CCCXXVI.—*The Decomposition of Bornyl Benzene- and Naphthalene-sulphonates by Heat. The Products of Hydrolysis of Bornyl and Menthyl Benzene- and Naphthalene-sulphonates. The Influence of Solvents on the Temperature of Decomposition of these Bornyl and Menthyl Sulphonates.*

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IN a recent paper (J., 1927, 349) we showed that the menthyl esters of benzene-, naphthalene-α- and naphthalene-β-sulphonic acids decomposed in two different ways according as they were (*a*) directly distilled under reduced pressure or (*b*) heated for some time before distillation. In the first case the main reaction was decomposition into menthene and the corresponding sulphonic acid, but in the second any menthene originally produced was converted into dimenthene and more complex substances.

These results seemed sufficiently interesting to make it worth while to extend the investigation to the behaviour of the corresponding bornyl esters, and for this purpose we have used mostly the *l*-bornyl derivatives, since *d*-borneol is not easily obtained in pure condition. We examined first, fairly completely, the naphthalene-β-sulphonic ester, as it is rather more easily obtained; the other esters were examined with less completeness, but sufficiently to establish similarity of behaviour in all three.

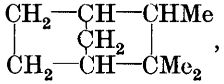
Decomposition by Distillation under Reduced Pressure.—When bornyl naphthalene-β-sulphonate was distilled from an oil-bath as rapidly as possible under a pressure of 18 mm., a small quantity (15—20% of the theoretical amount) of a clear, optically inactive liquid passed over at about 60°. This on redistillation boiled at 155—158° under ordinary pressure and solidified to a white substance, m. p. 51° (Found : C, 88·2, 88·1; H, 11·85, 11·8; *M*, cryoscopic in benzene, 137. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%; *M*, 136). The substance decolorised bromine and gave, when hydrogen chloride was passed through its solution in ether, a white precipitate which melted at 125—127° after recrystallisation from alcohol containing hydrogen chloride. These data indicate that the decomposition product is camphene.

The residue in the flask after the distillation of the camphene separated into two layers, the lower of which solidified. We found it best to separate these layers by dissolving the whole mass in warm water and extracting the solution with toluene. The extract was dried with calcium chloride and distilled under reduced pressure and after removal of the solvent a viscous, almost inactive liquid distilled at 168°/4 mm. (Found : C, 88·1, 88·2; H, 11·8, 11·8. Calc. for $C_{20}H_{32}$: C, 88·2; H, 11·8%). Since Tschugaev, on distilling bornyl methyl xanthogenate, obtained bornylene and a little camphene, and analogy seems to exist between the reactions of the xanthogenates and sulphonates under similar conditions (*e.g.*, menthyl xanthogenates and sulphonates), the substance we have obtained is presumably dibornylene, for which, however, there is no very satisfactory criterion beyond the analytical data. In addition to this liquid a certain amount of a gelatinous material of indefinite boiling point was obtained, but this we have not been able either to purify or identify.

The aqueous layer after the extraction with toluene was strongly acid : by neutralising it with barium carbonate a salt was obtained (Found : Ba, 24·1, 24·15%), showing that the other product of decomposition was naphthalene-β-sulphonic acid.

Bornyl naphthalene-α-sulphonate and bornyl benzenesulphonate distilled under reduced pressure gave the same volatile products, leaving behind naphthalene-α-sulphonic acid and benzenesulphonic acid respectively.

It thus appears that by distilling these sulphonic esters of borneol, a small quantity of camphene and a considerable quantity of dibornylene and a more complex product are obtained, whereas Tschugaev by decomposing bornyl methyl xanthogenate obtained mainly bornylene and a little camphene.

Bornyl naphthalene-β-sulphonate heated in a sealed tube (no pressure is developed) at 80—90° for 2—3 hours was completely separated into two layers. On cooling, the lower layer (B) solidified. The upper layer (A) on distillation under reduced pressure gave two fractions, b. p. 60—65°/4 mm. and 140—240°/4 mm. The former on redistillation boiled at 157—160° under ordinary pressure and ultimately solidified; m. p. 85° (Found: C, 86·7, 86·7; H, 13·2, 13·2; *M*, cryoscopic in benzene, 136·8. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%; *M*, 138). The substance did not decolorise bromine and would appear to be dihydrocamphene, since it corresponds closely with the behaviour given for that substance by Vavon (*Compt. rend.*, 1907, **149**, 997) and by Henderson and Pollock (J., 1910, **97**, 1620), and, if Wagner's formula for camphene is accepted, may be presumed to have the formula 

$$\begin{array}{l} CH_2-CH-CHMe \\ |\qquad CH_2 \qquad | \\ CH_2-CH-CMe_2 \end{array}$$

, but no more satisfactory method of identifying this compound seems to be available.

The higher-boiling portion on distillation under reduced pressure gave two fractions, one boiling at 168°/4 mm., and the other, a gelatinous mass which could not be purified or identified, boiling from 240—270°/4 mm. (Found for the former: C, 88·2, 88·2; H, 11·8, 11·8; *M*, cryoscopic in benzene, 268·7. Calc. for $C_{20}H_{32}$: C, 88·2; H, 11·8%; *M*, 272).

Since on decomposition, in sealed tubes, of the corresponding menthyl sulphonates, dimenthene was formed, the above substance is presumably dibornylene. It has the same physical properties as the substance obtained on decomposition by direct distillation.

The strongly acid, solid layer (B) was dissolved in water and boiled with animal charcoal, and a barium salt was precipitated by means of barium chloride and recrystallised from water [Found: Ba, 24·0, 24·15. Calc. for $Ba(SO_3{\cdot}C_{10}H_7)_2,H_2O$: Ba, 24·1%]. The solid is therefore naphthalene-β-sulphonic acid.

Bornyl naphthalene-α-sulphonate and bornyl benzenesulphonate decomposed in a strictly analogous fashion, yielding also what were probably dihydrocamphene, dibornylene, and a gelatinous mass of high boiling point, along with the corresponding sulphonic acid.

Decomposition in Solution.—When bornyl naphthalene-β-sulphonate was heated to boiling in 10% benzene solution for 6 hours there was no change in the rotation of the solution. If, however, toluene was substituted for benzene and the solution heated to 110°, definite decomposition took place and, on cooling, a solid separated. This was acid and gave the characteristic barium salt of naphthalene-α-sulphonic acid. On distillation of the filtrate a liquid, b. p. 285—

290°, or 168°/4 mm., was obtained identical with the high-boiling liquid presumed to be dibornylene.

The two corresponding esters decomposed in the same way, giving dibornylene and the corresponding sulphonic acid, when heated in solution in toluene. Bornyl benzenesulphonate gave a similar result even in boiling benzene.

Hydrolysis of Bornyl Benzene- and Naphthalene-sulphonates.—*d*-Borneol prepared from camphor by reduction contains a considerable proportion of *l*-*iso*borneol which renders the preparation of pure *d*-borneol rather difficult. We found that the bornyl naphthalene-β-sulphonate obtained from commercial *d*-borneol, unlike the naphthalene-α-sulphonate or the benzenesulphonate, could be completely purified by recrystallisation, and it seemed a comparatively simple matter to obtain pure *d*-borneol by hydrolysing the ester thus purified. These bornyl esters, however, cannot be hydrolysed in any of the usual ways, the products obtained being somewhat similar to those got by direct decomposition of the esters.

(1) *Action of water and aqueous potassium hydroxide.* When steam was blown through bornyl naphthalene-β-sulphonate suspended in water or in dilute aqueous caustic potash for 20—30 minutes, only water appeared to distil over and the ester seemed to be practically unchanged.

But when the ester was heated on the water-bath for 2—3 hours with either water or caustic alkali, decomposition took place, and steam now removed a colourless liquid. This did not solidify when separated from the water, and was ethereal in odour. Benzene extracted from it a liquid, b. p. 155—159°, which was optically inactive, gave on analysis results corresponding roughly to the formula $C_{10}H_{16}$, and from its odour seemed to be mostly camphene: it decolorised bromine water. It gave no solid hydrochloride when treated in ether with dry hydrogen chloride, but, on evaporation of the ether, the residue separated into a brown oil and a colourless portion. The latter solidified and had the melting point of camphene hydrochloride. Such camphene as was formed, however, was apparently mixed with other substances, it being very probable that even if hydrolysis gave different products from the simple heating of the ester the products of hydrolysis were almost certain, in the circumstances of the experiment, to be mixed with the products due to direct decomposition of the ester by heat. It was not found possible to identify definitely the substances present, but certainly no borneol was obtained.

(2) *Alcoholic potassium hydroxide.* A solution of bornyl naphthalene-β-sulphonate in a slight excess of alcoholic caustic potash, when heated on the water-bath for several hours, deposited

potassium naphthalene-β-sulphonate. The alcoholic solution was dried with potassium carbonate and most of the alcohol distilled off under reduced pressure. On pouring the residue into water a very small quantity of unchanged ester separated. No borneol was obtained, and we found it impossible completely to identify the products of hydrolysis. All that was noticeable was a strong odour of camphene—a substance extremely difficult to separate from its alcoholic solution.

We attempted this separation by distillation with an efficient fractionating column without success, but, by passing dry hydrogen chloride through the alcoholic solution and adding water, camphene hydrochloride was precipitated; it was rapidly filtered off and crystallised from alcohol containing hydrogen chloride, sufficient being obtained for identification. Any other substances present could not be identified.

In another attempt, the alcoholic solution was poured into a large excess of water, and the whole extracted with toluene, although this did not remove all the camphene. The toluene solution was dried with calcium chloride, and the toluene distilled off under reduced pressure. The main portion of the residue distilled at 155° and formed camphene hydrochloride, but some higher-boiling material had also been formed which could not be satisfactorily identified. The amount of terpene isolated in this manner was about 10% of the theoretical. Experiments to hydrolyse the ester with sodium ethoxide in alcohol and with barium hydroxide in aqueous alcohol were equally unsuccessful, the same products being again indicated. It seems very remarkable that, whereas such esters as bornyl acetate, bornyl *p*-nitrobenzoate (Henderson and Heilbron, P., 1913, 381), bornyl hydrogen phthalate (Pickard and Littlebury, J., 1907, **91**, 1973), and bornyl mandelate (McKenzie and Thompson, J., 1905, **87**, 1013) can easily be hydrolysed in a normal manner, bornyl benzene- and naphthalene-sulphonates decompose in an entirely different fashion, presumably similar to that in which they are decomposed by simple heating.

Hydrolysis of Menthyl Benzene- and Naphthalene-sulphonates.—On account of the peculiarities observed with the bornyl esters we examined also the hydrolysis of the corresponding menthyl derivatives.

(i) *Action of aqueous potassium hydroxide.* When menthyl benzenesulphonate was heated for several hours at about 80—85° with aqueous potassium hydroxide solution (10—15%), decomposition (which was not complete even after 5 or 6 hours) took place and a colourless oil separated. This was distilled over in steam and isolated by means of benzene. It boiled at 165°, gave on analysis figures corresponding almost exactly to the formula $C_{10}H_{18}$, decolorised bromine, formed a nitrosochloride, m. p. 115°, and was therefore menthene. No side reactions seemed to take place in this case.

Menthene was similarly formed when menthyl naphthalene-β-sulphonate was treated with aqueous potassium hydroxide, but even after heating for 6 hours 50% of the ester was recovered unchanged.

(ii) *Hydrolysis with barium hydroxide.* The three menthyl sulphonates were all decomposed by heating with aqueous-alcoholic solutions of barium hydroxide. The barium salt of the acid was formed almost quantitatively in each case. No menthol, however, could be obtained, but menthene was produced and was extracted from the aqueous-alcoholic solution by toluene; little, if any, of the higher-boiling dimenthene was formed. The decomposition, therefore, with aqueous caustic potash and with alcoholic barium hydroxide is practically identical with the decomposition of the esters when distilled rapidly under reduced pressure.

Temperature of Decomposition in Different Solvents.—From the experiments which have been detailed both here and in connexion with the menthyl esters, it appeared that the decomposition of these sulphonates took place more rapidly in certain solvents than in others, and we thought it worth while to examine this phenomenon systematically. We therefore made up 0·8 g. of ester to 10 c.c. with various solvents and heated the solution for one hour in a thermostat kept at a definite temperature. The solution was then cooled rapidly, diluted with 20 c.c. of absolute alcohol (distilled over quicklime), and titrated with alcoholic potash, a blank experiment being carried out in each case. The results are shown in the table on p. 2470.

It will be observed that not only does increase of temperature cause an increase in the velocity of the reaction, but that there is a great diversity of effect between the different solvents, the rate of increase being much greater in some than in others. The effect of the same solvent on the three esters, however, is, in general, fairly similar. Toluene causes little decomposition in 1 hour at any of the temperatures used, and the alcohols cause considerable decomposition at all temperatures, the percentage increasing with decrease in molecular weight of the alcohol. Although decomposition in the non-alcoholic solvents practically ceases below 85°, it continues to be quite appreciable in the alcohols at considerably lower temperatures. In fact, methyl alcohol at 65° causes more decomposition in a given time than the non-alcoholic solvents at 90—95°. Water would probably show the greatest effect, but this could not be proved owing to the insolubility of these esters even in aqueous-alcoholic solutions. Nitrobenzene causes little decomposition below 100°, but at 105° decomposition is practically complete in all cases. Ethylene dibromide causes little decomposition in menthyl benzenesulphonate even at 105°, but almost complete decomposition at this temperature in 1 hour in the two naphthalene-sulphonic esters.

Percentage of ester decomposed in one hour.

Temp.	C_7H_8.	$C_6H_5{\cdot}NO_2$.	$C_2H_4Br_2$.	C_5NH_5.	$Bu^{\beta}OH$.	$Bu^{\alpha}OH$.	Pr^{α} OH.	EtOH.	MeOH.
Menthyl benzenesulphonate.									
65°	—	—	—	—	—	—	—	3·73	8·95
70	—	—	—	—	—	—	3·17	5·13	—
75	—	—	—	—	—	4·10	5·88	8·73	—
80	—	—	—	—	—	6·77	10·70	—	—
85	0·98	2·37	—	2·37	9·89	10·85	16·42	—	—
90	1·04	2·75	2·48	3·19	16·20	17·27	25·74	—	—
95	1·06	5·88	2·67	4·72	27·17	28·15	38·39	—	—
100	2·23	12·87	4·20	9·80	43·12	45·14	—	—	—
105	2·37	82·15	9·18	14·08	54·44	60·23	—	—	—
Bornyl naphthalene-β-sulphonate.									
65	—	—	—	—	—	—	—	3·19	8·18
70	—	—	—	—	—	3·12	4·01	6·44	—
75	—	—	—	—	—	5·31	7·12	9·78	—
80	—	—	—	—	—	7·51	10·58	—	—
85	—	—	—	—	—	12·65	15·31	—	—
90	—	6·41	4·39	5·21	17·16	20·90	26·35	—	—
95	—	7·33	6·30	6·36	27·82	31·61	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	—	—	—
Menthyl naphthalene-β-sulphonate.									
65	—	—	—	—	—	—	—	4·92	12·92
75	—	—	—	—	—	5·62	8·27	13·53	—
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	—	—	—

EXPERIMENTAL.

l-*Bornyl Benzenesulphonate.*—Pure *l*-borneol (18·5 g.) recrystallised from light petroleum [m. p. 203°, $[\alpha]_{5461}^{17^{\circ}}$ (benzene, *c* = 5·25) — 42·81°] was dissolved in pyridine (60 g.) and cooled to 0°. Benzenesulphonyl chloride (21·1 g.) was then added very slowly with constant stirring, the temperature being kept below 3°. Crystals soon began to separate, and on continued stirring became very abundant. After 3 or 4 hours, a large quantity of water was added and ultimately the oil which first separated solidified; it was then filtered off and dried. In several preparations the oil would not solidify in contact with water. It was then extracted with benzene, the extract dried with calcium chloride, and the benzene removed by evaporation in air and finally over sulphuric acid in a vacuum desiccator; the residue then solidified to a pale yellow, crystalline mass.

l-*Bornyl benzenesulphonate* is very soluble in all common organic solvents; but may be crystallised from light petroleum, giving fine, white, slightly elongated crystals, m. p. 52°; $[\alpha]^{17°}_{5461}$ in benzene ($c = 2{\cdot}5$) $-$ 22·40°, in alcohol ($c = 2{\cdot}5$) $-$ 22·00°. Several crystallisations are necessary to obtain the substance free from borneol; the yield of pure product is about 25% [Found : S (fusion method), 10·7. $C_{16}H_{22}O_3S$ requires S, 10·95%].

d-*Bornyl benzenesulphonate*, m. p. 52°, is prepared and purified in exactly the same way as the *l*-ester. When prepared from crude *d*-borneol, a product is obtained the rotation of which is lower than that of the pure *l*-compound, + 21·30° (similar conditions), and we were unable to raise it by crystallisation.

l-*Bornyl naphthalene-β-sulphonate* was prepared from pure *l*-borneol (18·5 g.) in pure pyridine (90 g.) by means of naphthalene-β-sulphonyl chloride (27·2 g.) in a similar manner to the benzenesulphonate. It is soluble in all the common solvents, but may be recrystallised from methyl or ethyl alcohol, and from light petroleum, from which it separates in stellate masses of glistening, white, needle-shaped crystals. After three crystallisations it has m. p. 76°, and $[\alpha]^{17{\cdot}5°}_{5461}$ in benzene ($c = 3$) $-$ 16·50° and in alcohol ($c = 2{\cdot}5$) $-$ 16·00°. The yield of pure product is 60% [Found : S (fusion method), 9·2. $C_{20}H_{24}O_3S$ requires S, 9·3%].

d-*Bornyl naphthalene-β-sulphonate* was prepared, in exactly the same way as the corresponding *l*-ester, from commercial *d*-borneol, which contains *l*-*iso*borneol. Crystallisation from methyl or ethyl alcohol or light petroleum alone gave a product of m. p. 76°, the rotation of which, however, could not be raised beyond $[\alpha]^{17{\cdot}5°}_{5461}$ (in benzene, $c = 3$) $-$ 15·8°. But after the ester had been crystallised twice from a *mixture* of methyl alcohol and light petroleum the rotation rose to the value found for the *l*-ester.

l-*Bornyl naphthalene-α-sulphonate* was prepared and isolated in the way described for *l*-bornyl benzenesulphonate, naphthalene-α-sulphonyl chloride (27·2 g.) being used. The substance was difficult to purify owing to its great solubility, but after three to six recrystallisations from light petroleum it was obtained in fine, white crystals, m. p. 90°, $[\alpha]^{17{\cdot}5°}_{5461}$ in benzene ($c = 2{\cdot}5$) $-$ 23·20° and in alcohol ($c = 2{\cdot}5$) $-$ 26·4° (Found : S, 9·2. $C_{20}H_{24}O_3S$ requires S, 9·3%).

The corresponding *d*-ester was prepared from crude *d*-borneol but could not be completely purified.

Summary.

Menthyl esters of benzene-, naphthalene-α- and naphthalene-β-sulphonic acids, when directly distilled under reduced pressure, yield menthene and the corresponding sulphonic acid; but if they

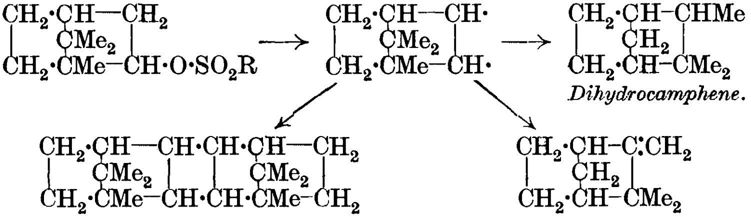
are heated for some time before distillation, dimenthene and more complex substances are produced, but no menthene.

The corresponding bornyl esters, when directly distilled, yield camphene, dibornylene, a more complex gelatinous material which we have been unable to purify or identify, and sulphonic acid.

The bornyl esters, when heated for 2 or 3 hours and then distilled, yield dihydrocamphene, dibornylene, a gelatinous material, and sulphonic acid.

The bornyl esters, heated to boiling in toluene solution, yield dibornylene and the corresponding sulphonic acid.

These changes may be represented thus :—



Dihydrocamphene.

Dibornylene.

Camphene.

if the current formulæ for camphene and dihydrocamphene be accepted.

The menthyl and bornyl esters of benzene- and the naphthalenesulphonic acids do not hydrolyse to yield menthol and borneol, but, on the contrary, decompose in somewhat the same way as when heated alone.

The rate at which these esters decompose in solution depends quite markedly on the nature of the solvent; and in the alcohols the velocity increases rapidly as the molecular weight diminishes. Tables are given showing this behaviour.

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