

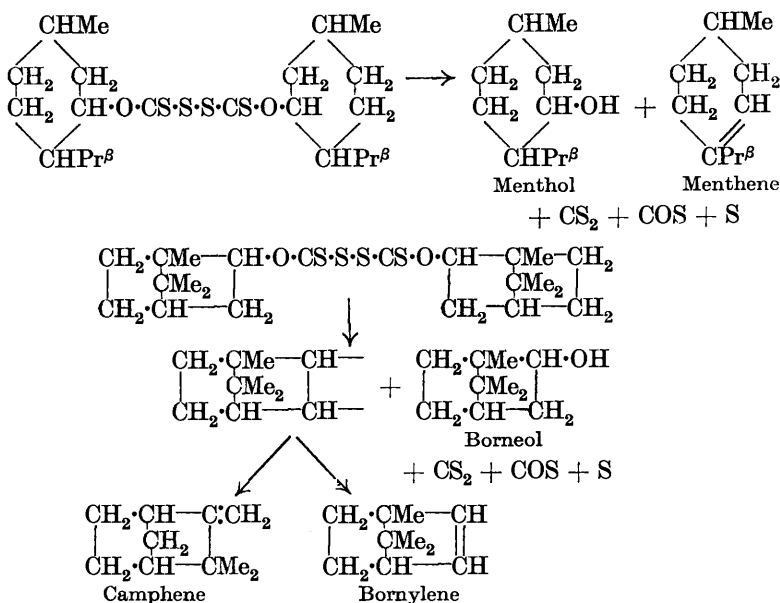
120. *Hydrolysis and Decomposition of Menthyl Dixanthide and of Bornyl Dixanthide.*

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DURING the investigation of the decomposition of menthyl methyl xanthate and of bornyl methyl xanthate (J., 1931, 1114) several distinct points of contrast were observed between these compounds and the corresponding sulphonates (Patterson and McAlpine, J., 1927, 349; 1928, 2464), with regard both to the temperatures used for similar decompositions and to the nature and rotation of the products obtained. It therefore seemed of interest to examine the corresponding dixanthides and to compare the results obtained with those from the sulphonates and xanthates under similar conditions, more especially since Tschugaev (*Ber.*, 1899, **32**, 3332) gives no indication of the temperature at which they decompose in a vacuum.

Menthyl dixanthide is hydrolysed by 40% aqueous potassium hydroxide and by alcoholic potassium hydroxide and baryta, but bornyl dixanthide only by the alcoholic reagents to pure terpene alcohol. They differ from the xanthates in that no "stable" form is obtained with alcoholic baryta.

The thermal decomposition of the dixanthides was studied under various conditions: (a) 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 more readily than the bornyl ester, the difference in temperature for (a) and (b) being fully 30°. In all cases the products are menthene and menthol, or bornylene and borneol, the former admixed with camphene, together with carbon disulphide, sulphur and carbonyl sulphide. The decompositions may be represented as follows:—



The effect of solvents on the decomposition of the esters is shown in Table I, which gives the values of α_{5461}^{17} ($l = 1$) for 10% solutions of the esters heated at the stated temperatures for given periods.

With the exception of bornyl dixanthide in toluene, there is considerable decomposition of both esters in all the solvents at 120°. The decomposition of the menthyl ester in 2 hours is extensive in all the solvents and nearly complete in pyridine and nitrobenzene. There is also considerable decomposition in all the solvents at 100°, and even at 70° there is decomposition in pyridine and nitrobenzene solutions. At this temperature pyridine has the greater effect, but increase of temperature aids decomposition in nitrobenzene to a larger extent. Decomposition of the bornyl ester is considerably slower even at 120°, pyridine causing the greatest amount in 2 hours. Decomposition in this solvent commences below 80°, but practically ceases in all the other solvents below 100°.

In all cases the products of decomposition are those shown in the equations with one possible exception. During the decomposition of both esters in ethylene dibromide solution substances were isolated which were identical with the original esters but were apparently stable to decomposition in that solvent but not stable to decomposition by distillation in a vacuum. No dimenthene or

TABLE I.

Time, hours.	Menthyl Dixanthide.				Bornyl Dixanthide.			
	Temperature.				Temperature.			
	120°.	100°.	80°.	70°.	120°.	100°.	80°.	70°.
In <i>n</i> -butyl alcohol (<i>c</i> = 4).								
0	-11.70°	-11.68°	-11.69°	—	-3.75°	—	—	—
2	4.53	10.84	11.28	—	3.64	—	—	—
4	2.40	8.73	10.83	—	3.53	—	—	—
In ethylene dibromide.								
0	-32.74	-32.72	-32.72	—	-5.14	-5.14°	—	—
2	5.45	27.80	32.25	—	4.42	5.07	—	—
4	2.40	23.25	32.02	—	3.76	5.01	—	—
In toluene.								
0	-25.51	-25.74	-25.74	—	-4.50	-4.50	—	—
2	9.72	22.75	25.71	—	4.45	4.48	—	—
4	5.40	19.55	25.69	—	4.40	4.47	—	—
In nitrobenzene.								
0	-25.80	-26.03	-26.00	-26.02°	-6.75	-6.75	-6.73°	—
2	+ 0.40	13.43	24.04	25.29	5.09	6.47	6.66	—
4	unread- able	7.38	22.27	24.81	4.65	6.18	6.53	—
In pyridine.								
0	-25.37	-25.37	-25.34	-25.34	-4.75	-4.82	-4.80	-4.79°
$\frac{1}{2}$	—	14.36	23.45	—	—	4.17	4.38	4.51
1	—	9.56	21.88	23.04	—	3.69	3.95	4.38
2	0.53	1.53	18.54	21.64	1.70	3.50	3.80	4.09
4	unread- able	unread- able	12.68	20.88	unread- able	unread- able	3.42	3.75

dibornylene was obtained. Nitrobenzene also caused carbonaceous decomposition.

The menthol obtained during these decompositions had always the full optical rotation, but the value for the menthene varied with the conditions of its preparation (see Table II). The same relation applied to the borneol and bornylene, but the latter was not in general sufficiently purified to justify tabulation of the rotations of the various specimens.

The xanthates greatly exceed the corresponding dixanthides in thermostability. Bornyl dixanthide, compared with menthyl dixanthide, shows an increased stability similar in degree to that existing between the xanthates: its stability under these conditions is approximately the same as that of menthyl methyl xanthate. The greatest difference between the two groups is shown in decomposition in solution. Menthyl dixanthide undergoes considerable decomposition in pyridine and nitrobenzene at 70° and in all the solvents at 100°, and decomposes more extensively at 120° in 2 hours than does menthyl methyl xanthate in 6 hours in the most reactive solvent. The action of solvents on bornyl dixanthide, although less vigorous, is distinctly more productive of decomposition in all cases than their action on bornyl methyl xanthate, the

decomposition of which is always very slow and is practically negligible in xylene, pyridine, and *n*-butyl alcohol. The most striking contrast between the two groups is found in the action of pyridine, which produces scarcely any decomposition of the xanthates but considerable decomposition of the dixanthides even at low temperatures.

Comparing the figures obtained for the action of solvents on bornyl dixanthide with those obtained for menthyl methyl xanthate, it is seen that, with the exception of pyridine, there is again approximate similarity of rate of decomposition at 120°.

On the other hand, the dixanthides are somewhat more thermostable than the sulphonates. Even though similar temperatures are used for decomposition in the homogeneous state and in a vacuum of menthyl dixanthide and the corresponding naphthalene-sulphonates, the decompositions take longer to accomplish in the former case. With decomposition in solution, more similarity is apparent between the dixanthides and sulphonates than exists between the former and the xanthates, with regard to the temperature at which the action begins, the rate of decomposition in various solvents at a given temperature, and the effect of increase of temperature on decomposition in the same solvent. The action of pyridine still forms an exception, the decomposition of the sulphonates in this solvent being appreciable, but slow compared with that in nitrobenzene, alcohol, and ethylene dibromide.

In their products of decomposition the dixanthides resemble the xanthates rather than the sulphonates, monoterpenes of fairly high rotation being the only products, whereas diterpenes are the principal products of the decomposition of the sulphonates, menthene and camphene resulting only on distillation in a vacuum, the former having a low rotation and the latter zero rotation. The dixanthides, however, differ from the xanthates in the absence of a definite compound corresponding to the "stable" form of the latter.

Comparison of the rotations of the menthenes obtained by the three methods from the different sources (Table II) shows that the menthene from the dixanthide usually has a lower rotation than that from the xanthate under the same conditions.

TABLE II.

Method of formation.	$\alpha_{5461} (l = 1).$	
	Menthene from menthyl xanthate.	Menthene from menthyl dixanthide.
Direct distillation	+ 113.64°	+ 112.18°
Decomposition by heating at 120°	90.63	80.00
Decomposition in nitrobenzene at 120°	84.30	65.79

These results, combined with those found for menthyl *isopropyl* xanthate and menthyl benzyl xanthate in the preceding paper, would seem to indicate that decrease in stability of the molecule tends to decrease the rotation of the menthene obtained on decomposition, but a satisfactory explanation of this phenomenon is not forthcoming. The results of the hydrolysis experiments prove that this is not due to racemisation during the formation of the esters, and other experiments prove that no racemisation takes place after formation of the menthene.

EXPERIMENTAL.

Menthyl Dixanthide.—*Hydrolysis.* Menthyl dixanthide does not distil or decompose in steam, but when boiled with 40% aqueous potassium hydroxide for 5–6 hours it gives pure menthol and no terpene. Alcoholic potassium hydroxide and baryta effect the same hydrolysis, the latter reagent also causing the separation of a “quasi-stable” form, which does not hydrolyse even on prolonged boiling but decomposes on distillation in a vacuum.

Decomposition. (a) *In the homogeneous state.* The ester, in tubes closed from atmospheric moisture, was heated at various temperatures. Decomposition was slow below 100°, proceeded fairly rapidly at 100°, and was complete at 120° in 6 hours. The products were menthene, menthol, carbon disulphide, carbonyl sulphide, and sulphur. The menthene, after repeated distillation over sodium, boiled at 167° (Found: C, 86.9; H, 13.1; *M*, cryoscopic in benzene, 136.9. Calc.: C, 87.0; H, 13.0%; *M*, 138), had $\alpha_{546}^{17^\circ} + 80.00^\circ$ ($l = 1$), and gave a colourless nitrosochloride, m. p. 117°. The menthol, purified by steam distillation and recrystallisation from light petroleum, melted at 40° and had $[\alpha]_{546}^{17^\circ} + 52.30^\circ$ ($c = 5$) in benzene. A small quantity of a sticky solid left after the steam distillation was extracted with benzene. The residue did not crystallise well for the determination of its constants, but on distillation in a vacuum it decomposed into the products already mentioned, and therefore appeared to be another modification of the original substance; it could not be further characterised.

(b) *Distillation in a vacuum.* Decomposition began at 130° (bath temperature), but nothing distilled below 145–150°. The distillate was fractionated in a vacuum. The portion obtained below 80°/20 mm. was distilled several times over sodium: it then boiled at 167–168° and had $\alpha_{546}^{17^\circ} + 112.18^\circ$ ($l = 1$), a slightly lower value than that given by Tschugaev for menthene from this source. The upper fraction, after the usual purification, was found to be menthol of full rotation.

(c) *In solvents. Nitrobenzene.* A fairly concentrated solution was completely decomposed by 4—6 hours' heating at 120°. The menthene was distilled off in a vacuum and found to have the usual constants and $\alpha_{5461} + 65.79^\circ$ ($l = 1$); in a second experiment, $\alpha_{5461} = 65.43^\circ$. The nitrobenzene solution showed a negative rotation after removal of all the menthene, but the menthol could not be easily isolated. The yield of menthene was not theoretical, carbonaceous decomposition also taking place.

Ethylene dibromide. A concentrated solution was decomposed in 8—10 hours at 130—135°. The menthene distilled over with the ethylene dibromide and was practically inseparable therefrom, the solution having $\alpha_{5461}^{17^\circ} 8.75^\circ$ ($l = 1$). Menthol was removed from the residue by steam distillation and showed full rotation. The remainder solidified to a sticky mass, crystallisable with extreme difficulty from alcohol; it then showed the same constants as the original ester, and was, like it, unstable to distillation in a vacuum.

Butyl alcohol, xylene, and pyridine. The rotations of the products obtained by decomposition in these solvents were not examined.

Bornyl Dixanthide.—Hydrolysis. Water and aqueous potassium hydroxide have scarcely any effect on this ester, but it is completely hydrolysed by alcoholic potassium hydroxide and by alcoholic baryta, barium sulphide being precipitated in this reaction and also a small quantity of a "quasi-stable" form similar to that obtained from the menthyl ester.

Decomposition. (a) *In the homogeneous state.* No decomposition took place below 120°. After 7 hours' heating at this temperature there was a trace of decomposition: the rate was slightly more rapid at 135°. At 155—160° decomposition proceeded at a moderate rate and was complete in 18—20 hours. The product was distilled under ordinary pressure to remove the terpene; the residue was then steam-distilled, pure borneol being isolated. On account of the expense of preparing the dixanthide in large quantities, decomposition was not carried out on a sufficiently large scale to enable the terpenic product of this and subsequent decompositions to be completely purified for identification by analysis, etc., but it appeared to consist mainly of bornylene and there were indications of the presence of camphene as in the case of the corresponding work on bornyl methyl xanthate.

(b) *Distillation in a vacuum.* Decomposition began at 160—165° (bath temperature), bornylene and camphene distilling slowly: the rate was more rapid at 170—175°. The crude product after two distillations over sodium had m. p. 102°, and $[\alpha]_{5461}^{17^\circ} + 12.30^\circ$ ($c = 5$) in benzene. The borneol remained in the reaction flask

and was purified by steam distillation and crystallisation from light petroleum; it had m. p. 205° and its full rotation in benzene solution. This method entails severe loss of the terpenic product owing to the extreme ease with which bornylene volatilises.

(c) *In solvents. Nitrobenzene.* Decomposition of a concentrated solution at 130° was complete in 6—8 hours, the terpenic product being again bornylene mixed with a large proportion of camphene. The borneol was not isolated.

Ethylene dibromide. Decomposition at 130° required 12—14 hours' heating. Removal of the ethylene dibromide and monoterpene as one fraction and then of the borneol by steam distillation left a sticky solid, which crystallised with difficulty from ethyl alcohol and proved to be identical in physical constants with the original ester (m. p., mixed m. p., analysis, molecular weight, etc.), and though stable to decomposition in this solvent was completely unstable to distillation in a vacuum.

Toluene, pyridine, and n-butyl alcohol. Decomposition was complete in pyridine solution in 6 hours at 120° , but the products were not examined. In both toluene and butyl alcohol the solutions were heated for 9 hours and the solvents removed: the residues on crystallisation showed the same constants as the original substances and were completely decomposed by distillation in a vacuum.

The author desires to thank Professor T. S. Patterson for the use of his polarimetric equipment and for his general interest in the work.

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[Received, November 10th, 1931.]
