108. *Alkyl–Oxygen Fission in Carboxylic Esters. Part I. Esters of αγ-Dimethylallyl Alcohol and other Substituted Allyl Alcohols.*

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Reactions of the optically active hydrogen phthalate and benzoate of αγ-dimethylallyl alcohol with acids and with alcohols, are described in which the products (esters and ethers) are extensively racemised. When the reaction is stopped before it reaches completion, the unreacted ester recovered is in many cases found to have undergone some racemisation.

Recorded instances of similar reactions of esters of other substituted allyl alcohols are quoted; in some of these, besides racemisation, rearrangement occurs in the substituted allyl residue. The rearrangement and racemisation are evidence that fission of the reacting molecule occurs at the bond joining the substituted allyl residue to the oxygen atom of the acid residue. This mechanism is in contrast to the usual mode of reaction of esters (particularly of saturated aliphatic alcohols), in which this bond remains undisturbed.

The convenient terms alkyl–oxygen fission and acyl–oxygen fission were introduced by Day and Ingold (*Trans. Faraday Soc.*, 1941, **37**, 686) to refer to the two alternative modes of fission, (I) and (II), which may be involved in reactions of carboxylic esters :

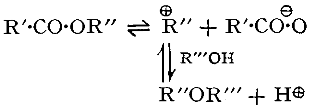
$R'\cdot CO\cdot O\downarrow R''$	$R'\cdot CO\cdot\downarrow OR''$
(I) Alkyl–oxygen fission.	(II) Acyl–oxygen fission.

Mechanism (II) is generally accepted as the common mode of reaction of esters, but mechanism (I) occurs, more commonly than has been realised, when the alkyl group R″ has electron-releasing properties. To the types of esters found to undergo alkyl–oxygen fission (see preliminary note, Balfe and Kenyon, *Nature*, 1941, **148**, 196), may be added the esters of *tert.*-butyl alcohol, which react with methyl alcohol to give methyl *tert.*-butyl ether (Cohen and Schneider, *J. Amer. Chem. Soc.*, 1941, **63**, 3383). When the alkyl group R″ separates as a kation, the occurrence of alkyl–oxygen fission may be demonstrated in two ways : if the carbon atom which in R″ is attached to oxygen is asymmetric, much racemisation will occur, and if the group R″ is unsaturated in the position βγ to the carbon atom which is attached to oxygen, rearrangement occurs. In acyl–oxygen fission, racemisation or rearrangement is not possible.

At an early stage in our investigations on the α- and γ-substituted allyl alcohols ,the occurrence of alkyl–oxygen fission was indicated by the racemisation occurring during saponification of the hydrogen phthalates of the optically active alcohols by dilute aqueous alkali. Kenyon, Partridge, and Phillips (J., **1936**, 85), in the case of γ-phenyl-α-methylallyl alcohol, indicated that a mechanism of type (I) was involved. Other recorded instances are the saponification of the hydrogen phthalates of αγ-dimethylallyl alcohol (Hills, Kenyon, and Phillips, J., 1936, 576) and of γ-methyl-α-ethylallyl alcohol (Airs, Balfe, and Kenyon, this vol., p. 18). The topic was discussed by Arcus and Kenyon (J., 1938, 1912), but no further instances have been recorded, because in experiments with other substituted allyl alcohols concentrated (5N) aqueous or aqueous-alcoholic sodium hydroxide was used for the saponification in order to obtain the alcohols with complete retention of optical purity, by the acyl–oxygen fission mechanism. Rearrangement, also, has been observed in the alkyl–oxygen fission reaction. Under weakly alkaline conditions of saponification, the hydrogen phthalate of α-phenyl-γ-methylallyl alcohol yields γ-phenyl-α-methylallyl alcohol (Kenyon, Partridge, and Phillips, J., 1937, 207).

We now describe solvolytic reactions of the optically active hydrogen phthalates and benzoates of αγ-dimethylallyl alcohol with acids and alcohols, and refer to cases of similar reactions of esters of other substituted allyl alcohols. The results obtained with the αγ-dimethylallyl compounds are summarised in the table. We are unable to attach any importance to the relative configurations of the optically active fractions of the products, since these are insignificant in amount, compared with the racemic fractions. Rearrangement in the reactions of αγ-dimethylallyl derivatives cannot be observed on account of the symmetrical substitution in the allyl residue.

These reactions have two characteristic features : (i) the extensive racemisation of the product; (ii) the racemisation found in the recovered portion of the reacting ester, when the reaction is stopped before it has reached completion. Both features indicate alkyl–oxygen fission, and the fact that the esters racemise more quickly than they react is in agreement with the known unimolecular mechanism of solvolytic reactions. The reacting ester ionises, a process which involves solvation, and the liberated and racemised carbonium kation may recombine with the anion, or combine with a solvent molecule, from which it expels a proton. The present experiments do not exclude the possibility that the reaction product undergoes continued racemisation by solvolysis, and our view of the mechanism of the reaction may be illustrated as follows :



$$\begin{array}{c} \mathrm{R'{\cdot}CO{\cdot}OR''} \rightleftharpoons \overset{\oplus}{\mathrm{R''}} + \mathrm{R'{\cdot}CO{\cdot}}\overset{\ominus}{\mathrm{O}} \\ \quad\quad\quad\quad \Big\updownarrow{\scriptstyle \mathrm{R'''OH}} \\ \quad\quad\quad\quad \mathrm{R''OR'''} + \mathrm{H}^{\oplus} \end{array}$$

At 66° the hydrogen phthalate of αγ-dimethylallyl alcohol reacts with methyl alcohol, giving a methyl ether of very low rotatory power, and if part of the phthalate is recovered, it is found to be extensively racemised. At 31°, in methyl alcohol, neither reaction nor racemisation occurs, a solution of the phthalate remaining unchanged in rotatory power during 3 months, but in nitromethane, the phthalate undergoes much racemisation and some decomposition during 2 months : presumably the higher dielectric constant of nitromethane facilitates ionisation of the ester, and hence racemisation and decomposition.

Reactions involving alkyl–oxygen fission have been recorded for the following hydrogen phthalates (those marked with an asterisk have been shown to involve rearrangement as well as racemisation): γ-phenyl-α-methylallyl with methyl alcohol, and α-phenyl-γ-methylallyl with methyl alcohol * and with acetic acid * (Kenyon, Partridge, and Phillips, *loc. cit.*); propenylallylcarbinyl with formic acid (Duveen and Kenyon, *Bull. Soc. chim.*, 1938, **6**, 704); γ-methyl-α-propylallyl with formic acid and with benzoic acid (Arcus and Kenyon, *loc. cit.*); α-phenylallyl with methyl and ethyl alcohols, and with formic * and acetic * acids (Duveen and Kenyon, J., 1939, 1697); γ-methyl-α-ethylallyl with methyl alcohol (Airs, Balfe, and Kenyon, *loc. cit.*).

During acid-catalysed etherification of αγ-dimethylallyl alcohol, much racemisation occurs also (three examples are recorded in the table). In etherification one or other of the reacting molecules must undergo alkyl–oxygen fission, and in the present cases this presumably occurs more readily in the unsaturated than in the saturated alcohol (methyl or *n*-butyl) with which it is reacting. The possibility that the ether itself is racemised in the presence of acid is not excluded by the present experiments.

In some of our early experiments we examined the reaction of hydrogen phthalates of optically active alcohols with sodium acetate in acetic acid solution, the products in all cases being racemic acetates. We discontinued these experiments because in this type of reaction there may be, not only alkyl–oxygen fission (interchange of anions) resulting in either racemisation or inversion of configuration, but also acyl–oxygen fission, as pointed out by Arcus, Balfe, and Kenyon (J., 1938, 485) with reference to the analogous case of sodium formate in formic acid solution, which results in retention of configuration. It is therefore not possible to draw any conclusion from the stereochemical nature of the products, which may be formed by concurrence of the two possible modes of reaction. This objection does not apply to the use of such mixtures in reactions with halides which can only react by replacement mechanisms analogous to the alkyl–oxygen fission of esters.

Reactions of the Optically Active αγ-Dimethylallyl Alcohols and their Esters.

Reacting ester of αγ-dimethylallyl alcohol.	Reactant.	Temp.	Duration.	Resulting cmpd. of dimethylallyl alcohol.	% Optical purity of resulting cmpd.	% Optical purity of recovered portion of reacting ester.
Hydrogen phthalate	$H\cdot CO_2H$ ‡	20°	5 mins.	Formate	0	0
		20	15 ,,	,,	1 †	93
		90	30 ,,	,,	0	11
	$Me\cdot CO_2H$	37	60 days	Acetate	1 †	23
		90	3½ hrs.	,,	0	0
	MeOH	64	21 hrs.	Methyl ether	6	6
		31	3 months	No reaction	—	100
	n-BuOH	90	30 hrs.	*n*-Butyl ether	9 †	19
	$Ph\cdot CH_2\cdot OH$	90	10 hrs.	Benzyl ether	2 †	8
	Ph·OH §	20	14 days	*Phenyl ether*	low	53
		90	1 hr.	,,	0	0
Benzoate	$H\cdot CO_2H$	90	6 hrs.	Formate	0	30
	$Me\cdot CO_2H$	90	50 ,,	Acetate	4 *	—
	MeOH	31	7 days	Methyl ether	4 †	98
		64	2½ ,,	,,	0	—
	n-BuOH	90	2½ ,,	*n*-Butyl ether	12 †	58
Acid catalysed reactions of (−)αγ-dimethylallyl alcohol	Dimethylallyl alcohol	20	12 hrs.	*Dimethylallyl ether*	18 *‖	—
	MeOH	20	24 ,,	Methyl ether	2 ¶	—
	n-BuOH	20	18 ,,	*n*-Butyl ether	0 ¶	—

* Retention of configuration.

† Inversion of configuration.

‡ In the first experiment a higher proportion of formic acid was used than in the second, and the proportion of formic acid used in the third was the lowest in the three.

§ In the experiment at 20°, the molar ratio of phenol to hydrogen phthalate was 3 : 1, and at 90° it was 1 : 1.

‖ % of maximum known rotation of the ether, which may not be optically pure.

¶ Hills, Kenyon, and Phillips (*loc. cit.*).

EXPERIMENTAL.

The preparation and rotatory powers of (+)αγ-dimethylallyl alcohol and its formate, acetate, and methyl, *n*-butyl, and benzyl ethers are recorded by Hills, Kenyon, and Phillips (*loc. cit.*). In the following experiments, the reacting esters had the rotatory powers of the optically pure substances, unless otherwise stated: (+) and (−) are used to refer to optically pure dextro- and lævo-rotatory substances, respectively.

Reactions of the Optically Active αγ-Dimethylallyl Hydrogen Phthalates.—(i) *With formic acid.* (*a*) At 20°. The (+)hydrogen phthalate (1 g.) dissolved instantly in formic acid (20 c.c.) with separation of phthalic acid. Within 5 mins. the filtered solution was found to be optically inactive. In the second experiment, the (+)phthalate (13 g.) was triturated with 20 g. of formic acid for 15 mins. Anhydrous ether (40 c.c.) was added, and phthalic acid (2·7 g.) filtered off. The filtrate was extracted with aqueous sodium carbonate, from which, after acidification, 8·6 g. of (+)αγ-dimethylallyl hydrogen phthalate were recovered with $[\alpha]_{5893}$ + 22·1°, $[\alpha]_{5461}$ + 28·0° in chloroform (*l*, 2; *c*, 5·24). From the ethereal residue, αγ-dimethylallyl formate was obtained, b. p. 122—123°, $n_{D}^{20^\circ}$ 1·4125; $\alpha_{5461}^{18^\circ}$ + 0·23° (*l*, 0·5).

(*b*) At 90°. The hydrogen phthalate (11·7 g.; $[\alpha]_{5461}$ − 26·0° in chloroform) and formic acid (2·5 g.) were warmed on the steam-bath for 30 mins. By the method described above, the following products were then isolated: phthalic anhydride (0·5 g.), αγ-dimethylallyl hydrogen phthalate (4·0 g., $[\alpha]_{5461}$ − 3·4° in chloroform), *dl*-dimethylallyl formate.

(ii) *With acetic acid.* (*a*) At 37°. A solution of 20 g. of the (+)hydrogen phthalate in 75 g. of glacial acetic acid was kept at 37° for 2 months, and the following products were then isolated by the method described above: αγ-dimethylallyl hydrogen phthalate (7 g., $[\alpha]_{5893}$ + 6·4°; $[\alpha]_{5461}$ + 7·0° in chloroform), αγ-dimethylallyl acetate (5 c.c., b. p. 41°/11 mm., $\alpha_{5893}^{17^\circ}$ + 0·23°, $\alpha_{5461}^{17^\circ}$ + 0·27°, $\alpha_{4358}^{17^\circ}$ + 0·50°, *l*, 0·5).

(*b*) At 90°. The hydrogen phthalate (5·8 g., $[\alpha]_{5461}$ − 13·4° in chloroform) and glacial acetic acid (1·7 c.c.) were heated on the steam-bath for 3½ hrs. The following products were then isolated as described above: phthalic acid (1·5 g.), *dl*-αγ-dimethylallyl hydrogen phthalate (2·1 g.), *dl*-αγ-dimethylallyl acetate, b. p. 137—138°. Phthalic anhydride (0·25 g.) was separated by filtration, being insoluble both in aqueous sodium carbonate and in ether.

(iii) *With methyl alcohol.* A solution of the (+)hydrogen phthalate (19 g.) in dry methyl alcohol (90 c.c.) was heated under reflux for 21 hrs., then concentrated. Addition of three successive portions of methyl alcohol (15 c.c.) to the solid residue, each followed by reconcentration, removed all volatile material. The solid residue was extracted with chloroform, from which αγ-dimethylallyl hydrogen phthalate (0·5 g., $[\alpha]_{5461}$ + 1·8° in chloroform) was isolated. Phthalic acid (9·3 g.) remained undissolved. The volatile fraction was diluted with dry ether (300 c.c.), and powdered anhydrous calcium chloride (160 g.) added to remove methyl alcohol. After 12 hrs. the solid was removed by filtration and washed with ether. On concentration of the filtrate, methyl αγ-dimethylallyl ether (4·0 c.c.) was obtained, b. p. 90—91°. It was redistilled until refractive index and rotatory power were constant, and then had $n_{5893}^{17^\circ}$ 1·4038; $\alpha_{5461}^{18^\circ}$ + 0·81°; $\alpha_{4358}^{18^\circ}$ 1·42° (*l*, 0·25) (Found: C, 71·1; H, 11·4. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·0%).

(iv) *With* n-*butyl alcohol.* A solution of the (+)hydrogen phthalate (20 g.) in *n*-butyl alcohol (60 c.c.) was heated on the steam-bath for 30 hrs., then diluted with ether and washed with dilute aqueous sodium carbonate from which, on acidification, αγ-dimethylallyl hydrogen phthalate (10·8 g.) was obtained with $[\alpha]_{5461}$ + 5·83° in chloroform. The ethereal solution was then washed with water, dried, and distilled. The fraction, b. p. 150—151°, was redistilled, yielding *n*-butyl αγ-dimethylallyl ether, b. p. 151—152°, $n_{5893}^{19^\circ}$ 1·4175; $d_{4^\circ}^{25^\circ}$ 0·7880; $\alpha_{5461}^{20^\circ}$ + 0·68°; $\alpha_{4358}^{20^\circ}$ + 1·10° (*l*, 0·25) (Found: C, 75·8; H, 12·0. Calc. for $C_9H_{18}O$: C, 76·1; H, 12·7%).

(v) *With benzyl alcohol.* A solution of the hydrogen phthalate (11·7 g.; $[\alpha]_{5461}$ − 26·0° in chloroform) in benzyl alcohol (7 g.) was heated on the steam-bath for 10 hrs., then cooled, and treated as in (iv), αγ-dimethylallyl hydrogen phthalate (3·2 g.) being recovered with $[\alpha]_{5461}$ − 2·0° in chloroform. The ethereal solution was washed with water, dried and distilled. The less volatile fraction was heated for 8 hrs. on the steam-bath with phthalic anhydride (8 g.) to remove benzyl alcohol, then diluted and washed as in (iv), and washed with water, dried, and distilled. Benzyl αγ-dimethylallyl ether (3·3 c.c.) was obtained, b. p. 117—119°/20 mm.; $n_{5893}^{16^\circ}$ 1·4994; $\alpha_{5461}^{20^\circ}$ − 0·16° (*l*, 0·25) (Found: C, 81·4; H, 9·1. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%).

(vi) *With phenol.* (*a*) At 20°. A solution of the (+)hydrogen phthalate (23·4 g., 1 mol.) and phenol (29 g., 3 mols.) in dry ether (50 c.c.) after 14 days at room temperature (during which phthalic acid separated) was made alkaline and extracted with ether. From the extract, *phenyl αγ-dimethylallyl ether* (3 c.c.) was obtained, b. p. 97°/13 mm.; $n_{5893}^{20^\circ}$ 1·5090; α_{5893} − 0·32°; α_{5461} − 0·34°; α_{4358} − 0·55° (*l*, 0·5) (Found: C, 81·7; H, 8·6. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%). From the aqueous residue, by acidification, αγ-dimethylallyl hydrogen phthalate (15 g.) was obtained, $[\alpha]_{5461}$ + 16·0° (*c*, 5·05) in chloroform.

(*b*) At 90°. The hydrogen phthalate (11·7 g., 1 mol.; $[\alpha]_{5461}$ − 26·0° in chloroform) and phenol (5·2 g., 1 mol.) were heated together on the steam-bath for one hour, then diluted with ether, filtered from deposited phthalic acid (6 g.), washed with dilute aqueous sodium carbonate (from which *dl*-αγ-dimethylallyl hydrogen phthalate was recovered), dried, and fractionally distilled; *dl*-phenyl αγ-dimethylallyl ether (1·3 c.c.) was obtained, b. p. 121—122°/22 mm., $n_{5893}^{19^\circ}$ 1·5107 (Found: C, 81·7; H, 8·6%).

The relative configuration and rotatory power of optically pure phenyl αγ-dimethylallyl ether could not be determined, as it was not possible to prepare it from the carbinol by methods unlikely to cause configurational change.

Reactions of αγ-Dimethylallyl Benzoate.—(i) *With formic acid.* The (+)benzoate (7 g.) and anhydrous formic acid (2 c.c.) were heated on the steam-bath for 6 hrs., cooled, diluted with ether, washed with dilute aqueous sodium carbonate and, after removal of the ether, fractionally distilled. From the more volatile fraction, on redistillation, *dl*-αγ-dimethylallyl formate (2 c.c.) was obtained, b. p. 122—123°; $n_{5893}^{15^\circ}$ 1·4163; $\alpha_{5461}^{20^\circ}$ − 0·22° (*l*, 0·5). The less volatile fraction yielded αγ-dimethylallyl benzoate (2·5 c.c.), b. p. 132—134°/19 mm.; α_{5461} + 1·94°; α_{4358} + 3·9° (*l*, 0·25). From 20·9 g. of the benzoate ($\alpha_{5461}^{20^\circ}$ − 4·46°; *l*, 0·25) and 5·4 g. of formic acid, heated on the steam-bath for 20 hrs., 3 c.c. of *dl*-formate were obtained (Found: C, 63·3; H, 8·8. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·8%).

(ii) *With acetic acid.* The benzoate (21·4 g.; $\alpha_{5461}^{20^\circ}$ − 7·56°, *l*, 0·5) and glacial acetic acid (7·3 c.c.) were heated together on the steam-bath for 50 hrs., then fractionally distilled. The more volatile fraction, dried and redistilled, yielded αγ-dimethylallyl acetate (2 c.c.), b. p. 136—137°; $n_{5893}^{15^\circ}$ 1·4218, $\alpha_{5461}^{20^\circ}$ + 0·36° (*l*, 0·25).

(iii) *With methyl alcohol.* (*a*) At 31°. A solution of the benzoate (19 g.; $\alpha_{5461}^{18^\circ}$ + 11·3°, *l*, 0·5) in 40 g. of dry methyl alcohol, after standing at 31° for 7 days, was distilled on the steam-bath, 20 g. of methyl alcohol being added in portions towards the end of distillation to facilitate removal of the methyl ether. The combined distillates were placed on powdered anhydrous calcium chloride overnight, and the resulting pasty mass lixiviated with dry ether. The ethereal extract was concentrated and the residue distilled, yielding: (i) methyl αγ-dimethylallyl ether (4 c.c.), b. p. 90°, $n_{5893}^{15^\circ}$ 1·4046, $\alpha_{5461}^{19^\circ}$ + 1·02°, $\alpha_{4358}^{19^\circ}$ + 2·0° (*l*, 0·5); (ii) methyl benzoate (6 g.), b. p. 199—200°, $n_{5893}^{20^\circ}$ 1·5148 (Perkin, J., 1896, **69**, 1174, gives b. p. 199°; Cotton and Moulton, *Ann. Chim. Phys.*, 1913, **28**, 214, give $n_{5893}^{18\cdot7^\circ}$ 1·5144); (iii) recovered αγ-dimethylallyl benzoate, b. p. 125—126°/14 mm., $\alpha_{5461}^{18^\circ}$ + 11·1° (*l*, 0·5); (iv) benzoic acid (4·7 g.).

(*b*) At 64°. The benzoate (6·3 g.; $\alpha_{5461}^{20^\circ}$ − 6·7°, *l*, 0·5) in methyl alcohol (50 c.c.) was heated under reflux for 60 hrs., then treated as in (*a*). *dl*-Methyl αγ-dimethylallyl ether (2 c.c.) was obtained, b. p. 90°; $n_{5893}^{15^\circ}$ 1·4046.

(iv) *With* n-*butyl alcohol.* The (+)benzoate (5·6 g.) and *n*-butyl alcohol (6 g.) were heated on the steam-bath for 60 hrs., then dissolved in ether, and the solution washed with dilute aqueous sodium carbonate, dried, and concentrated. From the residue, two fractions were obtained: (i) *n*-butyl αγ-dimethylallyl ether (2 g.), b. p. 151—152°, $n_{5893}^{17^\circ}$ 1·4180, $\alpha_{5461}^{20^\circ}$ + 0·19° (*l*, 0·5); (ii) αγ-dimethylallyl benzoate (1·5 g.), b. p. 134—135°/18 mm., $n_{5893}^{17^\circ}$ 1·4995, $\alpha_{5461}^{20^\circ}$ + 7·71° (*l*, 0·5), Benzoic acid (2·0 g.) was isolated from the sodium carbonate washings.

Preparation of Bis-αγ-dimethylallyl Ether of High Rotatory Power.—(+)αγ-Dimethylallyl alcohol (8·6 g.), methyl *p*-toluenesulphonate (20 g.), and anhydrous potassium carbonate (20 g.) were heated on the steam-bath for 7 hrs., poured into water, and extracted with ether. From the dried, concentrated ethereal extract, two fractions were isolated: (i) (+)αγ-dimethylallyl alcohol (2 c.c.), b. p. 120·5°; (ii) *bis-αγ-dimethylallyl ether* (2 c.c.), b. p. 156—157°, $n_{5893}^{16^\circ}$ 1·4290, $\alpha_{5461}^{20^\circ}$ − 14·26°, $\alpha_{4358}^{20^\circ}$ − 24·5° (*l*, 0·25) (Found: C, 77·6; H, 11·6. $C_{10}H_{18}O$ requires C, 77·8; H, 11·7%).

αγ-Dimethylallyl *p*-toluenesulphonate, formed by alkoxy-interchange, is presumably an intermediate in the formation of the ether, since no ether is formed when the alcohol is heated with anhydrous potassium carbonate only. In the absence of potassium carbonate the bis-αγ-dimethylallyl ether (b. p. 156—157°) obtained from the (+)alcohol and methyl *p*-toluenesulphonate is largely racemised (α_{5461} − 0·73°; *l*, 0·25), presumably by the concurrently formed *p*-toluenesulphonic acid.

Acid-catalysed Etherification of (−)αγ-Dimethylallyl Alcohol.—To (−)αγ-dimethylallyl alcohol (5 g.; $\alpha_{5461}^{18^\circ}$ −0·52°, $\alpha_{4358}^{18^\circ}$ −1·72°; *l*, 2) five drops of concentrated sulphuric acid were added, and the mixture left at room temperature for 12 hrs. It was then washed with dilute aqueous sodium carbonate, dried, and distilled, yielding bis-αγ-dimethylallyl ether (3 c.c.), b. p. 156—157°, $n_{5893}^{16^\circ}$ 1·4374, $\alpha_{5461}^{16^\circ}$ +0·93° (*l*, 0·25).

Optical Stability of αγ-Dimethylallyl Hydrogen Phthalate in Methyl-alcoholic Solution at 31°.—A solution of the phthalate (5·35 g.; $[\alpha]_{5461}$ +30·0° in chloroform) in methyl alcohol (100 c.c.) gave the following values for the specific rotatory power of the phthalate at room temperature: $[\alpha]_{5893}$ + 28·8°; $[\alpha]_{5780}$ + 31·1° $[\alpha]_{5461}$ + 35·5°; $[\alpha]_{4358}$ + 68·2°. These values were unchanged after the solution had been kept at 31° for 3 months.

Racemisation of αγ-Dimethylallyl Hydrogen Phthalate in Nitromethane at 31°.—A solution of the (+)phthalate (1·019 g.) in nitromethane (20 c.c.) had $\alpha_{5893}^{17^\circ}$ + 2·48°; $\alpha_{5780}^{17^\circ}$ + 2·72°; $\alpha_{5461}^{17^\circ}$ +3·10°; $\alpha_{4358}^{17^\circ}$ + 6·50°. This was kept at 31° and the rotatory powers gradually fell, after 61 days being $\alpha_{5893}^{20^\circ}$ + 0·26°; $\alpha_{5780}^{20^\circ}$ + 0·32; $\alpha_{5461}^{20^\circ}$ + 0·34°; $\alpha_{4358}^{20^\circ}$ + 0·70° (deposition of phthalic acid began at 20 days). After 61 days the solution was evaporated, leaving 0·65 g. of solid, which was separated by extraction with dry chloroform into phthalic acid (0·15 g.) and αγ-dimethylallyl hydrogen phthalate (0·44 g.), $[\alpha]_{5893}$ + 2·48°, $[\alpha]_{5461}$ + 3·16°. These results indicate that 20% of the phthalate had decomposed with liberation of phthalic acid, and the remainder underwent 90% racemisation.

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