36. *Retention of Asymmetry and Inversion of Configuration during Anionotropic Change. The Conversion of (—)α-Phenyl-γ-methylallyl Alcohol into (+)γ-Phenyl-α-methylallyl Alcohol.*

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IN 1933 Ingold and Wilson (J., 1493) began a series of investigations to ascertain whether asymmetry is retained during prototropic (I) and anionotropic (II) changes in which a proton

$[H]—\overset{*}{A}—B=C \rightleftharpoons A=B—\overset{*}{C}—[H]$

(I.)

$[X]—\overset{*}{A}—B=C \rightleftharpoons A=B—\overset{*}{C}—[X]$

(II.)

(I) or an anion (II) moves from one asymmetric centre to a new asymmetric centre arising as a result of the isomeric change. After a detailed discussion of the problem, and exploratory experiments with both prototropic and anionotropic systems (*loc. cit.*), the mutually interconvertible azomethines (III) and (IV)

(III.)

$$\mathrm{{}^{Me}_{Ph}\!>\!C[H]\cdot N{:}C\!<^{Ph}_{C_6H_4Cl\ (\mathit{p})}} \rightleftharpoons \mathrm{{}^{Me}_{Ph}\!>\!C{:}N\cdot C[H]\!<^{Ph}_{C_6H_4Cl\ (\mathit{p})}}$$

(IV.)

were selected for study, and from the equilibrium mixture obtained after the isomerisation of the optically active isomeride (III), the isomeride (IV) was isolated in an optically inactive condition. Later, kinetic studies of the rates of racemisation and of tautomeric change led Hsü, Ingold, and Wilson (J., **1935**, 1778) to conclude that the racemisation observed during the prototropic change of azomethines did not occur during the ionisation which precedes the tautomeric change, and therefore that mesomeric anions were capable of retaining their optical activity. Additional evidence in support of this conclusion was drawn from the influence of constitutional factors on the rates of racemisation of prototropic compounds (Wilson, J., **1934**, 98) and from comparisons of the rates of racemisation and bromination of optically active ketones (Ingold and Wilson, J., **1934**, 773; Hsü and Wilson, J., **1936**, 623).

Contemporaneously with the above investigations, we have studied the anionotropic system(V) $\rightleftharpoons$ (VI), mainly in order to throw light on the nature of the isomerism undergone by the more symmetrically substituted (+)$\alpha\gamma$-dimethylallyl alcohol (Hills, Kenyon, and

(V.) $(-)\mathrm{Ph\cdot CH[OH]\cdot CH{=}CHMe}$ $\qquad$ $(+)\mathrm{Ph\cdot CH{=}CH\cdot CH[OH]Me}$ (VI.)

Phillips, *Chem. and Ind.*, 1933, **52**, 660; J., **1936**, 580). We have been able to obtain evidence that when (V) is converted into (VI), asymmetry is maintained, and that the new asymmetric centre produced has the opposite configuration to that of the original asymmetric centre.

Conversion of (—)*α-Phenyl-γ-methylallyl Alcohol into* (+)*γ-Phenyl-α-methylallyl Alcohol.*—The preparation of the (+) and the (—) alcohol (VI) has already been described (Kenyon, Partridge, and Phillips, J., **1936**, 85); the (+) and the (—) alcohol (V) have now been prepared by the recrystallisation of the quinidine salt of dl-*α-phenyl-γ-methylallyl hydrogen phthalate* first from methyl acetate and secondly from acetone. The rotatory powers of the quinidine salts and the hydrogen phthalic esters are in Table I. The (—)α-phenyl-γ-methylallyl alcohol (see Table II) obtained by saponification of its hydrogen phthalic ester with alcoholic soda gave on reduction (+)phenyl-*n*-propylcarbinol with a rotatory power closely agreeing with that obtained by the direct resolution of *dl*-phenyl-*n*-propylcarbinyl hydrogen phthalate (Kenyon and Partridge, J., **1936**, 128). It is therefore probable that both the saturated and the unsaturated alcohol have been obtained optically pure. The rotatory power of (—)α-phenyl-γ-methylallyl alcohol remained unchanged during 15 weeks at room temperature.* It is also stable to alkalis, since it was not converted into its isomeride to any appreciable extent when it was (*a*) left in contact with 20 vols. of $0{\cdot}1N$-sodium hydroxide for 14 days, (*b*) boiled under reflux with aqueous sodium hydroxide, or (*c*) heated with anhydrous potassium carbonate at 100° for 2 hrs. In acid solution it changes fairly rapidly: a solution of the (—)alcohol, with $\alpha_{5461}^{20^\circ}$ $-14{\cdot}98^\circ$ (l, 0·25), in 0·5% aqueous acetic acid after standing at room temperature for 40 hrs. gave (+)γ-phenyl-α-methylallyl alcohol with $\alpha_{5461}^{20^\circ}$ $+\,0{\cdot}69^\circ$ (l, 0·5). Considerable racemisation occurred, therefore, since (+)γ-phenyl-α-methylallyl alcohol of the same degree of optical purity as that of the (—)alcohol used would have approximately $\alpha_{5461}^{50^\circ}$ $+\,21{\cdot}0^\circ$ (l, 0·5).

Conversion of Derivatives of (—)*α-Phenyl-γ-methylallyl alcohol into the Corresponding Derivatives of* (+)*γ-Phenyl-α-methylallyl Alcohol.*—In agreement with Burton's conclusions (J., 1928, 1650; 1929, 455) that the anionic stability of the migratory groups X (*i.e.*, the strengths of the acids HX) partly determines the ease of conversion, the esters of (—)α-phenyl-γ-methylallyl alcohol isomerised more readily than did the parent alcohol. Even at ordinary temperatures and under diminished pressure (—)α-phenyl-γ-methylallyl hydrogen phthalate

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* (Added in proof) After 18 months the rotatory power had fallen to $\alpha_{5461}^{20^\circ}$ $-\,15{\cdot}1^\circ$ (l, 0·25).

TABLE I.

	Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4359}$.
Quinidine salt of (−)α-phenyl-γ-methylallyl hydrogen phthalate	$CHCl_3$	4·64	+122·7°	+126·0°	+147·5°	+266°
Quinidine salt of (+)α-phenyl-γ-methylallyl hydrogen phthalate	$CHCl_3$	3·05	+131·0	+140·2	+160·2	+240
(−)α-Phenyl-γ-methylallyl hydrogen phthalate	Et_2O	5·00	− 17·1	− 20·0	− 22·4	− 47
(+) ,, ,, ,, ...	Et_2O	3·85	+ 15·5	+ 17·8	+ 20·0	+ 42

TABLE II.

The Observed Rotatory Powers (l, 0·5) *of* (—)*α-Phenyl-γ-methylallyl Alcohol.*

t.	α_{5790}.	α_{5461}.	α_{4359}.	*t.*	α_{5790}.	α_{5461}.	α_{4359}.
18·0°	−29·69°	−34·17°	—	50·0°	−22·90°	−26·55°	−47·8°
20·0	29·16	33·59	−64·0°	62·5	20·62	23·71	45·25
30·7	26·93	31·31	59·4	66·0	20·07	23·13	44·15
34·8	26·07	30·21	57·0	71·0	19·12	22·07	42·4
40·5	24·79	28·74	54·25	20·0 (after cooling)	29·15	33·69	64·0

t = 15·9°, 25·8°, 35·3°, 46·5°; $d_{4^\circ}^{t^\circ}$ = 1·0110, 1·0046, 0·9954, 0·9884 respectively.

slowly changed to a pasty mass which re-solidified after about 10 days. Viewed under the microscope the crystals maintained their shape, but their surfaces became covered with a viscous liquid. The liquid portions appeared to travel towards the centre of the crystal, which was finally composed of two forms of smaller crystals—fine hairs, corresponding to (+)γ-phenyl-α-methylallyl hydrogen phthalate, and rhombic crystals, corresponding to the *dl*-analogue, the whole mass retaining the essential shape of the original crystal. Similarly, when heated, the *dl*-hydrogen phthalic ester melted at 93—94°, but this was not its true m. p., for the resolidified ester was proved to contain *dl*-γ-phenyl-α-methylallyl hydrogen phthalate which can be readily detected since it forms a crystalline salt with cinchonidine (Kenyon, Partridge, and Phillips, *loc. cit.*) but not with quinidine. When mixed with *dl*-γ-phenyl-α-methylallyl hydrogen phthalate, the *dl*-α-phenyl ester melted at 92—93°. Details of other experiments in which the (—)α-phenyl ester was kept at various temperatures for different periods of time are given in Table III : it will be seen that as much as 70% of the (—)α-phenyl-γ-methylallyl hydrogen phthalate taken has been converted into its optically pure (+)γ-phenyl isomeride.

As is shown by the data given in Table IV (in which ε is the dielectric constant of the solvent), the isomerism undergone by the (—)α-phenyl ester in solution was more markedly affected by increase in temperature than by any change in the dielectric constant of the solvent, although, as in the case of the conversion of α-phenylallyl *p*-nitrobenzoate into cinnamyl *p*-nitrobenzoate (Burton, *loc. cit.*), the isomeric change was faster in solvents with high dielectric constants; *e.g.*, in benzonitrile the isomeric change was complete in 2 days, whereas in benzene 13 days were required.

Hyperbolæ were obtained when the rotatory powers of two solutions (Table V) of (—)α-phenyl-γ-methylallyl hydrogen phthalate, (i) *c*, 1·5 and (ii) *c*, 3·00 in carbon disulphide, were plotted against time. When t_n was plotted against $\log_{10}(A_0 - A_a) - \log_{10}(A_n - A_a)$, where t_n is time in hours, A_0 the initial rotation, A_a the final rotation, and A_n the rotation of the solution at time t_n, straight lines were obtained for each solution, and the velocity constant calculated from the slope of the lines proved to be in both cases 0·017, showing that the reaction was unimolecular.

In a similar manner the velocity constants (k) of the same reaction in benzene solution at different temperatures were calculated from the rotation data given in Table VI. The values of these constants when plotted against t_n gave a hyperbola, indicating that the rate of reaction approached infinity between 55° and 60°. When log k_T was plotted against T, the absolute temperature at which k_T was measured, a straight line was obtained with slope 2/0·0032, whence E, the energy of activation of the reaction, is 28,800 cals.

TABLE III.

Conversion of (—)α-Phenyl-γ-methylallyl Hydrogen Phthalate into (+)γ-Phenyl-α-methylallyl Hydrogen Phthalate at Different Temperatures in the Absence of Solvents.

Time.	Temp.	Rotatory power of final product in CS_2 (*l*, 2). $[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	*c*.	% Final product optically pure.*	
11 days	18—20°	+15·5°	+19·0°	+39·5°	2·20	42·5	*a*
15 ,,	,,	—	27·4	—	2·45	61·0	
18 ,,	24—26	27·8	30·6	58·6	2·40	67·0	
19 ,,	,,	28·0	33·0	69·0	2·65	73·0	
20 ,,	,,	30·3	33·8	72·0	2·80	74·6	
21 ,,	,,	31·4	33·0	68·0	2·65	73·0	
22 ,,	,,	31·1	33·7	—	2·54	74·5	
23 ,,	,,	30·3	33·2	65·6	2·66	73·6	
11 ,,	18—20	5·5	6·6	—	1·89	14·5	i *b*
20 ,,	20	—	25·5	—	2·50	57·0	ii
10 mins.	75	17·6	21·2	40·8	2·50	47·0	i *c*
5 ,,	77	20·4	21·8	45·0	2·50	49·0	ii
3 ,,	80—82	24·4	27·4	53·3	2·50	61·5	iii
5 ,,	,,	24·6	27·6	51·0	2·50	62·0	iv
10 ,,	,,	18·0	20·0	36·8	2·50	49·0	v
5 ,,	94	10·3	10·9	22·2	4·78	24·0	vi

(*a*) Portions of one preparation of the (—)ester, m. p. 80—81°, were sealed up in tubes: determinations of rotatory power were made after the periods stated.

(*b*) (i) Kept at 11 mm. in a desiccator; (ii) kept at <0·1 mm. in a sealed tube.

(*c*) Portions of a second preparation of the (—)ester, m. p. 80—81°. (iii) From the heated material (1·0 g.) there were isolated *dl*-γ-phenyl-α-methylallyl hydrogen phthalate, m. p. 93—94° (0·344 g.), and (+)γ-phenyl-α-methylallyl hydrogen phthalate, m. p. 68—69° (0·205 g.), with $[\alpha]_{5461}$ +45·0° (*c*, 1·025; *l*, 2) in CS_2.

* Calculated on $[\alpha]_{5461}$ as being the most accurate values.

TABLE IV.

Transformation of (—)α-Phenyl-γ-methylallyl Hydrogen Phthalate into (+)γ-Phenyl-α-methylallyl Hydrogen Phthalate at Different Temperatures in Solvents.

Solvent.	Initial [α] of soltn. $[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4359}$.	*c*.	Temp.	Time.	Final [α] of soltn. $[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	% Final product optically pure.	[α] of pure (+)γ-phenyl ester. $[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	*c*.	ε.
C_6H_{12} [10]	—	—	—		82°	0·5 min.	—	−20·0°[1]	—	0	—	—	—		2·05
,, ...	—	—	—		82	3 ,,	—	+10·0[2]	—	22	—	—	—		
,, ...	—	—	—		82	30 ,,	—	+20·0[3]	—	44	—	—	—		
C_6H_6	−12·1°	−13·3°	− 34·5°	3·06	20	13 days	+ 3·2°	+ 3·3[4]	+ 7·7°	30	+ 4·0°	+ 5·1°	+ 7·8°	5·00	2·28
CS_2..............	+ 0·3	+ 0·2	− 0·1	2·66	46	5 hrs.	+22·0	+26·0[5]	+50·7	58	+37·4	+44·7	+87·4	5·00	2·64
Et_2O	−17·1	−22·4	− 47·6	1·94	20	134 days	—	−14·0[6]	−26·7	33	−13·9	−16·3	−32·3	5·00	4·34
$CHCl_3$............	—	−15·7	− 34·1	5·12	20	22 hrs.	0	0[7]	0	39	+ 1·8	+ 2·2	+ 5·3	5·00	
C_6H_5Cl	—	+ 1·5	—	2·85	20	6 days	—	+ 9·0	+15·8	31	—	+29·2	—	3·25	
C_5H_5N	− 3·8	− 5·4	− 12·7	4·35	95	<30 mins.	+11·0	+13·4	+25·3	30	+19·8	+24·2	+43·0	5·00	12·50
$COMe_2$	−21·5	−26·0	− 54·6	3·85	20	17 days	—	− 6·7	—	52	−10·3	−12·6	−22·3	5·00	21·3
EtOH............	−44·3	−52·0	−109	1·50	20	5 ,,	—	− 4·7	− 6·7	—[8]	−13·5	−15·4	−28·0	5·00	25·70
PhCN............	—	−12·1	—	4·00	20	2 ,,	—	+ 5·9	—	27	—	+21·6	—	2·75	26·5
MeOH	−25·1	−33·0	− 65·3	4·04	20	67 hrs.	—	− 2·0	—	—[9]	− 7·2	− 8·4	−15·3	14·60	33·7
$CH_3{\cdot}CO_2Et$ ...	−26·7	−34·0	− 64·0	3·10	20	48 days	—	− 9·7	−17·0	41	−19·0	−23·7	−41·5	5·00	6·4
Dioxan	− 9·3	−12·7	− 22·6	5·13	20	13 ,,	− 9·3	−12·7	−22·6	0	− 7·2	− 9·2	−17·7	5·20	?
,, ...	,,	,,	,,	,,	95	10 mins.	—	+15·6	—	35[11]	—	—	—	—	

Ester recovered and rotatory power determined, [1] in ether (*c*, 1·14); [2, 3] in CS_2 (*c*, 2·50); [4] gave $[\alpha]_{5461}$ +13·6° in CS_2; [6, 7] gave $[\alpha]_{5461}$ +17·0° in CS_2; [11] gave $[\alpha]_{5461}$ +15·6° in CS_2 (*c*, 5·70); [8, 9] Ethers formed. [10] Esters insoluble in cold *cyclo*hexane.

TABLE V.

Transformation of (—)α-Phenyl-γ-methylallyl Hydrogen Phthalate into (+)γ-Phenyl-α-methylallyl Hydrogen Phthalate at Room Temperature in Carbon Disulphide (l, 2).

Time, hours.	(*c*, 1·5.) α_{5461}.	α_{4358}.	(*c*, 3·0.) α_{5461}.	α_{4358}.	Time, hours.	(*c*, 1·5.) α_{5461}.	α_{4358}.	(*c*, 3·0.) α_{5461}.	α_{4358}.
0	+0·10°	+0·21°	+0·20°	+0·43°	94	+0·47°	+0·86°	+1·00°	+2·01°
19	0·18	0·38	0·39	0·81	111	0·52	0·89	1·12	2·27
43	0·26	0·57	0·59	1·10	163	0·56	1·14	1·18	2·50
67	0·39	0·76	0·90	1·63	212	0·56	1·08	1·18	2·50

TABLE VI.

Influence of Temperature on the Rate of Change of (—)α-Phenyl-γ-methylallyl Hydrogen Phthalate into (+)γ-Phenyl-α-methylallyl Hydrogen Phthalate in Benzene Solution.

At 18°. c, 3·060; l, 2.		At 37°. c, 4·85; l, 2.		At 47°. c, 5·0; l, 2.		At 55°. c, 5·0; l, 2.	
t, hrs.	$\alpha_{5461}^{18^\circ}$.	t, mins.	$\alpha_{5461}^{37^\circ}$.	t, mins.	$\alpha_{5461}^{47^\circ}$.	t, mins.	$\alpha_{5461}^{55^\circ}$.
0	−0·74°	0	−0·88°	0	−0·47°	0	0·0°
19·5	0·43	10	0·85	6	0·42	3	+0·15
72·5	0·12	30	0·72	22	0·26	5	0·21
91·5	+0·02	60	0·57	48	0·02	10	0·35
236	0·16	90	0·47	60	0·00	15	0·46
308	0·20	180	0·15	70	+0·05	20	0·52
		210	0·00	95	0·12	25	0·52
$10^3 k$ = 0·39 (time units in minutes)		5·75		23		115	

The salts of (—)α-phenyl-γ-methylallyl hydrogen phthalate showed far less tendency to undergo isomeric change than did the acid ester. The rotatory power, $[\alpha]_{5461}^{20^\circ}$ + 11·0°, (c, 2·25; l, 2), of a solution of the hydrogen phthalic ester in ether containing ammonia remained unchanged during 9 days, after which the solution became cloudy, making accurate readings difficult: (+)γ-phenyl-α-methylallyl hydrogen phthalate under the same conditions had $[\alpha]_{5461}$ + 44·0° (c, 1·50; l, 2). Similarly, the quinidine salt of the (—)α-phenyl ester remains unchanged for many months, whilst the ester is quite stable in cold pyridine solution (see Table IV).

The relative stability of the hydrogen phthalic ester in pyridine solution is of particular interest because in the preparation of the ester by the action of a pyridine solution of phthalic anhydride on the alcohol it was found that unless the temperature of the reaction was kept below 45° the product consisted almost entirely of γ-phenyl-α-methylallyl hydrogen phthalate. It thus appears that in the course of its preparation the α-phenyl ester passes through a phase which favours its isomeric change.

A similar observation was made with the *p*-xenylurethane of the α-phenyl alcohol, which like the hydrogen phthalic ester readily underwent isomeric change. When (—)α-phenyl-γ-methylallyl alcohol and *p*-xenyl *iso*cyanate were mixed in molecular proportion and heated at 40—45° for 2·5 hours, (+)α-phenyl-γ-methylallyl *p*-xenylurethane with $[\alpha]_{5461}$ + 24·4° in chloroform was obtained. It was maintained molten (120°) for a few minutes, kept in boiling benzene solution for 4 hours, and kept in benzonitrile solution for 14 days at room temperature without its rotatory power, $[\alpha]_{5790}$ + 5·4°, $[\alpha]_{5461}$ + 7·3° (c, 1·30; l, 2), undergoing any change. On the other hand, when the original mixture of (—)alcohol and *iso*cyanate was heated on a steam-bath for ½ hour the solid product consisted entirely of (+)γ-phenyl-α-methylallyl *p*-xenylurethane, which after one crystallisation from benzene had $[\alpha]_{5461}$ + 175·4° in chloroform. Although some dl-*urethane* may have been removed during the crystallisation (the *dl*-urethane is not very soluble in benzene) this reaction is remarkable for the very high proportion, *i.e.*, 87·7%, of optical activity which survived the isomeric change.

The neutral esters of (—)α-phenyl-γ-methylallyl alcohol were more stable than the acid phthalic ester. The *p*-nitrobenzoic esters of the *dl*- and the (—)-alcohol were prepared in a pure condition with little difficulty (compare Burton, *loc. cit.*): the *dl*- and (+)-γ-phenyl-α-methylallyl *p*-nitrobenzoates have already been described (Kenyon, Partridge, and Phillips, *loc. cit.*). A specimen of dl-*α-phenyl-γ-methylallyl* p-*nitrobenzoate* changed but slightly when kept for a year in a closed bottle, and resolidified unchanged after being kept molten for ½ hour. After being kept at 100° for 2·5 hours it solidified immediately when inoculated with a crystal of *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate, the crystalline mass having m. p. 46—48° before recrystallisation, and after recrystallisation m. p. 58—59° either alone or mixed with authentic *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate. The (—)ester after similar treatment was separated by crystallisation into *dl*- and (—)-γ-phenyl-α-methylallyl *p*-nitrobenzoates; the latter ester had $[\alpha]_{5461}$ — 15·7° in chloroform; whereas the optically pure (—)-γ-ester had $[\alpha]_{5461}$ — 33·5° in this solvent. In solution the *p*-nitrobenzoate is more stable than the hydrogen phthalic ester, as is shown by the data given in Table VII.

The acetate of (—)α-phenyl-γ-methylallyl alcohol, prepared by the action of acetic acid-free acetic anhydride on a solution of the (—)α-phenyl alcohol in pyridine, was converted by acetic acid at room temperature into (+)γ-phenyl-α-methylallyl acetate (Kenyon, Partridge, and Phillips, *loc. cit.*), the rotatory power of the solution changing from $[\alpha]_{5461}$ + 3·0° to a maximum value of $[\alpha]_{5461}$ + 28·9° in 17 hours. After 54 hours (+)γ-phenyl-α-methylallyl acetate was isolated from the solution with $\alpha_{5461}^{26\cdot5^\circ}$ + 11·69° (*l*, 0·5), a value which is 14·1% of that of the optically pure (+)γ-phenyl-α-methylallyl acetate.

Stereochemical Aspects of the Anionotropic Changes and Replacement Reactions undergone by (—)*α-Phenyl-γ-methylallyl Alcohol and its Derivatives.*—A summary of the anionotropic changes studied is given in Fig. 1 (p. 214), which includes also reactions in which the anionic groups of the *p*-nitrobenzoic and hydrogen phthalic esters of (—)α-phenyl-γ-methylallyl alcohol were replaced by the anions -OAc and -OMe, by heating the esters with acetic acid and methyl alcohol respectively. From this scheme it will be seen that if the relative configurations of (+)phenyl-*n*-propyl- and (—)β-phenylethylmethyl-carbinols were known, it would be possible to deduce which of these changes were accompanied by inversion and which took place without configurative changes.

The relative configurations of these two alcohols can be decided from data already published if use is made of generalisations which have emerged from studies with optically active compounds. These include the experimental results of Pickard and Kenyon (J., 1911, **99**, 45, *et seq.*) on the determination of the rotatory powers of homologous series of alcohols and their esters, the work of Clough (J., 1918, **113**, 536, *et seq.*) showing that the rotatory powers of compounds of similar configuration are in general influenced similarly by changes in external conditions, and the investigations of Rule (J., 1924, **125**, 1121, *et seq.*) on the influence of the polarity of the substituent, X, on the magnitude of the rotatory powers of compounds of the series RX. From these investigations it can be concluded that the rotatory powers of the series of alcohols, Ph·CH(OH)·R, in which R is a lengthening alkyl chain, and also of the series, Me·CH(OH)·R, in which R contains a phenyl group becoming separated from the asymmetric carbon atom by an increasing number of methylene groups, should alter in a regular manner. The experimentally determined rotatory powers of some of the alcohols belonging to these two series both in the homogeneous state and also in benzene solution for light of three different wave-lengths are given in Table VIII.

TABLE VII.

Transformation of (—)*α-Phenyl-γ-methylallyl* p-*Nitrobenzoate into* (—)*γ-Phenyl-α-methylallyl* p-*Nitrobenzoate.*

				Initial values.			Final values.		
Solvent.	*t*.	Time.	*c*.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
C_6H_6 *	82°	3·5 hrs.	4·0	−39·7°	−44·0°	—	−30·0°	−36·0°	—
$CHCl_3$ †	15—20	3 months	4·6	−39·4	−45·0	−83·4°	0·0	0·0	0·0°
C_5H_5N	15	2 ,,	2·7	−46·3	−51·9	—	−46·3	−51·9	—
Et_2O	15	2 ,,	3·6	−34·0	−38·9	−73·6	−34·0	−38·9	−73·6
Et_2O + 1 drop conc. HCl.........	15	2 days	3·6	−34·0	−38·9	−73·6	−29·4	−34·0	—

* The recovered ester remained liquid.

† The recovered ester had m. p. 46—50° and was mainly *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate.

It will be seen that the rotatory powers of the (+)alcohols of the second series (1, 4, and 5) steadily decrease in magnitude both in the homogeneous state and in benzene solution. The decrease in the rotatory powers of the first series (1, 2, and 3) is not so regular, (+)phenylethylcarbinol, the middle member of the series, having slightly lower rotatory powers than either phenylmethyl- or phenyl-*n*-propyl-carbinol. This small irregularity is not serious, however, since the lack of simplicity in the rotatory dispersive powers of these alcohols makes a comparison under strictly comparable conditions difficult. (+)Phenylmethylcarbinol thus appears to be configuratively related to the alcohols of both series, and hence all the five alcohols have the same configuration. Confirmation of this conclusion is afforded by a comparison of the temperature–rotation curves of these alcohols (Pickard and

Kenyon; Kenyon and Partridge, *locc. cit.*). All five alcohols give temperature–rotation curves which tend to be concave to the temperature axis.

TABLE VIII.

The Specific Rotatory Powers of Related Semiaromatic Alcohols.

	$[\alpha]_\lambda^{40^\circ}$. Homogeneous state. λ.			$[\alpha]_\lambda^{17-20^\circ}$. In benzene ($c$, 5·00). λ.		
	5893.	5461.	4358.	5893.	5461.	4358.
1. Ph·CH(OH)Me *	+41·51°	+49·46°	+85·92°	+48·88°	+57·93°	+99·22°
2. Ph·CH(OH)·CH$_2$Me *	+30·24	+36·02	+60·49	+40·05	+47·78	+79·16
3. Ph·CH(OH)·CH$_2$Et †	—	+36·58	+63·00	+43·60	+52·20	+87·30
4. CH$_2$Ph·CH(OH)Me *	+27·58	+33·43	+61·22	+41·82	+50·82	+93·58
5. CH$_2$Ph·CH$_2$·CH(OH)Me *	+14·74	+17·46	+29·28	+19·41	+25·45	+42·79

* Pickard and Kenyon, J., 1914, **105**, 1110.

† From data given by Kenyon and Partridge, J., 1936, 128.

From these considerations it follows that (+)phenyl-*n*-propylcarbinol has the same configuration as (+)β-phenylethylmethylcarbinol, and since the two unsaturated alcohols were reduced by the same method, it can be concluded that (—)α-phenyl-γ-methylallyl alcohol has a configuration opposite to that of (+)γ-phenyl-α-methylallyl alcohol. Hence the new asymmetric centre produced by the isomeric change of (—)α-phenyl-γ-methylallyl alcohol has the opposite configuration to the asymmetric centre which is destroyed.

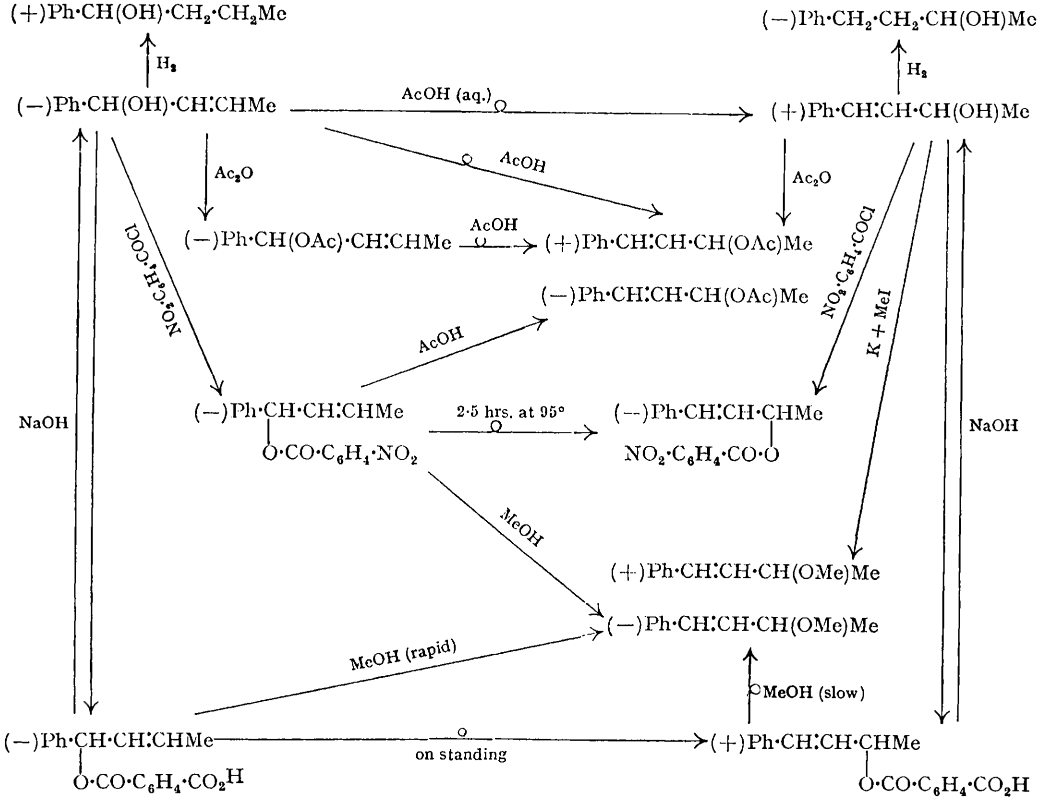
Furthermore, since the hydrogen phthalic, acetic, and *p*-nitrobenzoic esters are produced from the unsaturated alcohols by methods unlikely to lead to configurative change, the isomeric change of these esters of the α-phenyl alcohol into the corresponding esters of the γ-phenyl alcohol is accompanied by inversion of configuration.

Other conclusions can be drawn concerning the stereochemical changes which occur during reactions given in the scheme. For example, it can be assumed that the (+)*γ-phenyl-α-methylallyl methyl ether* produced from the potassio-derivative of the (+)alcohol by the action of methyl iodide possesses the same configuration as the parent (+)alcohol and also its (+)hydrogen phthalic ester. The (—)γ-phenyl-α-methylallyl methyl ether *slowly* produced when the (+)hydrogen phthalic ester was warmed with methyl alcohol arose, therefore, with inversion of configuration. On the other hand, if, as suggested, (—)α-phenyl-γ-methylallyl hydrogen phthalate and (—)α-phenyl-γ-methylallyl *p*-nitrobenzoate have a configuration opposite to that of (+)γ-phenyl-α-methylallyl hydrogen phthalate and (—)γ-phenyl-α-methylallyl *p*-nitrobenzoate, then they must have the same configuration as (—)γ-phenyl-α-methylallyl methyl ether. Hence both these esters undergo anionic replacement without the occurrence of inversion of configuration. It is also noteworthy that both these esters react *rapidly* with methyl alcohol: the anionic replacements are unlikely therefore to have been preceded by isomeric change, since the corresponding γ-phenyl esters react *slowly* with methyl alcohol.

The proposed configurational relationships between the compounds produced as indicated in Fig. 1 fit in with a relatively simple picture of the reaction mechanism. This is provided by assuming that the (—)α-phenyl-γ-methylallyl esters adopt a pseudo-cyclic configuration (see Fig. 2), in which the *cis*-form predominates. The arrangement of the groups around the γ-carbon atom will then be favourable to the adoption of a (+)configuration, *i.e.*, opposite to that of the α-asymmetric carbon atom, when the anion migrates.

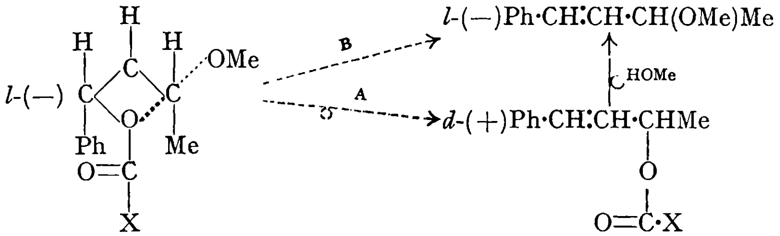
Isomerisation involves, then, the establishment of a link between the carboxyl oxygen atom and the γ-carbon atom, as indicated by the broken line; complete migration of the anion involves inversion of configuration. Anionic migration may be forestalled, however, by union of the γ-carbon atom with an external anion, *e.g.*, –OMe. When this occurs, as indicated by the dotted line, the new asymmetric centre acquires the same configuration as that previously possessed by the α-carbon atom. On the other hand, when the internal anion is attached to the γ-carbon atom and shows no tendency to migrate, but can nevertheless undergo displacement by an external anion, as when (+)γ-phenyl-α-methylallyl hydrogen phthalate is converted into (+)γ-phenyl-α-methylallyl methyl ether, then a Walden inversion occurs as in most other simple anionic replacement reactions.

FIG. 1.



In view of the fact that this picture of the space-mechanism of the isomerism and of the replacement reaction assumes the proximity of the ester-oxygen atom and the γ-carbon atom, it is of interest that α-phenyl-γ-methylallyl alcohol has a low parachor (360·6), whilst the parachor of γ-phenyl-α-methylallyl alcohol (367·4) is nearer the calculated value, which is 372·1 according to the constants of Sugden ("The Parachor and Valency," p. 38), or 368·2 according to those of Mumford and (J. W. C.) Phillips (J., 1929, 2113).

FIG. 2.



X = $-C_6H_4{\cdot}CO_2H$(*o*-) or $-C_6H_4{\cdot}NO_2$(*p*-)

(*l*- and *d*- denote configurations.)

If such a pseudo-cyclic configuration is adopted by anionotropic systems prior to anion migration, then a mechanism is provided by which an external anion can become attached to the γ-carbon atom of α-phenyl-γ-methylallyl alcohol without postulating the occurrence of complete ionic dissociation prior to isomeric change. This is a modification of the views of Burton (*loc. cit.*), who assumed that the formation of cinnamyl acetate resulting from the action of tetramethylammonium acetate on α-phenylallyl *p*-nitrobenzoate in acetic anhydride indicated that ionic dissociation proceeded sufficiently far to permit of direct competition between the internal and external anions for the electromeric cation. Our interpretation would, however, appear to be more in accord with the conclusions reached by Hsü, Ingold, and Wilson (J., 1935, 1778), from their studies of prototropic systems, namely, that the ionisation products of the system do not become kinetically free to such a degree as to allow of asymmetry being destroyed.

EXPERIMENTAL.

The phenylurethane of *dl*-α-phenyl-γ-methylallyl alcohol (b. p. 121—122°/12 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5525; Burton, *loc. cit.*) failed to crystallise, but its p-*xenylurethane* (0·8 g.), prepared by warming together for 2·5 hours at 40—45° *p*-xenyl *iso*cyanate (1 g.) and the alcohol (0·7 g.), separated from light petroleum and ether in radiating clusters of prismatic needles, m. p. 124° (Found : N, 4·25. $C_{23}H_{21}O_2N$ requires N, 4·1%).

dl-α-*Phenyl-γ-methylallyl* p-*nitrobenzoate* (20 g.), prepared by the interaction of the alcohol (14·8 g.) and *p*-nitrobenzoyl chloride (18·8 g.) in the presence of pyridine (10 g.), crystallised from a mixture of ether and light petroleum in radiating clusters of almost colourless, prismatic needles, m. p. 99° (Found : N, 4·8. $C_{17}H_{15}O_4N$ requires N, 4·7%). Mixed with *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate (m. p. 58—59°), it melts very indefinitely at 45—75°. dl-α-*Phenyl-γ-methylallyl acetate* (6·8 g.), b. p. 135—136°/21·5 mm., $n_{\mathrm{D}}^{25^\circ}$ 1·5087 (Found : C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), was readily obtained by the action of acetic anhydride (5·4 g., freed from acetic acid by Meisenheimer and Beutter's method, *Annalen*, 1934, **508**, 70) on a warm mixture of the alcohol (6·0 g.) and pyridine (5·0 g.).

dl-α-*Phenyl-γ-methylallyl hydrogen phthalate.* A solution of phthalic anhydride (30 g.) in hot pyridine (60 g.) was rapidly cooled and mixed with *dl*-α-phenyl-γ-methylallyl alcohol (30 g.); the resultant mixture was maintained at 40—45° for 2 hours and occasionally shaken. The homogeneous liquid was dissolved in ether and washed repeatedly with ice-cold dilute hydrochloric acid. When most of the ether had been removed by the aqueous acid, the hydrogen phthalic ester began to crystallise. On addition of a large volume of cold water, followed by vigorous shaking, it separated completely as small granules. These were finely triturated with cold dilute hydrochloric acid, filtered, washed with water, and dried in a vacuum, m. p. 77—79°; yield 54 g. dl-α-*Phenyl-γ-methylallyl hydrogen phthalate* separated from a mixture of ether and light petroleum in small needles, m. p. 93—94° (Found : C, 72·65; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%); mixed with *dl*-γ-phenyl-α-methylallyl hydrogen phthalate, it softened and melted at 92—94°. When saponified with alcoholic sodium hydroxide, the alcohol obtained distilled sharply at 119—120°/9·5 mm., and since it could not be induced to solidify, was relatively free from γ-phenyl-α-methylallyl alcohol (m. p. 33°). Very little transformation of the hydrogen phthalic ester to γ-phenyl-α-methylallyl hydrogen phthalate could therefore have occurred during either its preparation or saponification.

If, during the preparation of the ester, the precautions described above, particularly the avoidance of high temperature, were not taken, the product was not homogeneous. When a mixture of alcohol, phthalic anhydride, and pyridine was heated on the steam-bath for an hour complete transformation occurred, and the product consisted of the isomeric *dl*-γ-phenyl-α-methylallyl hydrogen phthalate, m. p. and mixed m. p. 92—94°, giving *dl*-γ-phenyl-α-methylallyl alcohol, m. p. 30—31·5°, when saponified.

Quinidine Salt of (—)α-*Phenyl-γ-methylallyl Hydrogen Phthalate.*—When quinidine (24 g.) was dissolved in a cold solution of *dl*-α-phenyl-γ-methylallyl hydrogen phthalate (22 g.) in methyl acetate (300 c.c.), a bulky mass of asbestos-like crystals separated immediately. These, after recrystallisation from methyl acetate (2300 c.c.), consisted of the optically pure quinidine salt of (—)α-phenyl-γ-methylallyl hydrogen phthalate (18·5 g.), m. p. 146—147° (decomp.).

Quinidine Salt of (+)α-*Phenyl-γ-methylallyl Hydrogen Phthalate.*—The filtrate from the quinidine salt, described above, after removal of the solvent yielded a gum (16 g.), which dissolved readily in hot acetone (60 c.c.). After cooling, this solution deposited bulky clusters of silky needles which, when recrystallised from acetone (60 c.c.), gave the quinidine salt of (+)α-phenyl-γ-methylallyl hydrogen phthalate (4·3 g.), m. p. 133—134° (decomp.).

(—)α-*Phenyl-γ-methylallyl Hydrogen Phthalate.*—The quinidine salt of m. p. 146—147° (62 g.), mixed with acetone (150 c.c.), was decomposed with ice-cold dilute hydrochloric acid, and the liberated hydrogen phthalic ester precipitated by addition of water and extracted with ether. The dried ethereal solution, mixed with warm light petroleum, deposited (−)α-phenyl-γ-methylallyl hydrogen phthalate as rosettes of long, fine, glistening needles (23 g.), m. p. 81—82°.

(+)*α-Phenyl-γ-methylallyl Hydrogen Phthalate.*—The quinidine salt of m. p. 133—134° (4·3 g.), when decomposed by the method described in the preceding paragraph, yielded (+)α-phenyl-γ-methylallyl hydrogen phthalate (1·75 g.), glistening needles, m. p. 80—81°.

(−)α-Phenyl-γ-methylallyl alcohol was obtained by adding (−)α-phenyl-γ-methylallyl hydrogen phthalate (19 g.) to a hot solution of sodium hydroxide (6·5 g.) in alcohol (300 c.c.) and then passing steam through the mixture. The steam-distillate (900 c.c.) on extraction yielded (−)α-phenyl-γ-methylallyl alcohol (8·5 g.), b. p. 126°/20 mm., $n_D^{20^\circ}$ 1·5525. Its *p*-xenylurethane, hairy needles, m. p. 120°, from methylene chloride and light petroleum, has $[\alpha]_{5893}$ + 20·0°, $[\alpha]_{5790}$ + 22·6°, $[\alpha]_{5461}$ + 24·4°, $[\alpha]_{4358}$ + 58·2° (*c*, 2·25; *l*, 2) in chloroform. When saponification was effected by a slight excess of aqueous 5*N*-sodium hydroxide, however, the liberated alcohol was a mixture, b. p. 122—128·5°/11 mm., from which by fractional distillation (+)γ-phenyl-α-methylallyl alcohol, m. p. 31°, $\alpha_{5461}^{20^\circ}$ + 0·35° (*l*, 0·25), was isolated. Similarly, when aqueous alcoholic sodium carbonate was used, the liberated alcohols were separated by distillation into : (i) b. p. 119—121·5°/11 mm., $\alpha_{5461}^{20^\circ}$ − 4·35° (*l*, 0·25), (ii) b. p. 128—129°/10 mm., $\alpha_{5461}^{20^\circ}$ − 2·14° (*l*, 0·25). Fraction (ii), when inoculated with *dl*-γ-phenyl-α-methylallyl alcohol, deposited crystals of (+)γ-phenyl-α-methylallyl alcohol, m. p. 33—34°, $[\alpha]_{5461}$ + 2·2° (*c*, 4·6; *l*, 2) in pyridine solution.

(−)*α-Phenyl-γ-methylallyl acetate*, b. p. 134—135°/20 mm., $n_D^{26\cdot5^\circ}$ 1·5064, $d_{4^\circ}^{22\cdot5^\circ}$ 1·016, $\alpha_{5893}^{23^\circ}$ − 0·34°, $\alpha_{5461}^{23^\circ}$ − 0·41°, $\alpha_{4358}^{23^\circ}$ − 1·23° (*l*, 0·25), was prepared by warming at 60—70° for an hour a mixture of the (−)alcohol ($\alpha_{5461}^{20^\circ}$ − 33·59°; *l*, 0·5; 3 g.), acetic acid-free acetic anhydride (2·7 g.), and pyridine (2·5 g.) (Found: C, 75·5; H, 7·8. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

(−)*α-Phenyl-γ-methylallyl* p-*Nitrobenzoate.*—A solution of *p*-nitrobenzoyl chloride (4 g.) in chloroform (15 c.c.) was added dropwise to a mixture of the (−)alcohol (3 g.) and pyridine (2 g.). The reaction mixture, which became warm, was left for 24 hours; the resulting *p*-nitrobenzoic ester was an oil, the rotatory powers of which are in Table VII.

Transformation of (−)*α-Phenyl-γ-methylallyl Alcohol into* (+)*γ-Phenyl-α-methylallyl Alcohol.*—A solution of (−)α-phenyl-γ-methylallyl alcohol (1·5 c.c.; $\alpha_{5461}^{20^\circ}$ − 14·98°, *l*, 0·25) in 0·5% aqueous acetic acid (500 c.c.) after standing 40 hours at room temperature was rendered slightly alkaline and extracted with ether. The dried extract yielded (+)γ-phenyl-α-methylallyl alcohol, b. p. 140°/20 mm., which crystallised immediately when inoculated with an authentic specimen, m. p. 33°, α_{5893} + 0·51°, α_{5461} + 0·69°, α_{4358} + 1·36° (*l*, 0·5).

Freshly distilled *dl*-α-phenyl-γ-methylallyl alcohol, b. p. 125—126°/15 mm. (5 g.), was shaken for 15 hours with 20% aqueous acetic acid (50 c.c.) and worked up as described in the preceding paragraph. The resulting product distilled completely at 136—138°/16 mm. and, when inoculated with *dl*-γ-phenyl-α-methylallyl alcohol, set to a crystalline mass, m. p. 28—29°. Its *p*-xenylurethane (prepared below 65°), small needles from benzene, had m. p. 162—163° alone or mixed with an authentic specimen.

Conversion of Derivatives of α-Phenyl-γ-methylallyl Alcohol into Derivatives of γ-Phenyl-α-methylallyl Alcohol.—*Conversion of* dl-*α-phenyl-γ-methylallyl acetate into* dl-*γ-phenyl-α-methylallyl acetate.* (*a*) The acetate, b. p. 123°/11 mm. (5 g.), and acetic anhydride (7·5 g.) were heated together on the steam-bath for 10 hours and then distilled. After removal of acetic anhydride, the main portion distilled at 132—133°/9 mm.; this product (2·5 c.c.) was heated under reflux for 1·5 hours with aqueous-alcoholic sodium hydroxide and subsequently removed in a current of steam. The volatile material, b. p. 123—124°/8·5 mm., crystallised completely when inoculated with *dl*-γ-phenyl-α-methylallyl alcohol and had m. p. 30—31°. (*b*) The acetate (5 g.) was heated with glacial acetic acid (5 g.) on the steam-bath for 2 hours; the main portion (3·5 g.) then had b. p. 133—134°/10 mm., and after saponification (as above) yielded *dl*-γ-phenyl-α-methylallyl alcohol (2 c.c.), b. p. 125—126°/9·5 mm., m. p. 30—31°.

Conversion of (−)*α-phenyl-γ-methylallyl acetate into* (+)*γ-phenyl-α-methylallyl acetate.* The (−)acetate, $\alpha_{5461}^{23^\circ}$ − 0·41° (*l*, 0·25), was dissolved in pure acetic acid, and the freshly prepared solution had $[\alpha]_{5893}$ + 2·6°, $[\alpha]_{5461}$ + 3·0°, $[\alpha]_{4358}$ + 4·2° (*c*, 5·10; *l*, 2). After this solution had stood for 17 hours at room temperature, its rotatory powers had changed to $[\alpha]_{5893}$ + 25·5°, $[\alpha]_{5461}$ + 28·9°, $[\alpha]_{4358}$ + 56·8°—values which remained unchanged after an additional 45 hours' standing. The isomeric (+)γ-phenyl-α-methylallyl acetate, prepared from (+)γ-phenyl-α-methylallyl alcohol (Kenyon, Partridge, and Phillips, J., 1936, 85), has $[\alpha]_{5893}$ + 145·0°, $[\alpha]_{5461}$ + 166·0°, $[\alpha]_{4358}$ + 321° (*c*, 1·12; *l*, 2) in acetic acid solution; hence the acetate formed by isomeric change of (−)α-phenyl-γ-methylallyl acetate in acetic acid possesses a rotatory power 17·2% of that of optically pure (+)γ-phenyl-α-methylallyl acetate. After removal of acetic acid the residual (+)γ-phenyl-α-methylallyl acetate had b. p. 150—151°/22 mm., $n_D^{26\cdot5^\circ}$ 1·525 and $\alpha_{5461}^{26\cdot5^\circ}$ + 11·69°, $\alpha_{4358}^{26\cdot5^\circ}$ + 22·86° (*l*, 0·5). The value $\alpha_{5461}^{26\cdot5^\circ}$ + 11·69° is 14·1% of that of optically pure (+)γ-phenyl-α-methylallyl acetate.

Conversion of (—)*α-phenyl-γ-methylallyl alcohol into* (+)*γ-phenyl-α-methylallyl acetate.* A mixture of (—)α-phenyl-γ-methylallyl alcohol (3 g.; $\alpha_{5461}^{20^\circ}$ — 14·98°; *l*, 0·25) and acetic acid (10 g.) after 4 days' standing at room temperature yielded (+)γ-phenyl-α-methylallyl acetate, b. p. 151°/24 mm., $\alpha_{5461}^{20^\circ}$ + 1·74°, $\alpha_{4358}^{20^\circ}$ + 3·6° (*l*, 0·5).

Conversion of (+)*α-phenyl-γ-methylallyl alcohol into* (—)*γ-phenyl-α-methylallyl acetate.* A specimen of optically impure (+)α-phenyl-γ-methylallyl alcohol ($\alpha_{5461}^{18^\circ}$ + 4·47°; *l*, 0·25; $n_D^{20^\circ}$ 1·5525), mixed with an equal weight of pure acetic anhydride, was heated on the steam-bath for 6·5 hours and then distilled. The main fraction had b. p. 136—138°/15 mm. and $\alpha_{5461}^{18^\circ}$ — 3·26°, $\alpha_{4358}^{18^\circ}$ — 6·25° (*l*, 0·25), $n_D^{20^\circ}$ 1·5324, and was accordingly partially racemised (see above) (—)γ-phenyl-α-methylallyl acetate. That the loss of optical activity was not due to the action of acetic anhydride on the (—)γ-phenyl-α-methylallyl acetate produced was proved by heating a specimen of this acetate (with $\alpha_{5461}^{17^\circ}$ — 9·88°; *l*, 0·5) with an equal weight of acetic anhydride for 8·5 hours on the steam-bath; when recovered it had $\alpha_{5461}^{15\cdot5^\circ}$ — 10·52° (*l*, 0·5), $n_D^{15\cdot5^\circ}$ 1·5310.

Transformation of α-Phenyl-γ-methylallyl p-*Nitrobenzoate into γ-Phenyl-α-methylallyl* p-*Nitrobenzoate.* (a) *In the homogeneous state.* A specimen of *dl*-α-phenyl-γ-methylallyl *p*-nitrobenzoate, m. p. 99°, after keeping in a closed vessel for a year had m. p. 96—97°; the amount of impurity (γ-phenyl-α-methylallyl *p*-nitrobenzoate ?) present was insufficient for separation by fractional crystallisation. The recrystallised ester after being kept molten for ½ hour resolidified unchanged to a crystalline mass, m. p. 98—99°; when, however, the molten material was kept at 100° for 2·5 hours, the cooled liquid did not solidify when inoculated with the original material but did so immediately when inoculated with *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate and had m. p. 46—48°; after recrystallisation from ether and light petroleum, it had m. p. 58—59° alone or admixed with authentic *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate.

(—)α-Phenyl-γ-methylallyl *p*-nitrobenzoate, after being kept at 100° for 2·5 hours, readily solidified on cooling and then had $[\alpha]_{5461}$ — 14·0°, $[\alpha]_{4358}$ — 33·7° (*c*, 3·65; *l*, 2) in chloroform. Crystallisation resolved this material into two fractions: (i) m. p. 50—52°, which when mixed with *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate (m. p. 58°) melted at 57—58°, and (ii) a more soluble portion, m. p. 45°, which when mixed with (—)γ-phenyl-α-methylallyl *p*-nitrobenzoate (m. p. 41°) melted at 42—44°, and had $[\alpha]_{5790}$ — 13·8°, $[\alpha]_{5461}$ — 15·7°, $[\alpha]_{4358}$ — 38·5° (*c*, 1·07; *l*, 2) in chloroform. Optically pure (—)γ-phenyl-α-methylallyl *p*-nitrobenzoate has $[\alpha]_{5790}$ — 27·52°, $[\alpha]_{5461}$ — 33·48°, $[\alpha]_{4358}$ — 87·4° (*c*, 5·00; *l*, 2) in chloroform.

(b) *In solution.* By heating *dl*-α-phenyl-γ-methylallyl *p*-nitrobenzoate with 1·5 times its weight of acetic anhydride for 6 hours (3·5 hours were insufficient) on the steam-bath, it was converted into *dl*-γ-phenyl-α-methylallyl *p*-nitrobenzoate, m. p. and mixed m. p. 57—58°. About 5% of *p*-nitrobenzoic acid was isolated from the reaction mixture. Other data are recorded in Table VII.

Transformation of α-Phenyl-γ-methylallyl Hydrogen Phthalate into γ-Phenyl-α-methylallyl Hydrogen Phthalate.—*dl*-α-Phenyl-γ-methylallyl hydrogen phthalate was heated with an equal weight of pyridine on the steam-bath for an hour and the cooled solution mixed with cold dilute hydrochloric acid. The liberated oil soon crystallised, m. p. 94—95°, either alone or admixed with authentic *dl*-γ-phenyl-α-methylallyl hydrogen phthalate; it crystallised from carbon disulphide and light petroleum in characteristic, large, glassy rhombs, and on saponification gave *dl*-γ-phenyl-α-methylallyl alcohol, m. p. 30—31°.

Preparation of (+)*γ-Phenyl-α-methylallyl Methyl Ether by a Method unlikely to lead to Inversion of Configuration.*—Potassium (3·9 g.) was dissolved in an ethereal solution of (optically impure) (+)γ-phenyl-α-methylallyl alcohol, $[\alpha]_{5893}$ + 10·7° in carbon disulphide, and the resulting solution mixed with methyl iodide (14·5 g.) and gently warmed. The resulting (+)*γ-phenyl-α-methylallyl methyl ether* (1·5 g.) had b. p. 102—103°/10·5 mm., $\alpha_{5893}^{18^\circ}$ + 6·61°, $\alpha_{5461}^{18^\circ}$ + 7·92°, $\alpha_{4358}^{18^\circ}$ + 13·93° (*l*, 0·25), $n_D^{18^\circ}$ 1·5327. (Found: C, 82·0; H, 9·0. $C_{11}H_{14}O$ requires C, 81·5; H, 9·0%). Attempts to prepare the isomeric methyl ether from α-phenyl-γ-methylallyl alcohol by a similar procedure were unsuccessful.

Conversion of (+)*γ-Phenyl-α-methylallyl Hydrogen Phthalate into* (—)*γ-Phenyl-α-methylallyl Ethyl Ether.*—(+)γ-Phenyl-α-methylallyl hydrogen phthalate (14·90 g.), made up to 100 c.c. with absolute ethyl alcohol, had $[\alpha]_{5893}$ — 12·3°, $[\alpha]_{5790}$ — 12·9°, $[\alpha]_{5461}$ — 14·7°, $[\alpha]_{4358}$ — 28·2° (*c*, 14·9; *l*, 2), and after 24 days' keeping at room temperature, $[\alpha]_{5461}$ — 14·1°. After 9 months' keeping at 25° the rotatory power had reached the constant value $[\alpha]_{5461}$ — 1·5°, the half-life period being about 60 days. This solution yielded (—)*γ-phenyl-α-methyllalyl ethyl ether* (7 g.),

b. p. 114°/11 mm., $n_D^{17°}$ 1·5262, $\alpha^{18°}_{5893}$ $-$ 2·20°, $\alpha^{18°}_{5461}$ $-$ 2·50° (*l*, 2) (Found : C, 82·1; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

Conversion of (+)*γ-Phenyl-α-methylallyl Hydrogen Phthalate into* (—)*γ-Phenyl-α-methylallyl Methyl Ether*.—The hydrogen phthalate (14·60 g.), made up to 100 c.c. with methyl alcohol (distilled from calcium), had $[\alpha]_{5893}$ $-$ 7·2°, $[\alpha]_{5790}$ $-$ 7·4°, $[\alpha]_{5461}$ $-$ 8·4°, $[\alpha]_{4358}$ $-$ 15·3° (*c*, 14·6; *l*, 2), and after being kept for 30 days at room temperature, $[\alpha]_{5461}$ $-$ 6·3°. After a further 3 months the constant value $[\alpha]_{5461}$ $-$ 72° was reached, half-life period about 34 days, and from the solution, which contained no unchanged hydrogen phthalic ester, (—)γ-phenyl-α-methylallyl methyl ether (7·5 g.), b. p. 124°/25 mm., $n_D^{17°}$ 1·5337, $\alpha^{24°}_{5893}$ $-$ 0·34°, $\alpha^{24°}_{5461}$ $-$ 0·38°, α_{4358} $-$ 0·59° (*l*, 0·25), was isolated. A second experiment showed that when the original solution was heated under reflux, the reaction was complete in 30 minutes, the resulting methyl ether having b. p. 103°/10 mm., $\alpha^{18°}_{5893}$ $-$ 0·48° (*l*, 0·5), $n_D^{19°}$ 1·5325.

Conversion of (—)*α-Phenyl-γ-methylallyl Hydrogen Phthalate into* (—)*γ-Phenyl-α-methylallyl Methyl Ether*.—A solution of (—)α-phenyl-γ-methylallyl hydrogen phthalate in methyl alcohol (freshly distilled from calcium) (*c*, 5·292; *l*, 2) gave the following changes in rotatory power (all negative) on standing at room temperature.

Time, mins.	0	20	45	70	165	260	320	480	1660	3 days
α_{5893}	2·51°	—	2·31°	2·23°	—	—	—	0·72°	0·17°	—
α_{5790}	2·67°	—	2·43°	—	1·44°	1·38°	1·10°	0·75°	—	0·10°
α_{5461}	3·05°	2·95°	2·81°	2·72°	1·66°	1·51°	1·20°	0·85°	0·19°	0·12°
α_{4358}	6·20°	—	5·67°	—	3·92°	3·00°	2·57°	1·72°	0·37°	0·35°

After evaporation of the solvent, there were obtained phthalic acid and (—)γ-phenyl-α-methylallyl methyl ether, b. p. 118°/20 mm., $\alpha^{20°}_{5790}$ $-$ 0·12°, $\alpha^{20°}_{5461}$ $-$ 0·20°, $\alpha^{20°}_{4358}$ $-$ 0·25° (*l*, 0·25), $n_D^{20°}$ 1·5322.

Transformations of (—)*α-Phenyl-γ-methylallyl* p-*Nitrobenzoate*.—(a) *Into* (—)*γ-phenyl-α-methylallyl acetate by the action of acetic acid at ordinary temperature.* A solution of (—)α-phenyl-γ-methylallyl *p*-nitrobenzoate in glacial acetic acid had $[\alpha]_{5790}$ $-$ 41·1°, $[\alpha]_{5461}$ $-$ 46·7°, $[\alpha]_{4358}$ $-$ 93·2° (*c*, 4·45; *l*, 2) when freshly prepared and, after standing for 24 hours at room temperature, the constant values $[\alpha]_{5790}$ $-$ 7·1°, $[\alpha]_{5461}$ $-$ 7·5°, $[\alpha]_{4358}$ $-$ 18·4°. From a parallel experiment using a larger amount (4 g.) of the *dl*-*p*-nitrobenzoate there was isolated *dl*-γ-phenyl-α-methylallyl acetate (1·5 g.), b. p. 147°/18 mm., $n_D^{19°}$ 1·534. Since optically pure (—)γ-phenyl-α-methylallyl acetate has $[\alpha]_{5461}$ $-$ 166° in acetic acid (*c*, 1·12; *l*, 2), it follows that the replacement of the *p*-nitrobenzoyl group by the acetyl group has been effected with the maintenance of some 4·5% of the optical activity of the new ester.

(b) *Into* (—)*γ-phenyl-α-methylallyl methyl ether by the action of methyl alcohol at ordinary temperature.* A solution of (—)α-phenyl-γ-methylallyl *p*-nitrobenzoate in methyl alcohol had $[\alpha]_{5790}$ $-$ 40·25°, $[\alpha]_{5461}$ $-$ 47·0°, $[\alpha]_{4358}$ $-$ 90·3° (*c*, 2·20; *l*, 2) when freshly prepared; after 6 days' standing the constant value $[\alpha]_{5461}$ $-$ 5·23° was reached. From a parallel experiment using the *dl*-*p*-nitrobenzoate (5 g.) there were isolated *p*-nitrobenzoic acid (2·5 g.) and *dl*-γ-phenyl-α-methylallyl methyl ether (2·0 g.), b. p. 112°/15 mm., $n_D^{22°}$ 1·5321.

Conversion of (—)*α-Phenyl-γ-methylallyl Alcohol into* (+)*γ-Phenyl-α-methylallyl* p-*Xenylurethane*.—A mixture of (—)α-phenyl-γ-methylallyl alcohol (0·7 g.) and *p*-xenyl *iso*cyanate (1 g.) was heated on the steam-bath for ½ hour. The resulting product, when crystallised from benzene, gave rosettes of hairy needles, (0·8 g.), $[\alpha]_{5790}$ + 147·6°, $[\alpha]_{5461}$ + 175·4°, $[\alpha]_{4358}$ + 369° (*c*, 2·25; *l*, 2) in chloroform, m. p. 176°; mixed with optically pure (+)γ-phenyl-α-methylallyl *p*-xenylurethane (m. p. 180°; $[\alpha]_{5461}$ + 200°, in chloroform) it melts at 182°.

Thanks are due to Mr. B. C. Platt for assistance in the preparation of the racemic alcohols, and also to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries, Ltd., for grants.

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