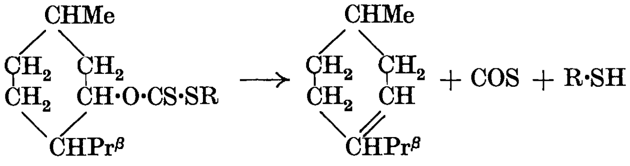
119. *Effect of Replacement of Methyl by Alkyl and Aryl on the Stability of the Xanthate Molecule.*

By IRENE MARY McALPINE.

DURING the work on menthyl and bornyl methyl xanthate (J., 1931, 1114) considerable variation was noticed in the rotation of the terpenic decomposition products, and also in the temperature of decomposition and in the conditions of formation of the " stable " modification of the xanthate. It therefore seemed advisable to prepare further derivatives, the ones chosen being those in which the *iso*propyl, benzyl, or *p*-nitrobenzyl group is substituted for methyl, and to study these esters under the same conditions as those used for the previous work.

Little difference was observed in the rate of hydrolysis of the two esters compared with that of the methyl ester.

The main decomposition reaction remained the same throughout, menthene, a mercaptan, and carbonyl sulphide being formed :



(R = Me, Pr^{β}, CH_2Ph, or $CH_2{\cdot}C_6H_4{\cdot}NO_2$.)

In general, the temperature required to decompose the iso*propyl* ester was higher than that required for the corresponding methyl ester under the same conditions. In the homogeneous state there is no decomposition of the *iso*propyl xanthate below 160°, whereas at 155—160° the methyl ester is decomposed completely in 12 hours, decomposition commencing at 120°. Similarly, an additional

15—20° is necessary to cause the decomposition of the *iso*propyl ester on distillation in a vacuum, and 12% of the " stable " form of the initial material, differing from the original only in its stability to distillation in a vacuum, is always obtained from this ester, whereas the " stable " form is only obtained under one special set of conditions from the methyl ester. On the other hand, the temperatures required to decompose the *benzyl* ester are approximately the same as those required for the methyl ester, the actual rate of decomposition being rather greater than with that ester. The *nitrobenzyl* ester was only examined in solution.

The results of decomposition in solvents are seen in Table I, which gives the values of $\alpha_{5461}^{17^\circ}$ ($l = 1$) for 10% solutions of the ester heated at 120° for given periods.

TABLE I.

Time (hrs.).	Ethylene dibromide.	Nitrobenzene.	*n*-Butyl alcohol, $c = 4\%$.	Pyridine.
		Menthyl iso*Propyl Xanthate.*		
0	−5·87°	−6·78°	−2·75°	−7·50°
6	4·70	4·76	2·58	7·10
12	3·87	3·66	2·40	6·48
18	3·43	2·40	2·38	6·13
		Menthyl Benzyl Xanthate.		
0	−2·73	−3·22	−1·48	−4·13
6	2·23	1·84	1·27	3·45
12	1·70	0·46	1·08	2·54
18	1·14	unreadable	1·01	1·65
		Menthyl p-*Nitrobenzyl Xanthate.*		
0	−1·75	−2·20	−0·68	−3·06
6	1·32	1·12	0·45	1·95
12	1·00	0·26	0·24	unreadable
18	0·62	+0·80	0·05	—

Decomposition occurs when the solutions in all the solvents are heated, but it is much slower in pyridine and in butyl alcohol than in the other two, nitrobenzene causing the greatest amount of decomposition. Comparisons can only be made roughly owing to the difference in initial readings in each case, but the rate of decomposition of the *iso*propyl ester compared with that of the methyl ester is distinctly less in all the solvents with the exception of pyridine, in which the rate is slightly increased. With the benzyl ester the opposite is the case, the speed of decomposition being distinctly increased, and a further increase takes place on the introduction of the *p*-nitrobenzyl group. Increase of temperature has little effect on these rates with the exception of those for solutions in nitrobenzene, in which it considerably accelerates the speed of decomposition.

Examination of the products of the reaction shows that, although nitrobenzene causes only decomposition of the methyl ester, it causes both decomposition and transformation of the *iso*propyl ester into the stable form below 155°; in ethylene dibromide a much larger yield of "stable" product is obtained (30%). Indication of the formation of diterpene in this case is more indefinite. Butyl alcohol also causes a larger percentage of transformation than is the case with the methyl ester. The product thus obtained has a boiling point 8° above that of the stable form of the methyl ester and is not decomposed in nitrobenzene solution below 155°, *i.e.*, fully 10° above the point at which decomposition of the stable methyl ester begins in that solvent. Nitrobenzene causes no transformation of the benzyl ester at any temperature examined, the only reaction being decomposition into menthene. After decomposition in ethylene dibromide solution no diterpene was indicated, but a small quantity of "stable" form (4—6%) was obtained. This was the only case of transformation of the benzyl xanthate, the residues from the reactions in the other solvents being identical with the original ester both in physical properties and in thermostability. On introduction of the nitrobenzyl group indications are found of a modification which is stable to the action of heat in ethylene dibromide solution, but its quantity is small and its thermostability not sufficiently great to enable it to be distilled in a vacuum.

Another interesting feature of this work is the variation in the rotation of the menthene obtained from the various experiments, and in particular from the action of nitrobenzene on the benzyl ester. As the temperature of decomposition of solutions in this solvent is increased, so also is the rotation of the menthene produced. This exceptional behaviour was also found in the case of the methyl ester, but here the values obtained for the rotation of the menthene are very much above the corresponding figures for the benzyl ester, though the decompositions take similar times to be accomplished. The variation is not due to the formation of a mixture of Δ^2- and Δ^3-menthene, the colourless nitrosochloride of Δ^3-menthene being the only one obtained, nor is it due to the racemisation of the product after formation. The values obtained from the various sources are summarised in Table II.

TABLE II.

	Rotation of menthene, $a_{5461}^{17^\circ}$ ($l = 1$).		
Method of decomp.	Methyl ester.	*iso*Propyl ester.	Benzyl ester.
Homogeneous state at 160°	+80·77°	+108·7° (170°)	+88·66°
Distillation in a vacuum ...	113·64	112·15	103·00
In nitrobenzene at 130° ...	84·30	—	49·95
,, ,, at 160° ...	107·60	—	75·64

Thus the effect of the replacement of the methyl group in menthyl methyl xanthate by the *iso*propyl group is to increase the tendency towards transformation into the " stable " form and to decrease the tendency towards decomposition, whereas the introduction of the benzyl group causes a decrease in the tendency towards transformation and instead causes an increase in the rate of decomposition in organic solvents, the rate under other conditions being practically the same as for the methyl ester. The introduction of the *p*-nitrobenzyl group still further decreases the tendency towards the formation of a " stable " modification and favours still further the decomposition reaction. The most striking effect of the introduction of the benzyl group is found in the rotation of the menthene formed during the various decompositions. The latter is much decreased, especially during decomposition in nitrobenzene solution.

EXPERIMENTAL.

Menthyl iso*Propyl Xanthate.*—This ester was prepared by Tschugaev's method (*Ber.*, 1899, **32**, 3332) for menthyl methyl xanthate, slightly more than the theoretical quantity of *iso*propyl iodide being used. The residue after removal of the toluene in a good vacuum solidified after prolonged keeping at 0°, and then crystallised from alcohol or light petroleum in white needles, m. p. 48°, $[\alpha]_{5461}^{16\cdot5^\circ}$ $-77\cdot60^\circ$ ($c = 5$ in benzene solution) (Found: C, 61·3; H, 9·5; S, 22·2; *M*, cryoscopic in benzene, 270. $C_{14}H_{26}OS_2$ requires C, 61·3; H, 9·5; S, 23·4%; *M*, 274). Yield, 50%.

Hydrolysis. No hydrolysis took place with 40% aqueous potassium hydroxide even after prolonged boiling, but alcoholic potassium hydroxide caused complete hydrolysis to pure menthol in 18—20 hours. Similar treatment with alcoholic baryta for the same time caused formation of menthol (isolated from the alcoholic mother-liquor) and barium mercaptide, and a white solid (precipitated during the reaction) which was physically identical with the original ester but distilled unchanged at 168°/11 mm. This is more fully characterised on p. 910.

Decomposition. (a) *In the homogeneous state.* No decomposition took place below 160° when the ester was heated in tubes protected from atmospheric moisture. At 170° decomposition was complete in 6 hours, the only products being menthene, b. p. 167—169°, $[\alpha]_{5461}^{17^\circ}$ $+108\cdot72^\circ$ ($l = 1$) (Found: C, 86·9; H, 13·1; *M*, cryoscopic in benzene, 136·7. Calc.: C, 87·0; H, 13·0; *M*, 138), *iso*propyl mercaptan, and carbonyl sulphide.

(b) *Decomposition by distillation in a vacuum.* Decomposition began at 165° (bath temperature), and distillation at 180—185°.

The distillate was separated into two fractions in a vacuum. The first after redistillation over sodium was proved by b. p., analysis, etc., to be menthene ($\alpha_{5461}^{17^\circ}$ + 112·15°; $l = 1$). The higher fraction distilled unchanged at 168°/11 mm. and solidified immediately. Analysis, etc., proved this to be the " stable " modification of the original ester, which is more fully characterised below. Yield, 12% of the original ester.

(c) *Decomposition in solvents. Nitrobenzene.* Decomposition of a saturated solution of the ester in this solvent required 30 hours at 130°. The menthene and nitrobenzene were removed and the residue was distilled in a vacuum; it passed over unchanged at 168—170°/11 mm. as a colourless liquid which solidified to white crystals. Yield, approximately 25% of the initial material. The product contained sulphur, had m. p. 47°, and gave $[\alpha]_{5461}^{17^\circ}$ − 77·57° in benzene ($c = 5$). Determination of other physical properties (analysis, molecular weight, mixed m. p., specific rotation in various solvents, etc.) confirmed its identity with the original ester in all respects except thermostability. Decomposition of this form in nitrobenzene solution does not take place below 155° and is not rapid even at 170°. The original ester is, however, completely decomposed by heating at 160° in this solvent.

Ethylene dibromide. Decomposition of a saturated solution of the ester in this solvent took 30 hours at 130°. Menthene was distilled off with the ethylene dibromide, and the residue, distilling unchanged at 168°/11 mm., was again proved to be the " stable " form of the original ester. Yield, 30%.

Pyridine, toluene, and n-*butyl alcohol.* Decomposition was slow in pyridine and after 24 hours' heating the solvent containing the menthene formed was removed : the residue, showing the usual constants, decomposed completely on distillation in a vacuum. Xylene caused but little more decomposition and no transformation into the stable form. The residue after 20 hours' heating in butyl-alcoholic solution was found to be completely transformed into the " stable " form.

Menthyl Benzyl Xanthate.—This ester was prepared by the same method as the methyl ester, the theoretical quantity of benzyl chloride being used instead of methyl iodide. The residue solidified in the refrigerator on prolonged standing, and was recrystallised from ethyl alcohol or light petroleum; it melted at 46·5—47°, and in benzene solution gave $[\alpha]_{5461}^{17^\circ}$ 43·50° ($c = 5$) (Found : C, 63·9; H, 8·1; S, 19·3; *M*, cryoscopic in benzene, 317. $C_{18}H_{26}OS_2$ requires C, 67·1; H, 8·1; S, 19·9%; *M*, 322). Yield, 40%.

Hydrolysis. The ester was only slightly hydrolysed after prolonged boiling with 40% aqueous potassium hydroxide, but was completely hydrolysed by alcoholic potassium hydroxide in 6 hours. Hydrolysis with alcoholic baryta was again partial, but the remaining solid, isolated as before, was completely decomposed by distillation in a vacuum.

Decomposition. (a) *In the homogeneous state.* Heating in tubes protected from atmospheric moisture for 12 hours at 120° had only a small effect, but heating for the same time at 160° caused complete decomposition; the resultant menthene had a rotation of $+ 87{\cdot}26°$ $(l = 1)$.

(b) *Distillation in a vacuum.* Decomposition began at 160—165° (bath temperature). The resultant menthene, freed with difficulty from sulphur compounds, had $\alpha_{5461}^{17°}$ $+ 103{\cdot}00°$ $(l = 1)$. No trace of stable compound was found in this decomposition.

(c) *In solvents. Nitrobenzene.* A saturated solution of the ester in nitrobenzene was heated at 125—130° for 25—30 hours. The menthene, isolated and purified in the usual way, showed $\alpha_{5461}^{17°}$ $+ 49{\cdot}95°$ $(l = 1)$. At 160° the time required for the decomposition was reduced to 12 hours: the menthene obtained had α $+ 75{\cdot}64°$ and 75·00° in two experiments. No "stable" form was obtained at either temperature.

Ethylene dibromide. Decomposition in this solvent at its b. p. for 30 hours gave menthene as usual and in addition a small quantity (4—6%) of a "stable" form, on removal of the solvent, which distilled without decomposition at 180°/12 mm. It decomposed in nitrobenzene solution above 140°, and otherwise appeared to be identical with the original ester. No trace of dimenthene was indicated.

In pyridine, toluene and butyl alcohol. After solutions in these solvents had been heated for 25 hours, the residues were isolated and examined in the usual way, their identity with the original unstable form of the ester being established.

Menthyl p-*Nitrobenzyl Xanthate.*—This ester was also prepared in the same manner as the two previous ones, *p*-nitrobenzyl bromide, which reacted very readily with the sodium xanthate in cold ethereal solution, being used. On recrystallisation from ethyl alcohol or light petroleum, it was obtained as yellowish-white needles, m. p. 60°, $[\alpha]_{5461}^{17°}$ $- 35{\cdot}20°$ $(c = 5)$ in benzene solution (Found: C, 58·8; H, 6·9; S, 16·9; N, 3·8; *M*, cryoscopic in benzene, 364. $C_{18}H_{25}O_3NS_2$ requires C, 58·85; H, 6·8; S, 17·4; N, 3·8%; *M*, 367). Yield, 30%.

Decomposition in ethylene dibromide solution. A saturated solution of this ester in ethylene dibromide was heated at 135° for 25 hours and then examined in the usual way. A small quantity of solid (5%) was left after removal of the solvent and menthene, m. p. 58°, $[\alpha]_{5461}^{17°}$ 35·17° ($c = 5$) in benzene solution, but this decomposed completely on distillation in a vacuum. No dimenthene was found.

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

UNIVERSITY OF GLASGOW. [*Received, November* 10*th* 1931.]