348. *The* d- *and* l-α-*Phenylallyl Alcohols and Some of their Reactions.*

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dl-α-Phenylallyl alcohol has been separated into its optically active forms by the fractional crystallisation of the quinidine salt of its hydrogen phthalate. A comparison of the reactivities of this alcohol and some of its carboxylic esters with those of α-phenyl-γ-methylallyl alcohol and its corresponding esters shows that the latter compounds undergo anionotropic changes far more readily than the former. This enhanced reactivity must be ascribed to the influence of the γ-methyl group.

IT has been found (Kenyon, Partridge, and Phillips, J., 1937, 207) that (—)-α-phenyl-γ-methylallyl hydrogen phthalate (I) is readily rearranged into (+)-γ-phenyl-α-methylallyl hydrogen phthalate (II) with a large retention of optical activity; further, that (—)-α-phenyl-γ-methylallyl alcohol and its esters readily undergo replacement reactions during which a similar rearrangement occurs although the retention of optical activity is of a lower order.

In discussing the mechanism of these and other replacement reactions in substituted allyl compounds, Arcus and Kenyon (J., 1938, 1912) concluded that a γ-methyl group contributes an inductive effect favourable to liberation of an anion in these compounds:

$$\mathrm{Me}\rightarrow\mathrm{CH{:}\overset{\curvearrowright}{CH}{-}CHR{-}\overset{\curvearrowright}{X}}.$$

$$\text{(I.)}\quad \mathrm{CHPhX{\cdot}CH{:}CHMe} \longrightarrow \mathrm{CHPh{:}CH{\cdot}CHMeX} \quad \text{(II.)}$$

$$(\mathrm{X} = {\cdot}\mathrm{O{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H})$$

In order to obtain comparative evidence of the influence exerted by the methyl group in (I), the optically active forms of α-phenylallyl alcohol have been prepared, and the behaviour of this compound and some of its derivatives examined.

Kamai (*J. Gen. Chem. Russ.*, 1931, **1**, 460) was unable to convert α-phenylallyl alcohol into its hydrogen phthalate, obtaining instead the isomeric γ-phenylallyl ester. As is shown in the experimental part, the former *compound* can be obtained in yields of over 90% when the combination of the alcohol and phthalic anhydride is allowed to take place at moderately low temperatures in pyridine solution. By fractional crystallisation from acetone its quinidine salt can be readily separated into the *quinidine* salts of the optically pure *d*- and *l*-α-phenylallyl hydrogen phthalates. The liberated *d*- and *l*-hydrogen phthalates when hydrolysed yield *d*-* and *l*-α-phenylallyl alcohols respectively. *l*-α-Phenylallyl alcohol is readily reduced catalytically to (+)-phenylethylcarbinol, the rotatory power of which is in good agreement with that of the carbinol obtained by direct resolution (Pickard and Kenyon, J., 1914, **105**, 1123). It thus appears probable that both the unsaturated and the saturated alcohols have been obtained optically pure. The results are in Table I and show quite clearly the marked difference in reactivity between the two series of compounds. The influence of the γ-methyl group in increasing the mobility of X in (I) is thus considerable and is perhaps most sharply shown in the relative stability of the two alcohols towards aqueous acids. Like Burton and Ingold (*loc. cit.*), we are unable to confirm Valeur and Luce's statement (*Bull. Soc. chim.*, 1920, **27**, 611) that α-phenylallyl alcohol is converted into cinnamyl alcohol by dilute sulphuric acid.

TABLE I.

Showing the difference in reactivity between

-X.	$\mathrm{Ph{\cdot}CHX{\cdot}CH{:}CHMe}$ and	$\mathrm{Ph{\cdot}CHX{\cdot}CH{:}CH_2}$.
$-\mathrm{CO_2{\cdot}C_6H_4{\cdot}CO_2H}$	(*a*) Changes spontaneously into the isomeric γ-phenyl-α-methylallyl ester	(*a*) Remains unchanged during many weeks both in homogeneous state and in inert solvents
	(*b*) With cold MeOH is rapidly converted into γ-phenyl-α-methylallyl methyl ether (A)	(*b*) Reacts exceedingly slowly with cold MeOH and EtOH
	(*c*) With cold AcOH is rapidly converted into γ-phenyl-α-methylallyl acetate (B)	(*c*) Remains unchanged to extent of 70% after a month
$-\mathrm{CO_2Me}$	With cold AcOH is rapidly converted into (B)	Stable to AcOH
$-\mathrm{CO_2{\cdot}C_6H_4{\cdot}NO_2}$	(*a*) With cold MeOH is rapidly converted into (A)	(*a*) Stable to AcOH, AcOH + HBr, HCl
	(*b*) With cold AcOH is rapidly converted into (B)	(See Burton, J., 1928, 1650.)
-OH	With cold 0·5% aqueous AcOH is converted into γ-phenyl-α-methylallyl alcohol	Stable to dilute aqueous $\mathrm{H_2SO_4}$ (confirms results of Burton and Ingold, J., 1928, 906)

The activating influence of the methyl group is most clearly noticeable in the reactions of the hydrogen phthalic esters:

$$\text{I.}\quad \mathrm{Ph{\cdot}CHX{\cdot}CH{:}CHMe} \longrightarrow \mathrm{Ph{\cdot}CH{:}CH{\cdot}CHYMe}$$

$$\text{II.}\quad \mathrm{Ph{\cdot}CHX{\cdot}CH{:}CH_2} \longrightarrow \mathrm{Ph{\cdot}CH{:}CH{\cdot}CH_2Y}$$

$$\text{III.}\quad \searrow \mathrm{Ph{\cdot}CHY{\cdot}CH{:}CH_2}$$

$$(\mathrm{X} = \mathrm{CO_2H{\cdot}C_6H_4{\cdot}CO_2{\cdot}};\ \ \mathrm{Y} = {\cdot}\mathrm{OAc\ or\ {\cdot}OMe}.)$$

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* For purposes of reference the (+)-alcohol is assumed to have the *d*-configuration.

Reaction (I) takes place readily with acetic acid (unpublished observation) and methyl alcohol, reaction (II) readily with formic acid and very slowly with acetic acid, and reaction (III) very slowly with methyl (and ethyl) alcohol.

Reaction (I) is accompanied by extensive racemisation (Kenyon, Partridge, and Phillips, *loc. cit.*); reaction (II) necessarily yields an inactive product, and the recovered hydrogen phthalate is partly racemised. The simple replacement reaction (III) yields an inactive product, but the unreacted hydrogen phthalate is recovered with almost unchanged rotatory power.

EXPERIMENTAL.

dl-α-Phenylallyl alcohol, obtained in 72% yield by the interaction of acraldehyde (0·9 mol.) and phenylmagnesium bromide (1 mol.), had b. p. 107°/17 mm., $n_D^{15°}$ 1·5404 (Klages and Klenk, *Ber.*, 1906, **39**, 2553, give b. p. 106°/18 mm., $n_D^{15°}$ 1·5406). Its *p*-nitrobenzoate had m. p. 44—45° (Burton and Ingold, *loc. cit.*, give m. p. 45—46°).

dl-α-*Phenylallyl Hydrogen Phthalate.*—The alcohol (67 g.) was added to a suspension of phthalic anhydride (74 g.) in pyridine (45 g.), and the mixture kept at about 50° for 3 hours. After working up in the usual manner, the *acid phthalate* was obtained (127 g.) in rectangular prisms, m. p. 73—74°, from carbon disulphide and light petroleum (Found by titration with N/10-NaOH: *M*, 279. $C_{17}H_{14}O_4$ requires *M*, 282).

Quinidine salt of l-α-*phenylallyl hydrogen phthalate.* Quinidine (484 g.) was dissolved in a warm solution of the *dl*-ester (422 g.) in acetone (1600 c.c.). On cooling, the salt was obtained as large masses of bulky asbestos-like crystals which, after being recrystallised thrice from methyl acetate, yielded the optically pure salt (233 g.); a further 74 g. were obtained by working up the various mother-liquors. The optically pure *salt* has m. p. 124° (decomp.), $[\alpha]_{5893}$ + 128·9°, $[\alpha]_{5461}$ + 155·8°, $[\alpha]_{4358}$ + 279·5° (*l*, 2; *c*, 5·010 in chloroform) (Found: N, 4·4. $C_{37}H_{38}O_6N_2$ requires N, 4·6%).

Quinidine salt of d-α-*phenylallyl hydrogen phthalate.* As much as possible of the salt of the *l*-acid ester was removed by concentration and crystallisation of the various filtrates from the above preparation: the liquors on standing for a fortnight then deposited compact glassy crystals of the quinidine salt of the *d*-hydrogen phthalate. Some solutions deposited a mixture of the two very different forms of crystals; but these were efficiently separated by taking advantage of the very much more rapid dissolution in warm acetone of the bulky needles of the *l*-acid ester salt than of its more compact diastereoisomeride. After one recrystallisation from acetone, the latter yielded the optically pure quinidine *salt*, m. p. 161—163° (decomp.), $[\alpha]_{5893}$ + 106·8°, $[\alpha]_{5461}$ + 127·9°, $[\alpha]_{4358}$ + 235·0° (*l*, 2; *c*, 5·101 in chloroform) (Found: N, 4·5%).

l-α-*Phenylallyl hydrogen phthalate.* The quinidine salt, m. p. 124°, was covered with acetone and decomposed with cold dilute hydrochloric acid in slight excess. The *l*-acid ester was precipitated as an oil which could not be induced to crystallise although the *dl*-ester crystallises readily. The rotatory powers are recorded in Table II.

TABLE II.

Specific Rotatory Powers of l-α-*Phenylallyl Hydrogen Phthalate in Various Solvents at Room Temperature* (l, 2).

Solvent.	*c.*	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
CS_2	5·376	+33·6°	+42·6°	—	+51·4°	+93·0°
C_5H_5N	5·002	—	+18·6	+19·5	+21·4	+33·8
C_6H_6	5·110	+15·2	+17·2	—	+20·2	+30·0
AcOH	5·115	—	+16·2	+17·3	+19·2	+29·0
$CHCl_3$	5·043	—	+ 8·9	—	+10·6	+15·2
MeOH	9·540	—	− 7·4	—	− 9·3	−23·0
EtOH	5·040	—	−14·0	−15·7	−18·4	−41·0

Advantage was taken of the active ester's being an oil to measure its optical rotatory power in the homogeneous state; a specimen which had $[\alpha]_{5461}$ + 51·4° in carbon disulphide (*l*, 2; *c*, 5·376) had $\alpha_{5893}^{20°}$ + 6·39°, $\alpha_{5461}^{20°}$ + 7·64°, $\alpha_{4358}^{20°}$ + 11·9° (*l*, 0·25) (Found, by titration with N/10-NaOH: *M*, 280. $C_{17}H_{14}O_4$ requires *M*, 282).

By crystallisation from carbon disulphide, the *d* + *dl*-hydrogen phthalate can be readily separated into the racemic and the highly dextrorotatory isomeride. A specimen of the oily *l*-ester was kept in a closed vessel, but the crop of small prismatic crystals which was deposited during 4 months proved to be γ-phenylallyl hydrogen phthalate; after recrystallisation from carbon disulphide, this had m. p. 95—97° alone or when mixed with an authentic specimen prepared by the interaction of molecular amounts of cinnamyl alcohol and phthalic anhydride in pyridine (Kamai, *loc. cit.*, gives m. p. 88—89°). The oily *l*-α-phenylallyl hydrogen phthalate decanted from the crystalline isomer was again set aside, and after several months, it set completely to a mass of the γ-phenylallyl hydrogen phthalate. In view of the ease with which the liquid optically active acid phthalic ester undergoes this anionotropic change completely, it is noteworthy that the crystalline *dl*-ester appears to be permanently stable.

d-α-Phenylallyl hydrogen phthalate was prepared in the same manner as its antipode and, like it, could not be induced to crystallise. It had $[\alpha]_{5893} - 42·3°$, $[\alpha]_{5461} - 51·3°$, $[\alpha]_{4358} - 92·6°$ (*l*, 2; *c*, 4·947 in carbon disulphide).

l-*α-Phenyallyl Alcohol.*—The *l*-acid ester was saponified with a slight excess of aqueous alcoholic potassium hydroxide (5N); the liberated alcohol, removed by steam distillation, had b. p. 106°/16 mm., $n_D^{19°}$ 1·5398, $\alpha_{5893} - 20·08°$, $\alpha_{5780} - 21·55°$, $\alpha_{5461} - 26·01°$, $\alpha_{4358} - 60·0°$ (*l*, 2; *t*, 18°), whence $\alpha_{4358}^{18°}/\alpha_{5461}^{18°} = 2·30$. The influence of temperature on rotatory power is shown by the following data (*l*, 0·25):

t.	21°.	26°.	30·5°.	35°.	40°.	47°.	50°.	55°.	60°.	67°.
α_{5893}	−2·48°	2·34°	2·20°	1·68°	1·44°	1·21°	1·10°	1·03°	0·80°	0·72°
α_{5461}	−3·71	3·20	2·97	2·16	1·86	1·46	1·41	1·33	1·04	0·93
α_{4358}	−8·52	7·59	6·88	4·90	4·27	3·46	3·24	3·05	2·39	2·10

d-α-Phenylallyl alcohol, similarly obtained from the *d*-acid ester, had b. p. 107°/16 mm., $n_D^{19·5°}$ 1·5391, $\alpha_{5893} + 20·0°$, $\alpha_{5461} + 25·7°$ (*l*, 2; *t*, 19°). Its specific rotatory powers in various solvents (*l*, 2) at room temperature are shown below.

Solvent.	*c*.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
CS_2	5·007	—	+12·1°	+12·8°	+13·8°	+18·9°
C_6H_6	5·143	—	8·2	9·0	9·6	10·1
$CHCl_3$	5·170	+3·1°	3·3	3·4	3·4	—
$CHCl_3$	2·585	3·2	3·2	3·2	3·3	—
EtOH	5·350	—	− 2·0	− 2·4	− 2·9	—

Reduction of l-*α-Phenylallyl Alcohol to* (+)-*Phenylethylcarbinol.*—The alcohol, dissolved in pure ether, was shaken with hydrogen at 2 atm. in the presence of Raney nickel catalyst. The resultant (+)-phenylethylcarbinol was completely without action on bromine water and had b. p. 105°/15 mm., $n_D^{20°}$ 1·5196, $\alpha_{5893} + 13·08°$ (*l*, 0·5; *t*, 20°) [Pickard and Kenyon, *loc. cit.*, give b. p. 115°/25 mm., $n_D^{20°}$ 1·5200, $\alpha_{5893} + 13·62°$ (*l*, 0·5; *t*, 17°) for the optically pure alcohol].

l-*α-Phenylallyl Acetate.*—A mixture of *l*-α-phenylallyl alcohol (6·7 g.; $\alpha_{5461}^{18°} - 26·00°$; *l*, 2) in pyridine (6·5 g.) and acetic anhydride was kept overnight and then warmed to 40° for an hour. The resulting *l*-α-phenylallyl acetate (8·5 g.), b. p. 111°/16 mm., had $\alpha_{6438} + 27·2°$, $\alpha_{5461} + 39·93°$, $\alpha_{5780} + 33·39°$, $\alpha_{4358} + 70·5°$ (*t*, 18°; *l*, 0·5), $n_D^{20°}$ 1·5092.

dl-*α-Phenylallyl acetate*, similarly prepared, had b. p. 114°/19 mm., $n_D^{22°}$ 1·5085 (Found: C, 74·6; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). This compound was prepared also by heating molecular proportions of the alcohol and acetic anhydride on the steam-bath for 3 hours. The resulting acetate distilled completely at 114°/19 mm., showing that no conversion into the isomeric γ-phenylallyl acetate had taken place.

dl-*α-Phenylallyl methyl ether* was prepared by dissolving potassium (2 g.) in a solution of *dl*-α-phenylallyl alcohol (7 g.) in dry ether and adding thereto methyl iodide (7·1 g.); it had b. p. 85°/18 mm., $n_D^{20°}$ 1·5105 (Found: C, 80·8; H, 8·2. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%). The γ-phenyl isomeride, prepared in a similar manner for purposes of comparison from cinnamyl alcohol, had b. p. 116°/15 mm. (Pschorr and Dickhauser, *Ber.*, 1911, **44**, 2640, give b. p. 115°/15 mm.).

Reactions of α-Phenylallyl Hydrogen Phthalate.—(a) *With methyl alcohol.* (i) A solution of the *dl*-ester (10 g.) in anhydrous methyl alcohol (25 c.c.) was slowly distilled during 2 hours. The partly crystalline residue was separated into phthalic acid (4 g.) and α-phenylallyl methyl ether (3 c.c.), b. p. 84—85°/19 mm., $n_D^{19°}$ 1·5104. (ii) A similar experiment with the *l*-ester yielded phthalic acid (4 g.) and *dl*-α-phenylallyl methyl ether (3 c.c.), b. p. 84—85°/19 mm. (iii) A solution of the *d*-ester (11 g.) in methyl alcohol (10 g.) was kept in a closed vessel for 3 weeks at summer room temperature. From the reaction mixture, which had developed the pleasant ethereal odour of the methyl ether, there were isolated the *d*-hydrogen phthalate (10 g.) of almost unchanged rotatory power and *dl*-α-phenylallyl methyl ether (0·6 c.c.), b. p. 87—89°/20 mm.

(b) *With ethyl alcohol.* A solution of the *l*-ester (1 g.) in absolute alcohol (20 c.c.) showed no alteration in rotatory power after 3 weeks, but after 18 months this had decreased to 25%, and after 33 months to 6%, of its original value. From the resulting solution, which had developed a pronounced ethereal odour, there were isolated phthalic acid (0·3 g.) and α-phenylallyl ethyl ether (0·3 c.c.), b. p. 90—95°/20 mm. Klages and Klenk (*loc. cit.*) give b. p. 203—205°/755 mm.

(c) *With formic acid.* Anhydrous formic acid (8 g.) was added to a solution of the *d*-ester (10 g.) in carbon disulphide (20 c.c.); within a few minutes phthalic acid began to separate and the amount rapidly increased. After 2 hours the reaction mixture was separated into (i) phthalic acid (5 g.), (ii) partly racemised hydrogen phthalic ester (1·3 g.; $[\alpha]_{5461} - 19{\cdot}3°$ in carbon disulphide solution), and (iii) γ-phenylallyl formate (3 g.), b. p. 132—139°/18 mm., m. p. 6° (Béhal, *Ann. Chim. Phys.*, 1900, **20**, 423, gives b. p. 138—139°/23 mm., m. p. 0°). Further confirmation was afforded by its hydrolysis to cinnamyl alcohol, m. p. alone and mixed with an authentic specimen, 32—33°.

(d) *With acetic acid.* (i) The observed rotatory power of a 5% solution of the *l*-ester in glacial acid changed from $\alpha_{5461} + 1{\cdot}96°$ to $\alpha_{5461} + 1{\cdot}34°$ during 16 days at room temperature. (ii) A solution of the *l*-ester (3·2 g.) in glacial acetic acid (20 c.c.) was heated on the steam-bath for several hours; from the reaction mixture there were obtained phthalic acid (0·6 g.), cinnamyl acetate, b. p. 143—145° (0·7 c.c.), and *l*-α-phenylallyl hydrogen phthalate (1·5 g.) having $[\alpha]_{5461} - 5{\cdot}4°$ in carbon disulphide solution.

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