removed on the water bath under reduced pressure. The residue distilled at 168° under 4 mm. pressure, or at 285° - 290° under ordinary pressure without decomposition taking place, and on analysis gave C = 88·19% and H = 11·80%, proving this liquid to be identical with the high boiling liquid presumed to be dibornylene.

Bornyl Benzenesulphonate.

This ester decomposed completely in benzene solution, the only products of the reaction being dibornylene and benzene sulphonic acid. Decomposition also took place exceedingly readily in toluene solution with the same result.

Bornyl Naphthalene-α-sulphonate.

When the decomposition of this ester was investigated in the manner already described, using toluene as solvent, the same diterpene, namely, dibornylene, was obtained along with naphthalene-α-sulphonic acid.

Thus the decomposition of the bornyl esters in solution results in the formation of only dibornylene, with no trace of the monoterpenes, bornylene or camphene, along with the sulphonic acid. Therefore with this method of decomposition both the menthyl and the bornyl esters show analogous behaviour.

Noticing that benzene would not decompose menthyl benzenesulphonate or bornyl naphthalene-β-sulphonate, but that toluene at 110° caused complete decomposition in both cases, the question arose as to whether this was purely a temperature effect or whether the solvent itself had some effect. The latter seemed possible from the observation that nitrobenzene decomposed menthyl naphthalene-β-sulphonate at 100°, while xylene required a temperature of 120° to

effect the same result. It was therefore thought of interest to investigate this quantitatively for several different solvents.

EFFECT OF SOLVENTS ON THE TEMPERATURE OF, AND AMOUNT OF DECOMPOSITION OF THE ESTERS.

Two methods were available for this purpose. Seeing that the esters are optically active and the products of decomposition almost completely inactive, it should be possible, by placing a tube containing a solution of known concentration in a thermostat on the polarimeter, and noting the change of rotation at given intervals of time, to determine the rate of reaction in the given solvent at the given temperature. Also seeing one of the products of decomposition is an acid, the percentage decomposition in a given time could be determined by making up a solution of the ester in the solvent, the concentration of which is known, heating the solution for a fixed time in a thermostat, cooling it and titrating the acid formed with alkali. Since the solutions in the hydrocarbons discolour during the decomposition, the latter method was chosen, for it might be difficult to obtain many readings on the polarimeter before the solution became too cloudy to read. In titration the discolouration could be reduced

by the use of a suitable diluent. The actual method used was to weigh out exactly 0·8 gm. of ester into a 10 cc. graduated flask and make up 10 cc. solution with the freshly distilled, pure solvent. The flask in which the reaction was to take place was placed in the thermostat, which had been carefully regulated to the required temperature, and allowed to acquire that temperature before the solution was poured in. This was done in order to enable the solution itself to attain the reaction temperature as quickly as possible after it was placed in the flask as the duration of the heating had to be timed from the pouring of the solution into the reaction flask. After heating the solution for one hour, it was withdrawn, cooled as rapidly as possible, and diluted with 20 cc. of absolute alcohol which had been distilled over quicklime to remove any traces of acid that might be present. It was then titrated with alcoholic KOH which had been carefully standardised with pure potassium bitartrate, using phenolphthalein as indicator. Alcoholic KOH was chosen in preference to baryta in spite of the fact that the latter is usually recommended for the titration of organic acids because barium hydroxide is not soluble in alcohol, and one would therefore be involved with partition coefficients during the titration. Also the sulphonic acids are sufficiently strong acids to enable

one to get a clear, sharp, end point, without this being marred by the hydrolysis of the potassium salt, particularly when only minute traces of water would be present. To reduce the error of the experiment, a burette with a very fine bore was used, and blank experiments carried out in all cases so that any slight correction could be made on the actual readings obtained. The reliability of the method was proved by carrying out the experiments in duplicate in several cases. Thereafter it was deemed unnecessary to do that in every case. For the first investigation it was decided to test the effect of a hydrocarbon, a nitrocompound, an amine, an alcohol, and a halogen compound at the temperatures 90°, 95°, 100°, and 105°, the solvents chosen being toluene, nitrobenzene, pyridine, n-butyl alcohol and ethylene dibromide. It was, however, noticed that the effect of the alcohol was more marked than that of the other solvents so the investigation was extended to include n-propyl alcohol, and iso-butyl alcohol. The former could, however, only be investigated for two temperatures, namely, 90°, and 95°, its boiling point being 98°. If the effect of this solvent were to be investigated at 100° and 105° in sealed tubes, there would be a change of conditions (the pressure would be greater than atmospheric) and the results obtained would not be comparable.

It may be remarked in passing that the results obtained for ethylene dibromide are not quite so accurate as those for the other solvents owing to the end point being slightly blurred, this being caused by the tendency of alcoholic KOH to react with the solvent itself if left long in contact with it. In the tables the results are given as percentage of decomposition. Table I gives the results obtained for pure menthyl benzenesulphonate with these solvents.

TABLE I.

Menthyl Benzenesulphonate.

Percentage of ester decomposed in one hour.

Temp.	Toluene	Nitro-benzene	Ethylene Dibrom-ide	Pyri-dine	N-Propyl Alcohol	Butyl Alcohol	Isobutyl Alcohol.
85	0·98	2·37	-	2·37	16·42	10·85	9·89
90	1·04	2·75	2·48	3·19	25·74	17·27	16·20
95	1·06	5·88	2·67	4·72	38·39	28·15	27·17
100	2·23	12·87	4·20	9·80	-	45·14	43·12
105	2·37	82·15	9·18	14·08	-	60·23	54·44

On examination of this table it will be seen that there is very considerable variation in the effect of different solvents at the same temperature, and also

in the effect of different temperatures on decomposition in the same solvent. For example, at 95° the percentage decomposition in toluene solution in one hour is 1·06, in nitrobenzene solution 5·88, and in alcoholic solutions 27 to 38. At 105° however, decomposition is greatest in nitrobenzene solution (82), with the alcohols next and only 2·3% in toluene. It may be remarked in passing, however, that prolonged heating at 100° - 105° does effect complete decomposition in toluene solution. With regard to the effect of temperature on decomposition in the same solvent we find that there is hardly any change in the amount of decomposition in toluene solution, but that it rises in nitrobenzene solution from 2·37 to 82·15, there being a very sudden rise between 100° and 105°. The most marked solvent effect is found in the case of the alcohols, these causing considerable decomposition even at 85° when the other solvents exert very slight action. This action seems to be proportional to the amount of OH group in the alcohol, that is, propyl alcohol, the lower homologue of the two used has a much greater effect than n-butyl alcohol. It may also be noticed that isobutyl alcohol has a smaller effect than the normal one. Since there is the same percentage of OH group in both these, the difference must be due to the branched chain. To see whether this relation was true throughout the lower

alcohols, the data on Table II was obtained using methyl ethyl, n-propyl, and n-butyl alcohols.

TABLE II.

Menthyl Benzenesulphonate.

Percentage ester decomposed in one hour.

Temperature	Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol.
65	8·95	3·73	-	-
70	-	5·13	3·17	-
75	-	8·73	5·88	4·10
80	-	-	10·70	6·77

It was thus found that at any given temperature the lower homologue in the alcohol series has the greater effect on the decomposition. This leads to the natural conclusion that if the esters were soluble in water this solvent would have the greatest effect of all. This, however, cannot be proved even by the addition of some water to an alcoholic solution, as quite small percentages of water cause the ester to precipitate completely. Another interesting point is, that while decomposition in most of the solvents practically ceases below 85°, it continues to take place at lower temperatures, in the alcohols, the temperature becoming lower as the percentage of hydroxyl group

in the alcohol increases till, with methyl alcohol at 65°, there is more decomposition taking place than with the non-alcoholic solvents at 95°.

The same experiments were carried out with bornyl naphthalene-β-sulphonate and the results embodied in Tables III and IV.

TABLE III.

Bornyl Naphthalene-β-sulphonate.

Percentage of ester decomposed in one hour.

Temp.	Toluene	Nitro-benzene	Ethylene Dibromide	Pyrid-ine	Isobutyl Alcohol	Butyl Alcohol	N-Propyl Alcohol.
90	0	6·41	4·39	5·21	17·16	20·90	26·35
95	0	7·33	6·30	6·36	27·82	31.6I	42·03
100	1·05	71·53	22·90	7·57	39.79	43·92	-
105	1·06	64·73 (½ hr.)	71·54	11·83	58·27	67·50	-

TABLE IV.

Bornyl Naphthalene-β-sulphonate

Percentage of ester decomposed in one hour.

Temperature	Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol.
65	8·18	3·19	-	-
70	-	6·44	4·01	3·12

TABLE IV. (Contd.)

Temperature	Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol.
75	-	9·78	7·12	5·31
80	-	-	10·58	7·51
85	-	-	15·31	12.65

Again it will be noticed that the same relation holds with regard to the effect of the various alcohols. The main difference in the effect of the solvents on these two esters is to be found in the action of nitrobenzene and ethylene dibromide. The former causes only a moderate percentage of decomposition with menthyl benzenesulphonate at 100°, but 71 with bornyl naphthalene-β-sulphonate, although at 105° the percentage is high in both cases. Ethylene dibromide, on the other hand, has a very moderate effect at all temperatures on the menthyl ester, 9% being the greatest amount of decomposition in this solvent, whereas in the case of the bornyl ester the percentage rises to 71.. With the other solvents the amounts of decomposition of the two esters are very similar, sometimes the one and sometimes the other ester giving slightly greater values for the same solvent. It is interesting to note, however, that no decomposition of the bornyl ester takes place in one hour in toluene solution at 90° and 95°,

and only 1% even at 105°, although, as in the case of the menthyl ester, prolonged heating at 100° to 105° can bring it almost to completion.

To effect a more accurate comparison the same experiment was carried out on menthyl naphthalene-β-sulphonate. One difficulty arose, however, owing to the smaller solubility of this ester in alcohols. With the exception of n-butyl alcohol it was impossible to make up 8% solutions even on heating. The effect of concentration on amount of decomposition was therefore examined in the case of butyl alcohol with the following results, the temperature used being 105°.

TABLE V.

Menthyl Naphthalene-β-sulphonate in Butyl Alcohol Solution at 105°.

Concentration	Percentage Decomposition.
8	66·06
6	63·04
5	62·92
4	62·84
2	59·69.

There is thus a slight fall in the amount of decomposition between 8 and 6 or 5, but not sufficient to make the results obtained with c = 5 incomparable with those obtained with the other esters at c = 8. To see whether this small effect of concentration on decomposition held for other solvents, butyl alcohol was replaced by nitrobenzene at the same temperature, with the following result:

TABLE VI.

Menthyl Naphthalene-β-sulphonate in Nitrobenzene Solution at 105°.

Concentration	Percentage Decomposition.
8	98·63
6	98·12
5	89·49
4	47·90
3	25·64
2	16·95

From these figures it will be noticed that concentration of solution in nitrobenzene has a very considerable effect on the amount of decomposition in that solvent at the same temperature, this being very marked below 5%. This, however, does not affect the reading in question as it is possible to make up a solution in nitrobenzene of c = 8.

The results obtained for menthyl naphthalene-β-sulphonate are given in Tables VII and VIII below.

TABLE VII.

Menthyl Naphthalene-β-sulphonate.

Percentage of ester decomposed in one hour.

Temp.	Toluene	Nitro-benzene	Ethylene Dibromide	Pyrid-ine	Isobutyl Alcohol	Butyl Alcohol	N-Propyl Alcohol.
95	1·50	9·30	7·02	6·20	26·96	30·77	41·68
100	1·50	63·23	28·14	9·11	41·21	45·02	-
105	1·55	98·63	99·56	13·86	56·13	62·92	-

TABLE VIII.

Menthyl Naphthalene-β-sulphonate.

Percentage of ester decomposed in one hour.

Temperature	Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol.
65	12·92	4·92	-	-
75	-	13·53	8·27	5·62.

By comparing these two tables with Tables III and IV, it will be seen that there is general agreement with regard to the effect of the different solvents at the different temperatures although the values are by no means

identical. The main difference noticeable is the much greater effect of ethylene dibromide on the menthyl than on the bornyl ester. Allowing for the slight reduction in decomposition due to decreased concentration, the values obtained for the alcohols are almost the same at all temperatures with the exception of methyl and ethyl alcohol, when the decomposition for the menthyl ester is higher than that obtained for the bornyl one.

Thus there is a distinct solvent effect on the temperature and on the rate of decomposition, and in general is similar for all the esters.

D. DECOMPOSITION BY HYDROLYTIC METHODS.

This was investigated in the first place in connection with bornyl naphthalene-β-sulphonate owing to the discovery that, starting with crude d-borneol containing l-isoborneol, it was possible to prepare the d- ester with the same rotation as that of the l-, when it was hoped to obtain a new method of purifying d-borneol.

(i) Action of Water and Aqueous KOH.

When steam was blown through bornyl naphthalene-β-sulphonate suspended in water or dilute aqueous caustic potash for a short time (20 - 30 minutes), only water distilled over, and the ester, after filtering and drying, was

found to be almost as pure as before, the melting point being the same and the rotation only slightly reduced.

When, however, the ester suspended in water or caustic alkali was heated on the water bath for two to three hours, reaction took place and brownish products rose to the surface. On passing in steam a colourless liquid was obtained in the distillate. This did not solidify, was ethereal in odour and on extraction with benzene and removal of the solvent was found to distil at 155° - 159°. It still did not solidify and was optically inactive. Analysis gave results which correspond roughly with the formula $C_{10}H_{16}$, but these were not so accurate as those generally obtained, in the other cases the carbon being lower and the hydrogen higher than that demanded by theory. This, taken in conjunction with the fact that the liquid did not solidify, seems to indicate that it is a mixture of two terpenes, the main one, however, being camphene, which has a distinctive odour. Testing with bromine water proved the unsaturated nature of the terpene as it was readily decolourised. To prove the presence of the camphene, some of the terpene was dissolved in ether and the solution saturated with dry HCl gas. There was a reaction and the solution darkened in colour but no hydrochloride precipitated. On evaporation of the ether in air the residue separated into a brownish oil and a

colourless portion which solidified and showed the melting point corresponding to camphene hydrochloride. From the analysis it seemed possible that the other terpene present was saturated. These usually give nitro compounds, so a portion of the liquid was heated with HNO_3, when a layer of a yellow compound formed on the surface of the liquors, which was most probably a nitro derivative although no such derivative of either dihydrocamphene or dihydrobornylene is indicated as being prepared by this method in the literature. The presence of the dihydrocamphene in the camphene can be readily explained by the fact that the former boils at 157° - 160°, that is, about two degrees above camphene, and it is almost impossible to separate two terpenes with such close boiling points by fractional distillation. The contamination of camphene with even small quantities of this, or any other terpene, also explains its liquid state and the difficulty of obtaining the hydrochloride in a crystalline state. It seems possible also that while camphene results from the action of the KOH on the ester, some of the ester may have decomposed purely on account of the temperature, this being very near that used in the decomposition of the ester in sealed tubes, when dihydrocamphene would naturally result along with higher boiling products. This seems the more likely when the contents of the distillation flask are examined.

Along with white glistening plates of what was afterwards proved to be the potassium salt of naphthalene-β-sulphonic acid (by converting it into the barium salt and analysing the latter) was some brownish material. This was extracted with benzene, the extract thoroughly dried with $CaCl_2$, and the solvent removed under reduced pressure. On attempting to distil the residue in vacuo carbonaceous decomposition set in at about 140°, so that it was impossible to isolate any product by this means. An attempt was therefore made to solidify the residue in a vacuum desiccator, but this having so far been unsuccessful, no further work can be done on it as there is no available test for the presence of dibornylene although it is very likely that some of this substance is present owing to decomposition in the homogeneous state having taken place to some extent as already suggested. No trace of borneol was obtained.

(ii) Alcoholic KOH.

This is the method usually found suitable for the hydrolysis of bornyl esters.

When bornyl naphthalene-β-sulphonate was dissolved in cold alcohol and KOH in slight excess of the quantity required by the equation

$$C_{10}H_{17}SO_3C_{10}H_7 + KOH \rightarrow C_{10}H_{17}OH + C_{10}H_7SO_3K$$

dissolved in a little water was added and the whole allowed to stand at the ordinary temperature for some days, crystals

finally separated: these were long, fine needles, and on determination of melting point, rotation, etc., were found to be the pure unchanged ester.

When, however, this solution, or a more concentrated one was boiled on the water bath for several hours, a white solid separated, quite different in appearance from that obtained in the previous experiment. When no more separation took place, heating was stopped and the solid filtered and dried. On weighing and estimating it by conversion into the barium salt, it was found that almost the theoretical amount of the potassium salt of the sulphonic acid had been formed. To isolate the borneol the alcoholic solution was dried with K_2CO_3, and most of the alcohol distilled off under reduced pressure. Nothing separated from the remainder so it was poured into water. A very small quantity of a solid separated, and, on drying and recrystallising, was found to be unchanged ester. No trace of borneol was obtained, but it was observed that the alcoholic distillate when poured into water became turbid, showing the presence of some foreign material. This did not solidify, and owing to the presence of the alcohol in the aqueous solution, extraction with any solvent was practically impossible. There was, however, a strong odour of camphene about the alcoholic solution.

This decomposition was carried out with the three bornyl esters with the same result. The naphthalene sulphonates requires three to four hours for this decomposition to take place, while bornyl benzenesulphonate requires six hours. Neither by changing the amount of KOH, nor by changing the temperature of the reaction was it possible to obtain any borneol. If there was any reaction at all it went in the manner indicated above.

(iii). Sodium Ethoxide in Alcohol.

The theoretical amount of metallic sodium was dissolved in absolute alcohol and the ester dissolved in the cold alcoholic sodium ethylate, with the addition of more alcohol if necessary. After allowing the whole to stand at room temperature for some days, long needle crystals again appeared, and were proved to be unchanged ester.

Heating on the water bath of this, or of a more concentrated solution prepared in the same manner, resulted in the same decomposition as that obtained with KOH, the only difference being the greater purity of the residue left after the removal of the alcohol by distillation. No trace of borneol could be obtained either mixed up with the potassium naphthalene-β-sulphonate, or in the alcoholic solution, but the odour of camphene was again apparent.

(iv). Barium Hydroxide.

The ester was dissolved in warm alcohol and a concentrated hot solution of baryta containing $1\frac{1}{2}$ times the quantity of barium hydroxide required completely to hydrolyse the ester according to the equation

$$2C_{10}H_{17}O.SO_2C_{10}H_7 + Ba(OH)_2 \longrightarrow 2C_{10}H_{17}OH + Ba(SO_3.C_{10}H_7)_2$$

was added, more alcohol being added if necessary to keep the ester in solution. The reaction which results in the separation of a glistening solid commenced almost at once, and was completed by heating on the water bath. Two to three hours were required in the case of the two naphthalene esters, but six for the benzenesulphonic ester. The whole was cooled, the solid filtered and dried, and the filtrate separated into aqueous and alcoholic layers by means of K_2CO_3, the former being discarded since borneol is insoluble in water and precipitated thereby. Any terpenes formed would also remain in alcoholic solution.

The solid was found to be nearly the theoretical amount of the barium salt of the sulphonic acid, this being proved by analysis of the recrystallised salt. To prove that no borneol was trapped among this salt, the salt before recrystallisation was extracted with hot benzene, and the benzene extract evaporated to dryness, when no residue was obtained.

The alcoholic layer of the filtrate was distilled

under reduced pressure until a solid began to separate in the distilling flask. The distillation was then stopped, and the residue allowed to crystallise. The amount of solid obtained was small even when the quantity of ester used was 25 to 30 grams. On attempting to crystallise this, it was found to consist mainly of the barium sulphonate, but traces of camphene M.P. 51°, dihydrocamphene M.P. 85°, and bornylene M.P. 113° were found. Sufficient quantity of any of these substances was not obtained at any time for purification and analysis. No borneol was present here either.

It being necessary to find some means of identifying the terpenes which had volatilised with the alcohol during distillation with the ordinary apparatus in the previous experiments, attempts were made to separate them by fractional distillation with an efficient fractionating column, but this was of no avail. Also precipitation with water was useless since they formed an emulsion with the alcohol water mixture, only very little if any separating out. It therefore became necessary to find if possible a derivative of camphene and bornylene which could be made in alcoholic solution, for it seemed reasonable to suppose that these were the substances formed, with, possibly, some dihydrocamphene and dibornylene. By passing dry gaseous HCl through the solution, camphene

hydrochloride was formed but did not crystallise owing to the solution being dilute. In spite of the fact that water decomposed camphene hydrochloride the agent had to be used to precipitate it from the solution, when it was filtered as rapidly as possible and recrystallised from alcoholic HCl. By this means sufficient was obtained to enable its melting point to be taken and found correct. None of the other substances mentioned gave any derivatives in alcoholic solution. This means of identification not being satisfactory, a final attempt to isolate the terpenes was made in the following manner. The alcoholic solution was poured into a large excess of water, and the whole extracted thoroughly with toluene. This by no means extracted all the terpene for the smell of camphene was still perceived strongly in the aqueous layer, and the latter had still the appearance of an emulsion. The extract was dried with $CaCl_2$, and the solvent removed by distillation under reduced pressure. The remainder was distilled at ordinary temperature when the main portion distilled at 155°, but some higher boiling material was also obtained. The portion boiling at 155° proved to be camphene, giving camphene hydrochloride in the usual way. The total amount of terpene isolated in this manner would not be more than 10%.

Hence one decomposition taking place in all these experiments is the splitting off of the sulphonic acid and the molecular transformation of the residue into camphene. There also seems to be an indication of the formation of some dibornylene but this cannot be proved owing to the lack of any known derivative. It is remarkable that the methods which hydrolyse other bornyl esters such as bornyl acetate, bornyl p-nitrobenzoate (Henderson and Heilbron, J.C.S., 1913, Proc., 381), bornyl hydrogenphthalate (Pickard and Littlebury, 1907, T., 1973), and bornyl mandelate (Mackenzie and Thompson, 1905, T., 1013) should cause the reaction to go further in the case of the sulphonic esters, with not even a trace of borneol in the resultant product.

Observing this peculiarity in the bornyl sulphonic esters, it seemed to interest to see whether the corresponding menthyl esters were normal or otherwise. Only two of the methods of hydrolysis were carried out in this case, the action of aqueous KOH, and the action of barium hydroxide.

(i) Action of aqueous KOH.

When menthyl benzenesulphonate was suspended in aqueous KOH (10 - 15% solution) and heated on the water bath for several hours decomposition finally took place and on passing in steam a colourless oil distilled with the

water. This was extracted with benzene, the extract dried with $CaCl$, and the solvent removed at ordinary pressure. The product boiled at 165 at ordinary pressure, and gave analysis corresponding almost exactly with the formula $C_{10}H_{18}$, indicating that in this case practically no saturated terpene, if indeed any at all, had been formed from decomposition of the ester by the action of heat alone. This was to be expected since in the homogeneous decomposition of this ester the steam bath was necessary. Bromine proved the terpene to be unsaturated, and formation of the nitrosochloride by the usual method which melted at 115°, proved the liquid to be menthene.

Examination of the contents of the reaction flask showed that, in addition to the potassium benzene-sulphonate, there was also some unchanged ester, the reaction not taking place so readily even after heating for five or six hours as it does in the case of the bornyl ester. Raising the temperature of the reaction would almost certainly decompose all the ester, but the reaction would most likely not take just the direction desired.

When menthyl naphthalene-β-sulphonate was treated in the same way, some decomposition also took place with the formation of menthene and the sulphonic acid, or rather its potassium salt, but the amount of this decomposition was not large even after heating for six

hours, at least 50% of the ester being recovered unchanged. Boiling with caustic potash solution would probably effect more complete decomposition without side reactions taking place, but this was not further investigated.

(ii) Barium Hydroxide.

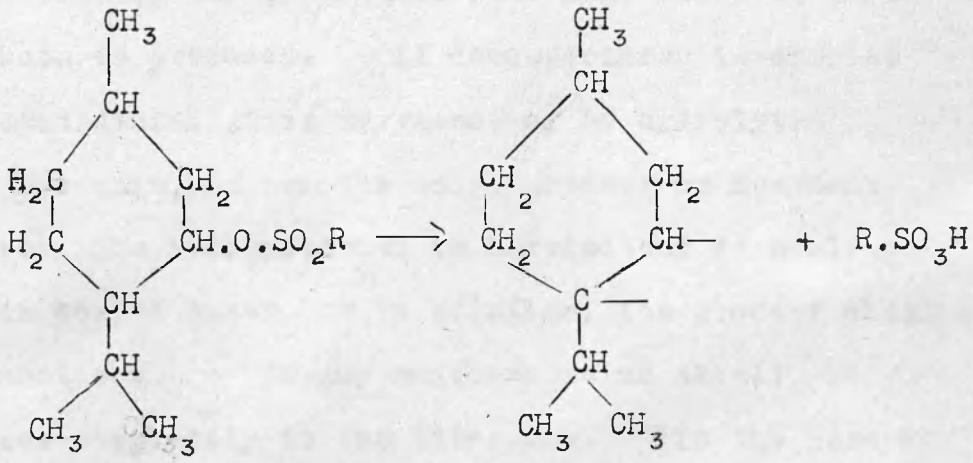
This experiment was carried out exactly as described for the bornyl esters (see page 59) using all the menthyl sulphonates. The times required for their decomposition were approximately the same as those for the corresponding bornyl esters, but if anything, slightly more time is necessary for complete decomposition of the menthyl esters. The barium salt of the acid was formed almost quantitatively in every case and was estimated as before. No menthol could be obtained at all though every precaution was taken to prevent overlooking it, but the alcoholic distillate contained a terpene which could not be separated from it by distillation or precipitation with water. From analogy with the previous work this was probably menthene, and the odour of the solution strengthened this belief. Since menthene does not give any derivative in alcoholic solution, the distillate was poured into excess water and extracted with toluene as before. On removal of the solvent and distilling the

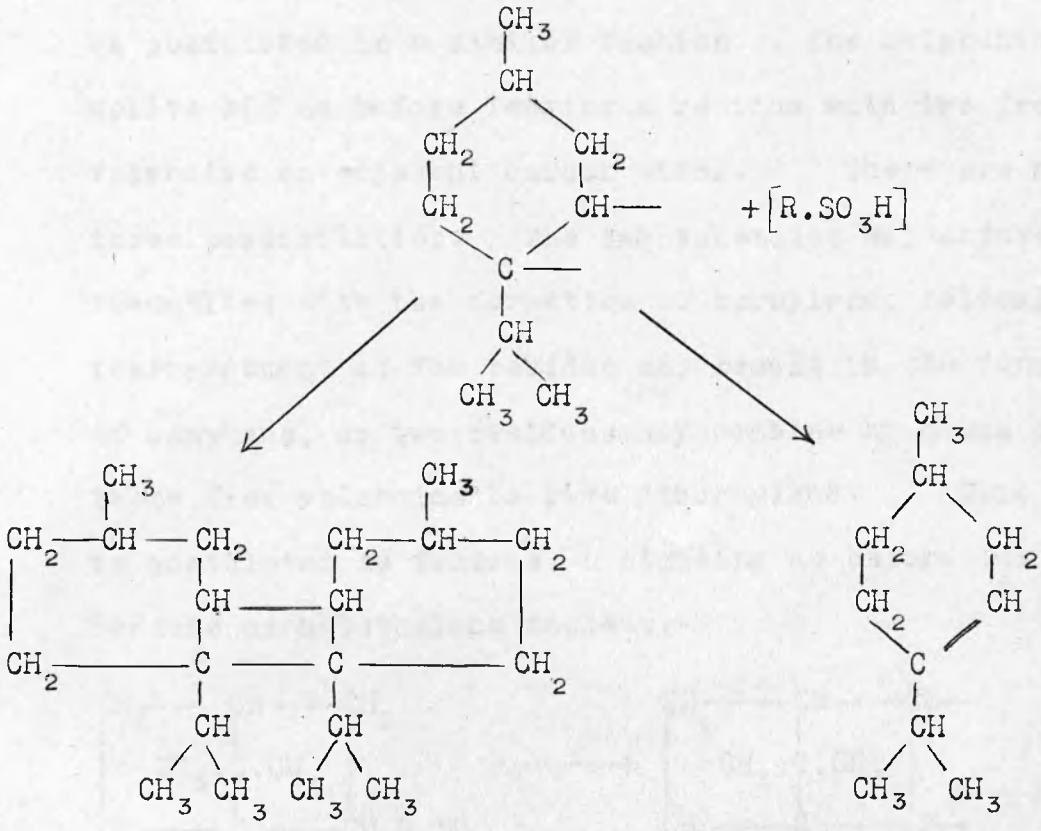
residue, practically the whole quantity distilled at about 164°. Little if any high boiling material was obtained, although the percentage of terpene extracted was higher than that obtained in the bornyl experiment. The liquid thus obtained was readily proved to be menthene by the formation of the nitrosochloride.

Thus the action of baryta and of aqueous KOH on the menthyl esters results in the formation of menthene as practically the only terpenic product, the other product being the salt of the sulphonic acid. Side reactions do not occur to complicate the issue. This decomposition is practically identical to that found when the esters are distilled rapidly in vacuo. The same may also be said of the decomposition of the bornyl esters by these hydrolytic agents, with the exception of the formation of the dihydro-compound by decomposition in the homogeneous state owing to the temperature used.

CONCLUSION.

The reaction taking place during the decomposition of the menthyl esters by the various methods employed, may be represented as occurring in two stages. In the first stage the sulphonic acid radicle splits off along with a hydrogen atom from the adjacent carbon atom, giving the sulphonic acid and a residue with two free valencies. This residue can now stabilise itself in two ways. The two free valencies may saturate each other when the double-bonded compound menthene results, or, alternatively, two residues may combine together by means of these free valencies when the saturated dimenthene results. This may be represented as follows:- R stands for the benzene or naphthalene nucleus.

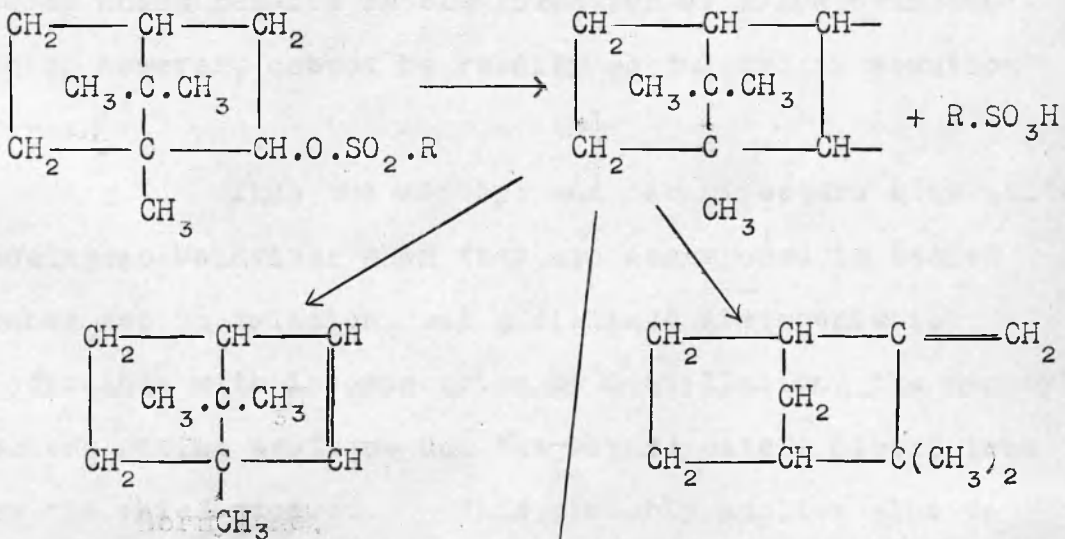




Dimenthene. Menthene.

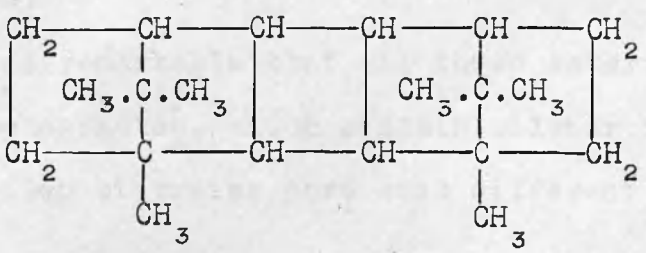
The conditions of the experiment determine which of these two products is produced. If decomposition is carried out by rapid distillation in vacuo, or by hydrolytic methods, the main, if not the only, product is menthene. If, however, the decomposition is carried out by prolonged heating in sealed tubes, or in solution, the product obtained is dimenthene. If any menthene forms at all, it polymerises completely to the diterpene. In the case of decomposition in sealed tubes hexahydrocymene (or menthane) results as a product of some secondary reaction which cannot be readily postulated.

The decomposition of the bornyl esters may be postulated in a similar fashion. The sulphonic acid splits off as before leaving a residue with two free valencies on adjacent carbon atoms. There are now three possibilities. The two valencies may saturate themselves with the formation of bornylene, molecular rearrangement of the residue may result in the formation of camphene, or two residues may combine by means of these free valencies to give dibornylene. This may be postulated as follows, R standing as before for the benzene or naphthalene nucleus:-



Bornylene

Camphene.



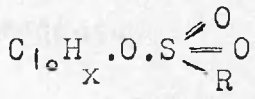
Dibornylene.

The conditions of the experiment again determine whether dibornylene or camphene is formed, but in no circumstances does bornylene seem to be formed - at least none can be isolated. Hydrolytic methods give both camphene and dibornylene, but the proportions of these compounds could not be obtained. Distillation in vacuo also gives these two products, but dibornylene is the main one. Decomposition in sealed tubes and in solution leads to the formation of dibornylene only of the above-mentioned compounds, there, however, being some secondary reaction in the case of heating in sealed tubes which results in the formation of dihydrocamphene. This, however, cannot be readily postulated in equation form.

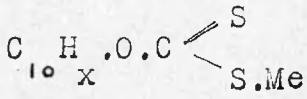
Thus the menthyl and bornyl esters show quite analagous behaviour when they are decomposed in sealed tubes and in solution, but a distinct divergence is noticeable with decomposition by distillation, the menthyl esters giving menthene and the bornyl esters dibornylene as the chief product. This probably applies also to the decomposition by hydrolytic methods, but it cannot be definitely proved.

It is remarkable that all these esters, sulphonates and xanthogenates, which contain sulphur in the acid group but which otherwise have such different structures,

the terpenic group being linked through oxygen to sulphur in the former and by oxygen to carbon in the latter, according to the structures



and



Sulphonate Xanthogenate

should show such instability and that the former should decompose readily under such varied conditions. The fact that menthol can be easily dehydrated by the action of acids, especially dibasic acids, at high temperatures does not explain the decomposition of these esters in the homogeneous state a few degrees above their melting points, for the conditions necessary are quite different. These were studied by Zelokoff (Ber., 1904, 37, 1374), who found that with tartaric, succinic, citric, phthalic, and terephthalic acids the mechanism of the reaction was:-

menthol + acid = acid ester + normal ester

normal ester + acid = acid ester

acid ester ⟶ menthene + acid.

Excess acid was essential and the temperature of the decomposition was 200° or above. It seems therefore that the sulphur present in the acid group acts as an unstabilising agent, although a reason for this is not apparent.

This view is strengthened by the hydrolysis of diethyl sulphite (B., 1898, 31, 406) with NaOH, when, instead of obtaining the sodium salt of ethyl hydrogen sulphite, the isomer sodium ethyl sulphonate is found to be the product.

ROTATION of MENTHYL SULPHONIC ESTERS in VARIOUS SOLVENTS.

The rotations of the three menthyl esters whose decomposition under various conditions were investigated in Part I, were examined for three colours of light, namely, mercury yellow ($\lambda = 5790$), mercury green ($\lambda = 5461$), and mercury violet ($\lambda = 4358$), and in six solvents, ethyl alcohol, benzene, pyridine, nitrobenzene, ethylene dibromide, and quinoline. Since the object of the investigation was to obtain a general oversight, only one solution was examined in each case, the concentrations ranging between C = 4·45, and C = 1·0. The results obtained are tabulated below.

Table I.

Specific Rotations of Menthyl Sulphonates in Various Solvents.

t = approximately 17.5 throughout.

a = ethyl alcohol.

b = benzene.

c = pyridine.

d = nitrobenzene

e = ethylene dibromide.

f = quinoline.

Table I. (Contd.)

Menthyl Benzenesulphonate.

Solvent	a	b	c	d	e	f
Concent-ration	4·0	4·5	4·0	4·0	4·0	4·0
y	-74·75	-65·50	-67·95	-67·44	-72·67	-64·42
g	-84·64	-74·05	-76·34	-75·94	-82·64	-72·82
v	-142·17	-123·92	-128·41	-127·90	-138·60	-122·78

Menthyl Naphthalene-α-sulphonate.

Solvent	a	b	c	d	e	f
Concent-ration	1·0	1·0	1·0	3·0	1·0	3·0
y	-101·81	-81·40	-87·27	-92·16	-145·19	-84·77
g	-114·77	-93·25	-98·45	-104·63	-163·53	-97·23
v	-194·27	-158·10	-166·00	-178·08	-276·18	-165·11

Menthyl Naphthalene-β-sulphonate.

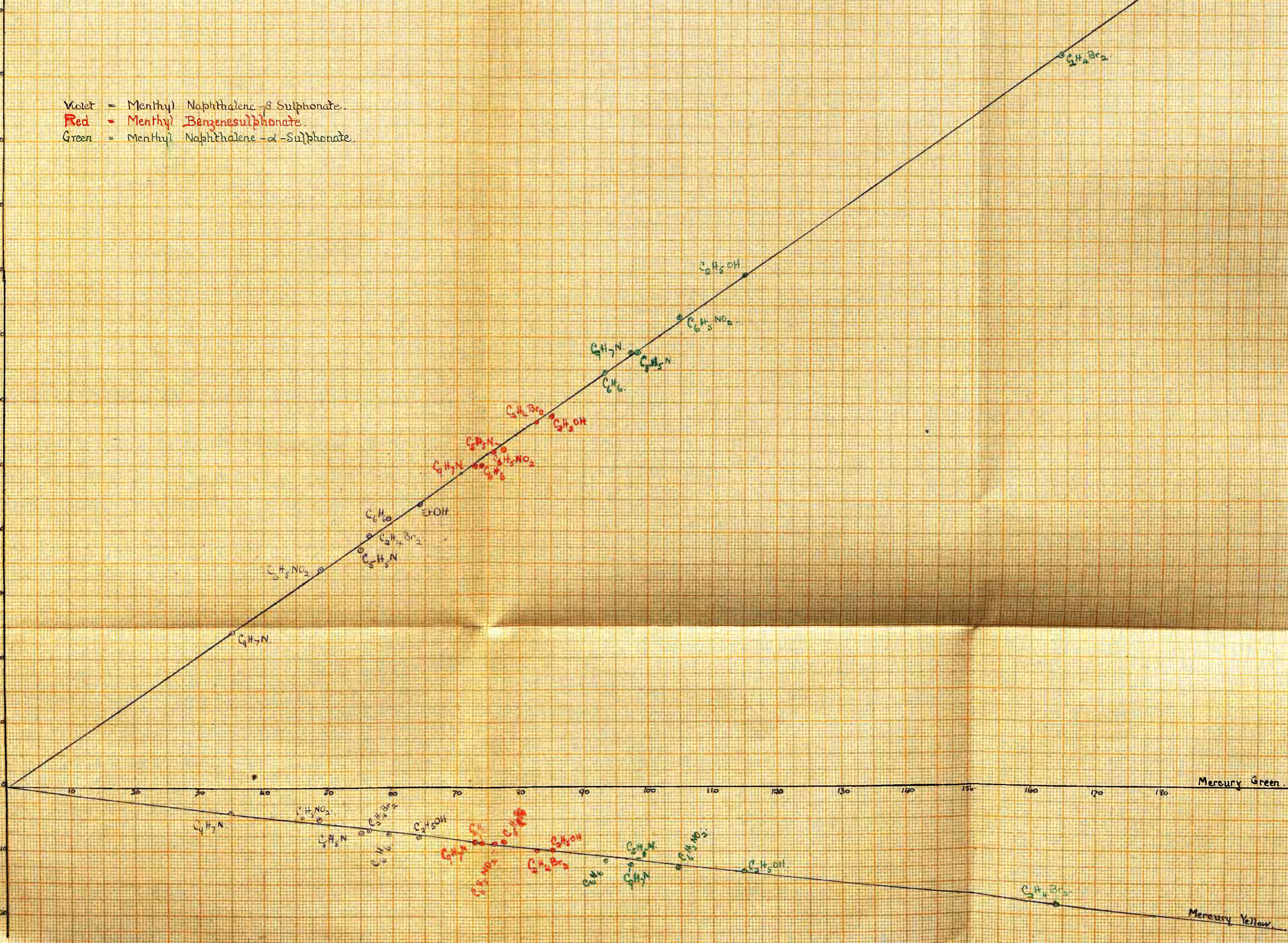
Solvent	a	b	c	d	e	f
Concent ration	1·0	1·0	1·0	3·0	1·0	3·0
y	-56·15	-51·89	-47·70	-43·87	-49·34	-31·21
g	-64·00	-59·34	-55·01	-48·67	-56·33	-35·10
v	-108·00	-101·94	-92·18	-82·64	-95·75	-59·07

Although the rotations vary considerably in each case with change of solvent, the change is not sufficient to cause any overlapping, so that the solutions of each substance form a separate group, the rotations of menthyl naphthalene-β-sulphonate being the lowest, and those for menthyl naphthalene-α-sulphonate the highest. The rotations for the benzenesulphonate solutions lie wholly between the others. It may also be noticed that the different solvents do not influence the rotations in the same way, although there is some similarity. Quinoline, which usually has a powerful effect either towards exaltation or depression, produces the lowest rotation in menthyl naphthalene-α-sulphonate and in menthyl benzenesulphonate, and the second lowest in menthyl naphthalene-β-sulphonate. Ethylene dibromide, on the other hand, which usually has a powerful influence of the opposite character to quinoline, produces the highest rotation in menthyl naphthalene-α-sulphonate, the second highest in menthyl benzenesulphonate, and the third highest in menthyl naphthalene-β-sulphonate. On the whole this general tendency is recognisable.

These values were then plotted on a characteristic diagram according to Patterson's method, and lay with fair agreement along lines intersecting one another

Characteristic Diagram
for.
Menthyl Sulphonic Esters
in Various Solvents.

Violet = Menthyl Naphthalene-β Sulphonate.
Red = Menthyl Benzenesulphonate.
Green = Menthyl Naphthalene-α-Sulphonate.



very close to the origin of the diagram (see diagram I), and in such a way, as far as can be judged when extrapolation has to be carried out through some 35° of rotation, as to indicate little or no region of anomalous rotation dispersion. It follows from this that the dispersion coefficients for all these compounds calculated by the ordinary method ought to be almost the same throughout. That this is the case is shown by the following table of dispersion ratios.

Table II.

Dispersion Ratios.

	Menthyl benzene Sulphonate		Menthyl Naphthalene-α-sulphonate		Menthyl Naphthalene -β-sulphonate.	
Solvent	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g.
Alcohol	1·680	0·883	1·692	0·887	1·687	0·878
Benzene	1·664	0.884	1·695	0·873	1·716	0·875
Pyridine	1·669	0·890	1·686	0·887	1·676	0·852
Nitrobenzene	1·685	0·888	1·703	0·881	1·698	0·902
Ethylene Dibromide	1·665	0·879	1·689	0·888	1·700	0·876
Quinoline	1·685	0·885	1·709	0·872	1·683	0·889.

PART II.

ROTATION of MENTHYL and BORNYL ESTERS of BENZENE and NAPHTHALENE-α- and -β- SULPHONIC ACIDS in VARIOUS SOLVENTS.

Kenyon and Pickard (1915, T., 35) have plotted a characteristic diagram for most of the menthyl derivatives known, and find that the majority of these lie on the same diagram with the ordinary dispersion coefficient, ranging mainly between $^{V}/_{G}$ = 1·634 and 1·675. The exceptions found by them were the esters of the various nitro and halogen nitro benzoic acids. The characteristic diagram for the latter does not show the lines intersecting near the origin, and the dispersion coefficients therefore vary from $^{V}/_{G}$ = 1·77 to 2·59. The sulphonic esters therefore lie approximately on the same characteristic diagram as the normal menthyl esters.

Rotation of Bornyl Sulphonic Esters in Various Solvents.

The rotations of these esters were examined for the same colours of light and in the same solvents as in the previous case. Only one solution was examined in each case, the concentrations ranging from 2·5 to 3·5. The data obtained are as follows.

Table III.

Specific Rotations of Bornyl Sulphonates in Various Solvents.

t = approximately 17·5 throughout.

a = ethyl alcohol.

b = benzene.

c = pyridine.

d = ethylene dibromide

e = quinoline

f = nitrobenzene.

Bornyl Benzenesulphonate.

Solvent	a	b	c	d	e	f
Concentration	2·5	3·0	3·5	3·5	3·5	3·5
y	-19·00	-19·98	-21·84	-25·60	-26·56	-18·85
g	-22·00	-23·15	-24·84	-29·43	-30·57	-21·74
v	-36·40	-38·30	-41·13	-49·00	-51·13	-36·00

Bornyl Naphthalene-α-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	2·5	3·0	3·5	3.5	3·5	3·5
y	- 22·80	-20.51	-18·14	-26.28	-27·14	-20·00
g	-26·40	-23.50	-20·71	-30·00	-31·14	-22·83
v	-43.60	-38·80	-34·11	-49·57	-51.43	-38.28

Bornyl Naphthalene-β-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	2·5	3·0	3·5	3·5	3·5	3·5
y	-14·00	-14·25	-14·99	-19·43	-17·29	-13·14
g	-16·00	-16·50	-17·28	-22·43	-20·00	-15·14
v	-26·40	-27·17	-28·56	-37·14	-33·14	-25·14

The rotations vary considerably in each case with change of solvent, and this change causes overlapping of one set of readings with another. The solutions of bornyl naphthalene-β-sulphonate show the lowest rotations, and form a group almost by themselves, the only solution overlapping those of the other esters being that in ethylene dibromide, which suffers a large exaltation. Solutions of the other two esters in the different solvents give values which overlap each other completely, the range of variation being greater with the naphthalene-α-sulphonate than with the benzenesulphonic ester. This is quite different from the behaviour of the menthyl esters in these solvents, each of the latter, as already pointed out, forming a group by themselves.

Another interesting point is the fact that while

the introduction of the sulphonic acid groups into menthol causes an increase in rotation, the introduction of the same groups into borneol causes a decrease in the rotation. In both cases the naphthalene-β-sulphonate shows the lowest rotation and the naphthalene-α-sulphonate the highest, with the benzenesulphonate in between. It follows that the introduction of the same group into these two terpenic alcohols does not effect a similar change in rotation but rather the opposite, the naphthalene-α-sulphonic radicle producing the greatest change in the case of the menthol, and the naphthalene-β-sulphonic radicle in the case of borneol.

It may also be noticed that the different solvents do not influence the rotations in the same way, although there is some similarity. Quinoline, which usually has a powerful influence either towards exaltation or depression, produces in this case the highest rotation in bornyl naphthalene-α-sulphonate and in bornyl benzenesulphonate, and the second highest rotation in bornyl naphthalene-β-sulphonate. Ethylene dibromide, which should have a powerful influence in the opposite direction to quinoline, has with these esters a similar effect, and produces the highest rotation in bornyl naphthalene-β-sulphonate, and the second highest with the other two esters, while nitrobenzene produces the lowest rotation in bornyl

naphthalene-β-sulphonate and in bornyl benzenesulphonate, and the second lowest in bornyl naphthalene-α-sulphonate, the lowest rotation in that case being produced by pyridine. There is thus some similarity in the action of the same solvent on the three esters.

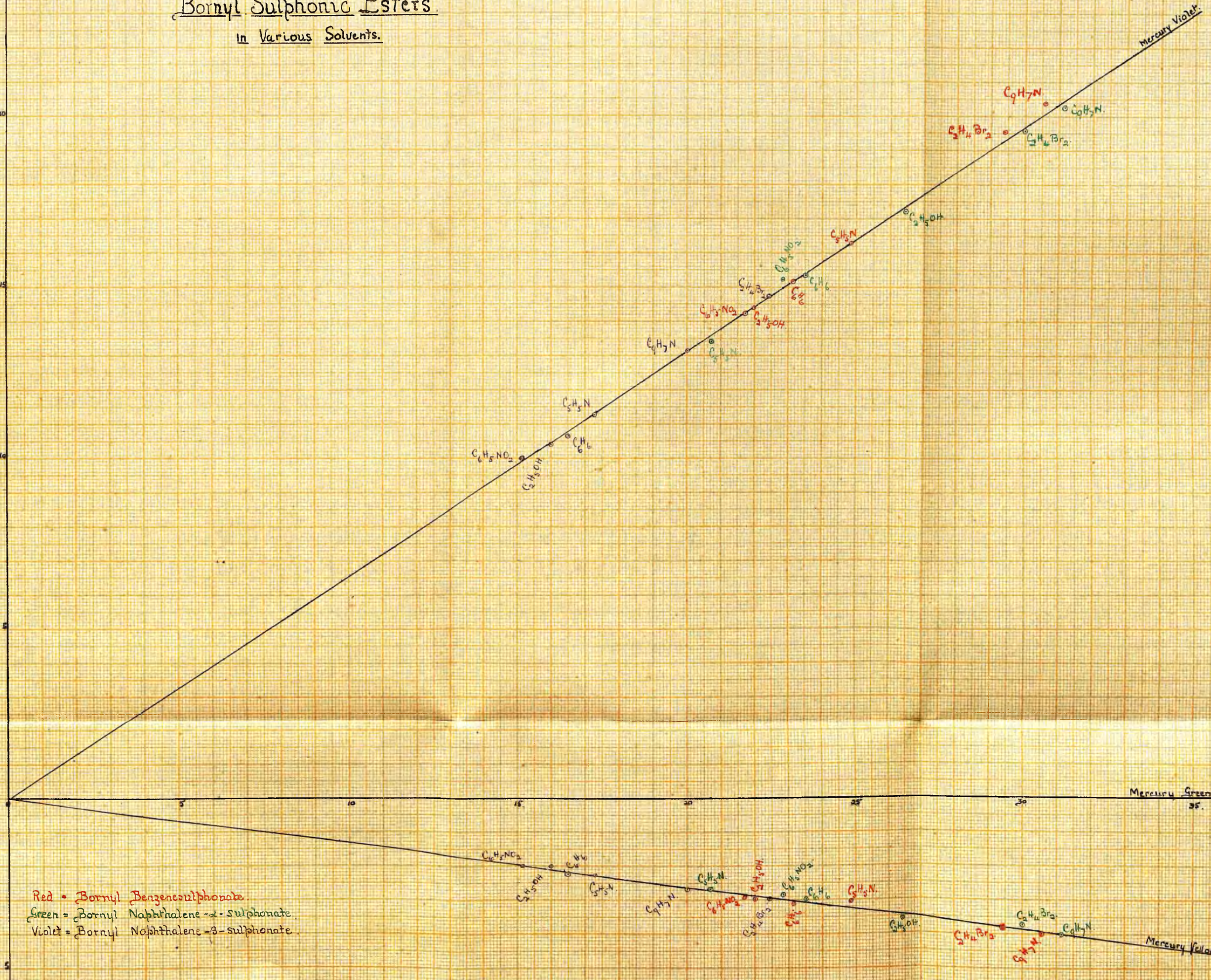
The values obtained for the rotation of the three esters in the various solvents were plotted on a characteristic diagram in the same manner as before, and lay with good agreement along lines intersecting one another very near the point of origin of the diagram. These esters therefore afford another example of compounds which should give constant dispersion coefficients when these are calculated by the ordinary method. This is seen by the following table to be roughly the case.

Table IV.

Dispersion Ratios.

	Bornyl Benzene Sulphonate		Bornyl Naphthalene-α-sulphonate		Bornyl Naphthalene-β-sulphonate.	
Solvent	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g
Alcohol	1·655	0·864	1·625	0·875	1·651	0·863
Benzene	1·654	0·863	1·646	0·863	1·650	0·873
Pyridine	1·655	0·879	1·652	0·868	1·647	0·876

Characteristic Diagram for Bornyl Sulphonic Esters in Various Solvents.



Red = Bornyl Benzenesulphonate.
Green = Bornyl Naphthalene -α- Sulphonate.
Violet = Bornyl Naphthalene -β- sulphonate.

Table IV. (Contd.)

Solvent	Bornyl Benzene Sulphonate		Bornyl Naphthalene-α-sulphonate		Bornyl Naphthalene-β-sulphonate	
	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g	Hg_v/Hg_g	Hg_y/Hg_g
Ethylene Dibromide	1·665	0·868	1·656	0·866	1·652	0·876
Quinoline	1·683	0·878	1·658	0·864	1·667	0·871
Nitrobenzene	1·655	0·867	1·661	0·868	1·675	0·875.

Comparing these ratios with those found for the menthyl esters (Table II, page 76), it will be seen that they are similar, but that the values obtained for the bornyl esters are slightly lower than those found for the menthyl esters, this being more apparent with the ratio $V/_G$. Nevertheless, it is obvious that all these sulphonic esters lie approximately on the same characteristic diagram, this being the one found by Kenyon and Pickard to include most of the menthyl esters. This is unexpected since the bornyl esters that they had plotted on a characteristic diagram (see same paper) gave the same type of diagram but dispersion coefficient $V/_G$ = 1·707 to 1·871, and one would naturally expect the esters to lie on that diagram.

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