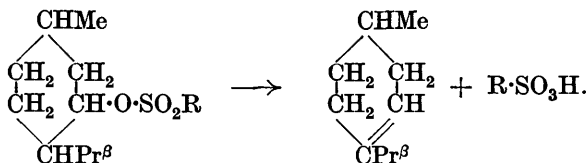


LIII.—*The Decomposition Products of Menthyl Esters of Sulphonic Acids.*

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WHILE engaged in an examination of the optical rotation of menthyl benzenesulphonate and menthyl naphthalene- β -sulphonate, Patterson and Frew (J., 1906, **89**, 332) noticed that these compounds decompose at temperatures just above their melting points, both in the homogeneous state and in nitrobenzene solution, whereas

many other menthyl esters are much more stable, and are distillable at considerably higher temperatures. We have recently investigated this decomposition more fully and have found that, on direct distillation of menthyl benzene- and naphthalene- α - and - β -sulphonates under reduced pressure, the main reaction is decomposition into menthene and the corresponding sulphonic acid according to the equation

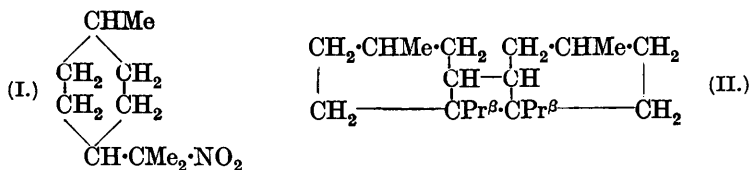


But when the heating of the homogeneous ester is carried out in sealed tubes at ordinary pressure, secondary decompositions take place with formation of hexahydrocymene, carbonaceous matter, and tarry products, whilst the menthene which is possibly first formed polymerises to dimenthene and a more complex gelatinous substance. None of the menthene appears to survive, if indeed it is formed at all.

EXPERIMENTAL.

Menthyl benzenesulphonate (m. p. 80°) was prepared as described in the paper quoted above, and was then decomposed in various ways.

I. On heating the ester at 85 — 90° for 6 hours in a tube, which, although no pressure developed, was sealed, complete separation into two layers took place. On cooling, the lower brown layer solidified to form a low-melting, deliquescent solid. The upper layer in the crude condition had a slight positive rotation; it was separated, by distillation at 4 mm. pressure, into two fractions of b. p. 72 — 75° and 150 — 240° . The lower-boiling fraction (A) was a clear, colourless, optically-inactive liquid, distilling at ordinary pressure from 167 — 169° (Found: C, 85.7, 85.6; H, 14.4, 14.4; M , cryoscopic in benzene, 142. d_4^{20} 0.7962, n_D^{20} 1.44009; whence $[R_L]_D = 46.35$. $\text{C}_{10}\text{H}_{20}$ requires C, 85.7; H, 14.3%; M , 140). The substance appears thus to be a saturated ring compound. With nitric acid (d 1.075), a yellow nitro-derivative was obtained, b. p. 135 — $137^\circ/25$ mm., n_D 1.46241, presumably therefore tertiary nitromenthane (I). The original liquid thus appears to be hexahydrocymene, which has been shown to form a tertiary nitro-compound corresponding to that which we obtained (Konowalov, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 237).



The higher-boiling fraction was separated by distillation under reduced pressure into a viscous, oily liquid (B), b. p. $174^\circ/4$ mm., and a gelatinous mass (C), b. p. $240\text{--}270^\circ/4$ mm. The fraction (B) (Found: C, 86.8, 86.8; H, 13.2, 13.15; *M*, cryoscopic in benzene, 273.1. d_4^{17} 0.8845, n_D 1.48704; whence $[R_L]_D = 88.14$. $\text{C}_{20}\text{H}_{36}$ requires C, 86.9; H, 13.1%; *M*, 276; $[R_L]_D$, 87.96) had a slight dextrorotation, $[\alpha]_{5461}^{17}$ ($c = 5$ in benzene) = $+2.29^\circ$, and did not decolorise potassium permanganate solution on standing; on treatment with bromine, hydrogen bromide was evolved. This compound closely approximates to that obtained by Tolloczko (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 39; *Chem. Zentr.*, 1898, I, 105) by treating menthol with sulphuric acid (except that his product was completely inactive), and thus appears to be dimenthene (II) (Kanonnikov, *Chem. Zentr.*, 1899, II, 860). A gelatinous compound corresponding to that (C) obtained by us was also observed by Tolloczko. Owing to the difficulty of purifying this compound, we have been unable to identify it.

Solid product. The solid substance constituting the lower layer after the heating of menthyl benzenesulphonate was deliquescent and of low melting point. We were unable to crystallise it from any solvent. It was easily soluble in water and the solution gave a strongly acid reaction. The barium salt prepared from the aqueous solution after boiling with animal charcoal was purified by recrystallisation from water [Found: H_2O , 3.9, 3.9; Ba, 29.0, 29.0. Calc. for $\text{Ba}(\text{SO}_3 \cdot \text{C}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$: H_2O , 3.8; Ba, 29.3%]. The solid substance which separates on heating menthyl benzenesulphonate is therefore mainly, or exclusively, benzenesulphonic acid.

II. *Decomposition by Direct Distillation.*—If, instead of being heated in a sealed tube, menthyl benzenesulphonate be directly distilled at a pressure of 4 mm., a vapour condensing to a colourless liquid passes over at 68° (the substance, heated in an oil-bath, being meanwhile at a temperature a little above its melting point), and a brown, deliquescent solid remains in the flask.

The liquid (D) boiled at 165° under ordinary pressure and had the rotation $[\alpha]_{5461}^{20} = +9.56^\circ$ (Found: C, 86.8, 86.8; H, 13.15, 13.2; *M*, cryoscopic in benzene, 138.4. $\text{C}_{10}\text{H}_{18}$ requires C, 86.9; H, 13.1%; *M*, 138. d_4^{17} 0.8130, n_D 1.45162; whence $[R_L]_D = 45.72$. Calc. for $\text{C}_{10}\text{H}_{18}$ + one ethylene linking, 45.71). It formed a nitroso-

chloride, m. p. 117°, and thus appears to be the same menthene as obtained by Zelikov (*Ber.*, 1904, **37**, 1374) by the action of various dibasic acids such as succinic acid, tartaric acid, citric acid, phthalic acid, terephthalic acid on menthol at high temperatures, and by Tschugaev (*Ber.*, 1899, **32**, 3332) by distilling menthyl xanthates in a vacuum. The rotation of the menthene formed in such experiments varies greatly; that obtained by Tschugaev had the high rotation $[\alpha]_D = 114.77^\circ$, 116.06° , which may have been due to the fact that his menthyl xanthate had a fairly low melting point, 39°.

In our experiment the higher-boiling dimenthene does not appear to be formed, whilst the other product of decomposition was found, from analysis of its barium salt, to be benzenesulphonic acid.

III. *Decomposition in Solution.*—Patterson and Frew (*loc. cit.*) had already noticed that menthyl benzenesulphonate also decomposed on heating in nitrobenzene solution. We ascertained that, when it is heated in benzene solution under reflux, little decomposition takes place, whereas in toluene decomposition appears to be complete. A brown solid separated which proved to be benzenesulphonic acid; the toluene solution acquired a positive rotation, and, after distillation of the solvent, a fraction was obtained, b. p. 190°/20 mm., presumably dimenthene. No lower-boiling decomposition product appeared to be formed.

I. *Menthyl naphthalene- β -sulphonate* (m. p. 114.5°), which had been examined by Patterson and Frew, was prepared again and heated in a sealed tube at 120°. Decomposition took place, and, as in the case of the benzenesulphonate, three distillable liquids were obtained. The most easily volatile fraction (A) boiled between 167° and 169° under ordinary pressure (Found: C, 85.75, 85.6; H, 14.2, 14.4%). The liquid was inactive and was identical with the hexahydrocymene obtained from menthyl benzenesulphonate.

The middle fraction, b. p. 174°/4 mm., had a slight positive rotation (Found: C, 86.8, 86.7; H, 13.1, 13.2%). It was the same as the dimenthene, $C_{20}H_{36}$, obtained from the benzenesulphonic ester. Some of the gelatinous substance, b. p. 240—270°/4 mm., was also obtained, but was not further examined.

In this case the solid which was produced on heating crystallised with difficulty from chloroform; m. p. 80°. From it a barium salt was prepared crystallising in flat, glistening plates [Found: H_2O , 3.2, 3.2; Ba, 24.1, 24.0. Calc. for $(C_{10}H_7 \cdot SO_3)_2Ba, H_2O : H_2O$, 3.2; Ba, 24.1%]. The decomposition product is therefore naphthalene- β -sulphonic acid.

II. When menthyl naphthalene- β -sulphonate, instead of being heated in a sealed tube, was distilled directly under 4 mm. pressure, a liquid boiling at 68° passed over and a yellow solid residue was

left in the flask. The liquid boiled at 165° under ordinary pressure, had a positive rotation of $[\alpha]_{5461}^{20} = +9.4^\circ$, and on analysis gave values corresponding to the formula $C_{10}H_{18}$, proving it to be the menthene obtained in the corresponding experiment with menthyl benzenesulphonate. The solid was naphthalene- β -sulphonic acid, which was characterised by the analysis of its barium salt.

III. Menthyl naphthalene- β -sulphonate, heated in nitrobenzene solution at 100° or in xylene solution at 120°, decomposed and, on cooling, naphthalene- β -sulphonic acid separated. The reaction products were not further examined.

I. *Menthyl naphthalene- α -sulphonate* (m. p. 116.5°, decomp.) was prepared in 60% yield in the same way as the other two sulphonic esters, and was crystallised from alcohol. It is soluble in most common solvents and has $[\alpha]_{5461}^{17.5}$ (in benzene; $c = 1$) = -93.25° and $[\alpha]_{5461}^{17.5}$ (in alcohol; $c = 1$) = -114.8°.

When it was decomposed in a sealed tube at 120°, two layers were formed. The liquid, on distillation and analysis, yielded the same three fractions as before, namely, hexahydrocymene (b. p. 167—169°/ordinary pressure. Found: C, 85.6; H, 14.4%); dimenthene (b. p. 174°/4 mm. Found: C, 86.6; H, 13.1%), and a gelatinous mass boiling from 240—270°/4 mm. The lower layer consisted of naphthalene- α -sulphonic acid, as was proved by the analysis of its barium salt [Found: Ba, 24.2, 24.1. Calc. for $(C_{10}H_7 \cdot SO_3)_2Ba, H_2O$: Ba, 24.1%].

II. On decomposition of this ester by direct distillation in a vacuum, menthene and naphthalene- α -sulphonic acid were the only products obtained and were characterised as before.

III. The ester also decomposed when heated in solution in much the same way as in the other two cases.