53. *The Rotatory Powers of the Chlorides produced by heating Certain Chloroformates in Solvents.*

By (MISS) MARY B. HARFORD, JOSEPH KENYON, and HENRY PHILLIPS.

THE decomposition of the chloroformates of ethyl *l*-mandelate and *l*-β-octanol, when heated, producing lævorotatory chlorides (Kenyon, Lipscomb, and Phillips, J., **1931**, 2275; Houssa and Phillips, J., **1932**, 108, 1232), $RO{\cdot}COCl = RCl + CO_2$, is of particular interest, since it probably occurs without inversion. On the other hand, when these chloroformates decompose in the presence of a tertiary base, the chlorides produced are dextrorotatory and an inversion of configuration occurs. In order to throw light upon the mechanism of the two processes, the decomposition of the two chloroformates in different solvents has been studied.

Lævo-β-octyl chloroformate and lævo-ethyl phenylchloroformoxyacetate were prepared as previously described (*loc. cit.*); the lævo-mandelic acid required was isolated from amygdalin * and both chloroformates were purified by distillation at less than 0·1 mm.

In each expt., a solution of the ester (1 mol.) in the solvent (10 mols.) was heated at the lowest temp. at which a vigorous evolution of CO_2 occurred. When this ceased, the chloride produced was isolated by fractional distillation; the purity of the final fraction was checked by the determination of its Cl content. The approx. temp. at which each decomp. occurred, the obs. rotatory power ($l = 1{\cdot}0$) and Cl content of the chloride obtained, and the dielectric const. (" International Critical Tables," **1929**, VI, 83) of the solvent used are given in Table I.

TABLE I.

The Observed Rotatory Powers of the Lævo-chlorides obtained by the Decomposition of Lævo-ethyl Phenylchloroformoxyacetate and Lævo-β-octyl Chloroformate in the Presence of Solvents.

Solvent.	Approx. temp. of decomp.	Duration of decomp.	Chloride obtained.		Dielect. const. of solvent at 20°.
			α_{5461} ($l = 1{\cdot}0$).	Cl, %.	
		Lævo-ethyl phenylchloroacetate.			
Nitrobenzene	145—150°	45 min.	7·00°	17·9	36·1
Benzonitrile	145—155	30 ,,	19·08	17·9	26·5
Acetophenone	135—140	150 ,,	34·28	17·8	18·3
m-Dinitrobenzene	110—130	150 ,,	48·96	17·8	2·8
Bromobenzene	145—155	360 ,,	60·12	17·9	5·4
p-Tolylethylsulphone	145	—	61·92	17·9	—
Ethyl *p*-toluenesulphonate	140—150	60 ,,	66·28	17·9	—
Decalin	170—180	slow	68·92	17·1	—
Phenetole	150—160	90 min.	74·12	17·9	4·56 (21°)
Ethyl benzoate	155—165	vigorous	75·12	17·9	6·2
None [1]	150	—	57·4	18·2 [4]	—
		Lævo-β-chloro-octane.			
Nitromethane	105	30 min.	16·84	23·8	39·4
Benzonitrile	120	vigorous	19·08	23·8	26·5
p-Benzoquinone	135—140	30 min.	19·12	23·8	—
Nitrobenzene	115—135	20 ,,	19·80	23·8	36·1
α-Bromonaphthalene	140—150	60 ,,	20·04	22·0	5·1 (19°)
Diphenyl ether	130	vigorous	21·52	23·9	3·9 (28°)
Ethyl benzoate	145	60 min.	20·56	23·9	6·2
Benzophenone	130—140	60 ,,	21·72	23·9	13·3
α-Cyanonaphthalene	130	—	22·00	23·8	19·6 (22°)
Ethyl *p*-toluenesulphonate	140—150	60 ,,	22·08	23·8	—
α-Nitronaphthalene	145	60 ,,	22·32	23·9	3·9 (<28°)
None [2]	130	14 hr.	17·50	23·5 [3]	—

[1] Kenyon, Lipscomb, and Phillips, *loc. cit.* [2] Houssa and Phillips, *loc. cit.* [3] Calc., 23·9%. [4] Calc., 17·9%.

In repetition expts., in every case the same or almost the same rotatory power was observed, *e.g.*, $[\alpha]_{5461}$ 59·00° for ethyl phenylchloroacetate in bromobenzene and 19·8° for lævo-β-chloro-

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* The amount of lævo-mandelic acid isolated from amygdalin (100 g.) by Kenyon, Lipscomb, and Phillips (*loc. cit.*) was 20 g. and not 40 g. as stated.

octane in nitrobenzene. The max. obs. rotatory power (α_{5461}) recorded for ethyl phenylchloroacetate is 122·0° ($l = 1{\cdot}0$) (Kenyon, Lipscomb, and Phillips, *loc. cit.*), and for β-chloro-octane 36·68° ($l = 1{\cdot}0$) (Houssa, Kenyon, and Phillips, J., **1929**, 1711).

HCl was evolved during the decomp. of both esters, particularly the β-octyl ester. In order to estimate this, and also the CO_2 produced, the inactive chloroformate (about 1 g.; 1 mol.) in the solvent (10 mols.) was heated under reflux in a slow current of CO_2-free air, which then passed through two wash-bottles containing 0·666*N*-NaOH. The absorbed CO_2 was determined by titration of the alkali with 0·1*N*-H_2SO_4, with phenolphthalein and methyl-orange as indicators, and the HCl produced was estimated in an aliquot portion of the alkali solution by Volhard's method. The temp. of decomp. was more carefully regulated than in the expts. just described and, together with the time, is given in Table II.

TABLE II.

The Proportion of CO_2 *to* HCl *evolved during the Decomposition of Ethyl Phenylchloroformoxyacetate and β-Octyl Chloroformate in the Presence of Solvents.*

Solvent.	Temp. of decomp.	Time, hr.	CO_2 evolved, as % of ester taken.	HCl evolved, as % of ester taken.	Ester decomposed with liberation of	
					CO_2 + HCl.	CO_2 alone.
		Ethyl phenylchloroformoxyacetate.				
Nitrobenzene	160°	3·0	18·03[1]	0·38[2]	2·5	97·5
Benzonitrile	160	2·5	15·67	1·09	8·4	91·6
,,	160	3·5	15·60	1·08	8·5	91·7
Acetophenone	160	2·5	17·22	1·48	10·4	89·6
Bromobenzene	150—160	2·5	17·90	1·91	12·8	87·2
Ethyl *p*-toluenesulphonate	150—160	2·5	18·20	1·96	13·0	87·0
Phenetole	170	3·0	18·11	2·02	13·4	86·6
Ethyl benzoate	140—150	2·0	14·42	1·43	12·0	88·0
,, ,,	160	4·0	18·20	2·61	17·3	82·7
None	150—160	3·0	18·03	1·70	11·3	88·7
		β-Octyl chloroformate.				
Benzonitrile	150—160	2·0	21·30[3]	7·51[4]	42·5	57·5
Nitrobenzene	150—160	2·0	21·29	7·46	42·2	58·7
,,	125	2·0	21·69	7·42	41·1	58·9
α-Bromonaphthalene	150—160	2·0	18·90	6·26	39·9	60·1
Ethyl benzoate	150—160	2·0	22·40	7·52	40·4	59·6
,, ,,	135—140	2·0	22·90	7·27	38·3	61·7
Benzophenone	150—160	2·0	19·32	7·59	47·2	52·8
α-Nitronaphthalene	150—160	2·0	15·24	7·85	61·9	38·1
dl-β-Chloro-octane	140	2·0	22·20	10·42	57·0	43·0
,,	140	2·0	18·03	8·79	58·6	41·4
None	—	—	20·60	6·80	39·7	60·3

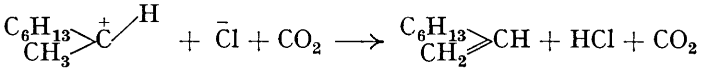
100% Ester decomposition would give: [1] 18·15%. [2] 15·06%. [3] 22·85%. [4] 18·98%.

The CO_2 and HCl produced during each decomp. are also recorded in this table as percentages of the total ester taken. On the assumption that both esters, when they decompose, yield either the corresponding chloride and CO_2, or HCl and CO_2 in equimolecular amounts, the total amount of ester decomposed during each reaction and the percentage of this amount decomposed with evolution of HCl as well as CO_2 have been calculated. The amount of the total ester converted into chloride has been obtained by difference.

In Table II the solvents are arranged in the same order as those in Table I, where the order is that of increasing rotatory power of the chloride produced. The results obtained for the decomposition of lævo-ethyl phenylchloroformoxyacetate in benzonitrile for 2·5 and 3·5 hours and for the decomposition of lævo-β-octyl chloroformate in nitrobenzene for 2 hours at 150—160° and 125° respectively and in ethyl benzoate for hours at 150—160° and 135—140° respectively show that the experiments can be repeated to give fairly concordant results, which are not seriously influenced by small variations in the temperature at which the decompositions occur. The results obtained with *dl*-β-chloro-octane as solvent suggest that the products of the decompositions influence the course of the reactions.

The amount of hydrogen chloride evolved during the decomposition of the esters varies only slightly from solvent to solvent. It is probable, therefore, that, though solvents may alter the rate at which the esters decompose, they have but little influence on their mode of decomposition. Nevertheless solvents can effect large alterations in the magnitude of the rotatory power of the chloride obtained from the ethyl mandelyl ester, but only small alterations in the case of the chloride obtained from the β-octyl ester.

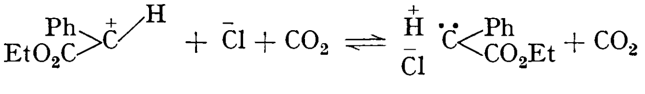
The behaviour of the lævo-β-octyl ester is consistent with the view that it decomposes along two routes, one giving rise to octyl chloride with some racemisation but without inversion, the other to octylene and hydrogen chloride. Octylene is produced, to a greater or less extent, during all the reactions of lævo-β-octyl derivatives that are known to occur with inversion. There is also considerable evidence for the assumption that during such reactions the β-octyl radical passes through the cationic state. The octylene therefore probably arises by the irreversible transformation of those cationic radicals which momentarily become free :



$$\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!>\!\overset{+}{C}\diagup^{H} + \overset{-}{Cl} + CO_2 \longrightarrow \begin{matrix}C_6H_{13}\\CH_2\end{matrix}\!\geqslant\! CH + HCl + CO_2$$

When the lævo-β-octyl chloroformate decomposes to yield octylene and hydrogen chloride, it is probable, therefore, that it is the inversion reaction which is being side-tracked : if this reaction occurred smoothly, it would yield either a racemic or a dextrorotatory chloride.

The decomposition of the lævo-ethyl mandelyl ester by a mechanism which leads either to a racemic or a dextrorotatory chloride cannot be side-tracked in a similar manner, because if this radical becomes free in the cationic state, it cannot pass into an unsaturated hydrocarbon. The cation may lose a proton, but, unless some involved change occurs to dispose of the residual organic radical, recombination to produce the racemic chloride is the



$$\begin{matrix}Ph\\EtO_2C\end{matrix}\!>\!\overset{+}{C}\diagup^{H} + \overset{-}{Cl} + CO_2 \rightleftharpoons \begin{matrix}\overset{+}{H}\\\overset{-}{Cl}\end{matrix}\;\ddot{C}\!<\!\begin{matrix}Ph\\CO_2Et\end{matrix} + CO_2$$

most likely sequel. On this view solvents influence the magnitude of the rotatory power of the chloride obtained from the *l*-ethyl mandelyl ester mainly because they alter the amount of dextrorotatory chloride produced by the decomposition which may be accompanied by inversion : they have little influence on the magnitude of the rotatory power of the chloride obtained from the lævo-β-octyl ester because this type of decomposition is side-tracked. The magnitude and the sign of rotatory power of the chloride obtained from this ester are therefore determined by the type of decomposition which yields a lævo-chloride and occurs without inversion. In the case of both esters it is possible that solvents do not influence the magnitude of the rotatory power of the chlorides produced by this type of decomposition.

Thanks are due to the Royal Society and Imperial Chemical Industries, Ltd., for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11.

[*Received, October* 19*th*, 1932.]