

CXLIII.—*Hydrolysis and Decomposition of Menthyl Methyl Xanthate and of Bornyl Methyl Xanthate.*

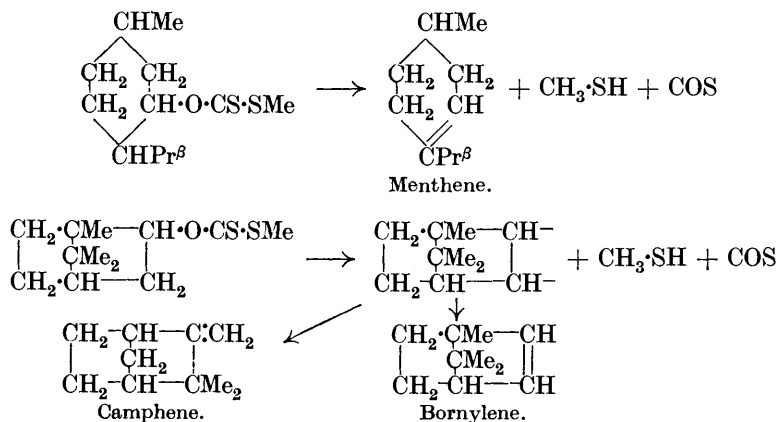
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IT has been shown (Patterson and McAlpine, J., 1927, 349; 1928, 2464) that the menthyl and bornyl esters of benzene- and naphthalene-sulphonic acids cannot be hydrolysed without further decom-

position, the products being mainly monoterpenes; also, that distillation under reduced pressure gives similar products of small rotation, whereas prolonged heating under ordinary pressure affords diterpenes. According to Tschugaeff (*Ber.*, 1899, **32**, 3332), the corresponding xanthates decompose to monoterpenes without much racemisation. As his conditions were not specified, it was decided to investigate the decomposition of these esters under conditions similar to those used for the sulphonates.

In regard to hydrolysis, the xanthates differed from the sulphonates in that (i) aqueous potassium hydroxide under all conditions was without appreciable action upon them (contrast *isobornyl* xanthate), and (ii) alcoholic potash readily effected hydrolysis to the terpene alcohol; further, (iii) baryta caused only partial hydrolysis, some of the ester undergoing transformation to a more stable form (see p. 1118).

Thermal decomposition of the xanthates was studied under various conditions: (a) by heating the dry ester alone, moisture being excluded, (b) by distillation in a vacuum, and (c) by heating solutions in various solvents. Under all conditions, the menthyl ester decomposes at least 30° below the bornyl ester. Except in one solvent, the products are menthene and bornylene (the latter admixed with camphene), together with mercaptan and carbonyl sulphide; in ethylene dibromide, however, some dimenthene accompanies the menthene, whereas bornylene is entirely replaced by its dimeride. The main decompositions may be represented as:



The effects of solvents are shown in the following tables, which relate to 10% solutions of the esters when heated at 120° for given periods.

*Menthyl Methyl Xanthate.*

Time of heating, hours.	$\alpha_{5461}^{25} (l = 1).$					
	Nitrobenzene.	Ethylene dibromide.	Xylene.	Pyridine.	<i>n</i> -Butyl alcohol.	Methyl alcohol.*
0	- 8.45°	- 7.26°	- 7.73°	- 9.50°	- 8.42°	+ 4.77°
6	6.56	5.22	7.26	9.28	7.77	4.65
12	unreadable	3.56	6.91	9.25	7.43	4.60
18	—	2.34	6.91	—	7.07	—
24	—	1.24	—	—	7.05	—

*Bornyl Methyl Xanthate.*

0	- 5.31	- 4.84	- 4.78	- 3.24	- 4.38	—
6	5.16	2.58	4.76	3.22	4.34	—
12	5.10	1.22	4.72	3.20	4.33	—
18	—	- 0.38	—	—	—	—
24	—	+ 0.04	—	—	—	—
30	—	+ 0.06	—	—	—	—

\* Methyl-alcoholic solutions were heated at their boiling point, and not at 120°.

It will be seen that xylene, pyridine, and *n*-butyl alcohol cause but slight decomposition of the menthyl ester and none of the bornyl ester. Ethylene dibromide and nitrobenzene effect considerable and roughly equal decomposition of the menthyl ester, but the former solvent is far more effective than the latter in decomposing the bornyl ester. (Increase in temperature has but little influence except on the nitrobenzene solutions, in which it accelerates decomposition.)

The solvents also affect the products formed. The alcohols cause only slight decomposition but transform the esters into the "stable" form, this tendency being more pronounced the lower the molecular weight of the alcohol. Xylene and pyridine do not possess this ability. Ethylene dibromide not only causes both decomposition and transformation, but is also the only solvent studied which gives rise to diterpenes.

Nitrobenzene decomposes the menthyl ester to menthene, the rotation of which is higher the higher the temperature, *i.e.*, the more rapid the decomposition; moreover, since blank tests showed that menthene is not racemised under these conditions, this higher rotation cannot be ascribed to any shorter period of racemisation after formation. This phenomenon is the reverse of the general experience and is contrary to what occurs on decomposition of the homogeneous ester. The observed rotations of the various specimens of menthene are tabulated below.

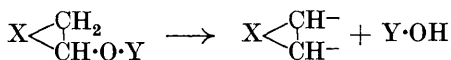
Method of formation.	$\alpha_{5461}$ ( $l = 1$ ).
Direct distillation	+ 113.64°
Decomposition in nitrobenzene solution	
at 130°	+ 84.30
at 155—160°	+ 107.09
at 170°	+ 107.60
Decomposition in the homogeneous state	
at 130—135°	+ 90.63
at 155—160°	+ 80.77

Nitrobenzene both transforms and decomposes the bornyl ester, but above about 200° the former effect vanishes.

The xanthates greatly exceed the sulphonates in thermal stability under all conditions. (a) In the homogeneous state the latter decompose in 3—6 hours a few degrees above their m. p.'s, *i.e.*, at 116° for the menthyl naphthalenesulphonates and below 100° for the other esters, whereas the xanthates (m. p.'s 42° and 56°) require 15 hours' heating at 160—190°. (b) On distillation in a vacuum, the sulphonates decompose rapidly at 125—140°, whereas the xanthates require a temperature of 170—200°. (c) The greatest differences between the two types, however, are shown in the decomposition in solutions. For instance, although the sulphonates show at least 50% decomposition in 1 hour at 105° in nitrobenzene, ethylene dibromide, or *n*-butyl alcohol, yet even 6 hours' heating at 125—130° in the same solvents has much less effect on the xanthates. Similarly, the sulphonates are decomposed in 6 hours at 105° in toluene, whereas prolonged heating in boiling toluene or xylene has but little effect on the xanthates.

Moreover, these differences extend to the products of decomposition on distillation. Under low pressure, the menthyl sulphonates gave mainly racemised menthene, and the bornyl esters underwent deep-seated decomposition but gave no bornylene, and at ordinary pressures these sulphonates gave principally diterpenes. On the other hand, in spite of the use of much higher temperatures, the xanthates gave monoterpenes showing little racemisation, diterpenes being obtained only from ethylene dibromide solution.

No explanation can be offered for these differences, for the primary reaction in each case must be of the type



and any polymerisation would be expected to be more pronounced in the xanthates owing to the higher temperatures used, whereas the reverse is the case.

Considerable difficulty was encountered in this work owing to the formation of a substance identical with the original ester in

analysis, molecular weight, and physical properties, but differing from it solely in possessing an increased thermal stability, requiring a higher temperature for decomposition, but giving the same products as the original ester under otherwise similar conditions. This "stable" form of menthyl methyl xanthate is obtained only by the action of alcohols and of ethylene dibromide and under certain conditions by distillation in a vacuum, but the bornyl ester gives rise to its stable form under all conditions of decomposition except in nitrobenzene at 200°.

A satisfactory explanation is not forthcoming for this phenomenon, which was not encountered in the parallel case of the sulphonates.

#### EXPERIMENTAL.

##### *Menthyl Methyl Xanthate.*

*Hydrolysis.*—Prolonged boiling with 40% aqueous potassium hydroxide had no effect, but substitution of concentrated alcoholic potash caused complete hydrolysis in 12—18 hours, the resulting pure menthol having maximum rotation. Similar treatment with alcoholic baryta yielded barium mercaptide admixed with some barium sulphide and a substance physically identical with the original ester, except that it distilled unchanged at 164°/15 mm. (see p. 1119). The alcoholic mother-liquor contained pure menthol, together with what appeared to be menthene, but the quantity obtained was insufficient for definite characterisation.

*Decomposition.*—(a) *In the homogeneous state.* The ester, in tubes closed from atmospheric moisture, was heated at various temperatures. At 120° reaction was slow; at 130° 40% was decomposed in 30 hours, and at 160° decomposition was complete in 12 hours. Menthene, mercaptan, and carbonyl sulphide were the only products. The rotation of the menthene decreased with increase of temperature of decomposition.

(b) *By distillation in a vacuum.* Evolution of mercaptan and the distillation of a clear liquid commenced when the temperature of the surrounding bath was 160—165°. As the temperature rose, the liquid distilling became syrupy. On standing, the distillate partly crystallised, but the whole was redistilled in a vacuum over sodium, and the portion boiling at 45° (about one-half) was proved by analysis, etc., to be menthene. Distillation of the remainder was impossible owing to the precipitation of sodium mercaptide, and the residue was therefore treated with methyl alcohol, whereupon the bulk solidified and on recrystallisation and distillation proved to be the "stable" xanthate (see below). Tschugaëff (*loc.*

*cit.*) having made no mention of the formation of this high-boiling product, a modified procedure was adopted, the menthene being removed from the original distillate in a vacuum on the water-bath without the addition of the sodium; the residue thus obtained was unstable to distillation and gave a further yield of menthene, so if Tschugaëff used this method he would not have obtained the "stable" form.

(c) *In solvents. Nitrobenzene.* A concentrated solution was completely decomposed by 12 hours' heating at 160°. Fractionation afforded menthene, which, after redistillation over sodium, had  $D$  0.8122, b. p. 167—169°,  $\alpha_{5461}$  107.09°, 106.97° [Found: C, 86.87, 86.90; H, 13.08, 13.06;  $M$  (cryoscopic in benzene) 137.2. Calc.: C, 87.0; H, 13.0%;  $M$ , 138]; it formed a nitrosochloride, m. p. 117°. Heating at 170° gave substantially the same results. At 130°, 25 hours' heating was necessary to effect 50% decomposition, and the resulting menthene had  $\alpha_{5461} + 84.30^\circ$ ,  $+ 86.45^\circ$ . Under identical conditions a specimen of menthene showed at 130° no decrease in rotation, proving that the lower rotation was not due to racemisation after formation.

*Butyl alcohol, xylene, and pyridine.* After 18 hours' heating, the solvents were removed, and the residues examined; their physical constants were unchanged in every case, but whilst the products from the last two solvents decomposed below their b. p.'s on distillation in a vacuum, that from the butyl alcohol distilled unchanged at 164°/15 mm.

*Ethylene dibromide.* The sign and magnitude of the rotation of the menthene produced by decomposition in nitrobenzene solution show that, had it been possible to follow the reaction throughout, the values would have crossed the zero of rotation, whereas those for the ethylene dibromide solution converge towards the zero. The ester was therefore heated in the latter solvent for 25 hours at 135°, and then fractionated; the menthene and ethylene dibromide separated as one fraction with  $\alpha_{5461} + 10.45^\circ$  ( $l = 1$ ), and the residue distilled without decomposition at 164°/15 mm., and solidified to moist needle-shaped crystals, m. p. 41°, having a distinct odour of dimenthene. Recrystallisation removed the latter, and the product contained sulphur, and was apparently identical with the original ester (analysis, molecular weight, mixed m. p., density in solution in benzene and in pyridine, index of refraction in benzene, specific rotation in several solvents). Nevertheless, examination of the decomposition of this "stable" form in nitrobenzene solution showed that no decomposition took place below 145°, whereas with the original ester decomposition began below 120°; when decom-

position did take place, however, menthene was again isolated as the only product. Decomposition in the homogeneous state also commenced at a higher temperature (by some 30°). No other distinguishing characteristics could be discovered, nor could any trace of impurity be detected in the original ester which might act as a catalyst for the decomposition reactions.

*Bornyl Methyl Xanthate.*

*Hydrolysis.*—Water and aqueous potassium hydroxide have no effect at all on this ester. Alcoholic potash causes complete hydrolysis, whereas baryta gives borneol, barium mercaptide, and the "stable" form of the ester (see below).

*Decomposition.*—(a) *In the homogeneous state.* Decomposition does not occur below 170° and is slow below 190°. After 30 hours' heating at this temperature, the residue was distilled under atmospheric pressure until the monoterpenic fraction was removed, and then in a vacuum. The products were bornylene, largely contaminated with camphene and having  $\alpha_{5461} + 4.39^\circ$  (in ethyl alcohol), and also the stable form of the original ester.

(b) *By distillation.* Distillation of the ester in a vacuum from an oil-bath at 190—200° gave a mixture of two solids. Redistillation under atmospheric pressure yielded bornylene, b. p. 163°,  $\alpha_{5461} + 14.90^\circ$ ; the residue was distilled under low pressure and consisted of about 50% of the stable form of the original ester. Decomposition by Henderson and Caw's modification (J., 1912, **101**, 1416) also failed to secure complete decomposition of the ester into bornylene, although it yielded a purer product.

(c) *In solvents. Nitrobenzene.* A concentrated solution in this solvent was heated at 160° for 25 hours, and distilled in a vacuum. After repeated refractionation, some monoterpene was obtained as an unsaturated, volatile, white solid, m. p. 70°,  $[\alpha]_{5461} - 13.75^\circ$  ( $c = 4$  in ethyl alcohol) [Found: C, 88.20, 88.18; H, 11.78, 11.74;  $M$  (cryoscopic in benzene), 136.9. Calc.: C, 88.2; H, 11.8%;  $M$ , 136]. No hydrochloride could be obtained, and the rotation of the substance indicates that it is a mixture of bornylene ( $[\alpha]_{5461} + 22.27^\circ$ ) and camphene ( $[\alpha]_{5461} - 92.37^\circ$ ).

After removal of the monoterpene and the nitrobenzene, the residue distilled at 154°/15 mm., and solidified when pure to a white solid, m. p. 55°, having  $[\alpha]_{5461} 32.60^\circ$  in benzene solution. Analysis, molecular-weight determination, and several physical properties (as in the case of the menthyl ester) confirmed the identity of this substance with the original ester in all respects except stability to distillation in a vacuum. Decomposition of the stable

form in nitrobenzene solution does not take place below 200°, but it is then complete although slow. A higher temperature is also necessary for its decomposition in the homogeneous state, but the products were the same monoterpenes as those obtained from the original ester.

*In ethylene dibromide.* This was carried out in 30—35 hours at 140°. After removal of the solvent, which did not contain any monoterpene, the residue distilled at 155—160°/15 mm., but did not solidify. The syrupy liquid smelt strongly of dibornylene, but contained much combined sulphur. Repeated fractionation failed to effect any separation, but the liquid,  $\alpha_{5461} + 10.66^\circ$  ( $l = 1$ ), is presumed to consist of dibornylene and the "stable" bornyl methyl xanthate.

*In xylene, pyridine, or butyl alcohol.* After 18 hours' heating in each case, the products recovered from the first two solvents were found to be the original form of the ester, whilst that from the butyl alcohol was the stable form.

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