Some Reactions of Optically Active 1-*Phenylpent*-1-*en*-3-*ol and* 1-*Phenylpent*-2-*en*-1-*ol.*

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The dibromo-alcohols formed by addition of bromine to optically active 1-phenylpent-1-en-3-ol yield, on oxidation, optically active 1 : 2-dibromo-1-phenylpentan-3-ones. These reactions are analogous to those observed by Kenyon and Partridge (*J.*, 1936, 1313) with (+)-4-phenylbut-3-en-2-ol. Evidence is now obtained that *both* the 1- and the 2-carbon atom contribute to the optical activity of the dibromo-alcohols and dibromo-ketones derived from the alkenols.

(+)- and (−)-1-Phenylpent-2-en-1-ols rearrange with complete racemisation to 1-phenylpent-1-en-3-ol, and a similar rearrangement of the hydrogen phthalates occurs with extensive, but incomplete, racemisation.

(+)- and (−)-1-PHENYLPENT-1-EN-3-OL and (+)- and (−)-1-phenylpent-2-en-1-ol are readily obtained by the usual method of fractional crystallisation of alkaloidal salts of their hydrogen phthalates: details are given in the experimental section and rotatory data in Tables 1 and 2.

TABLE 1. *Specific rotatory Powers of* (+)-1-*ethyl*-3-*phenylprop*-2-*enyl* (1-*phenylpent*-1-*en*-3-*yl*) *hydrogen phthalate in various solvents at room temperature* (1, 2).

Solv.	c	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$	Solv.	c	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
CS_2	1·40	+53·4°	+80·5°	+127°	Me_2CO	2·02	−6·2°	− 9·1°	−13·1°
AcOH	2·27	26·1	32·1	63·5	Et_2O	2·00	−7·8	− 9·0	−13·9
C_5H_5N	1·61	17·0	19·8	38·2	EtOH	13·85	−4·4	− 5·0	− 7·2
CCl_4	2·16	11·5	14·3	30·4					
$CHCl_3$	2·38	9·4	12·2	26·2		(−)-isomeride			
C_6H_6	2·32	+7·3	+11·4	+20·6	$CHCl_3$	1·60	−9·5°	−12·0°	−26·7°

TABLE 2. *Specific rotatory powers in the homogeneous state.*

(*a*) 1-*Phenylpent*-1-*en*-3-*ol* (d_4^{20} 0·9980)

	l	t	$[\alpha]_{5893}$	$[\alpha]_{5780}$	$[\alpha]_{5461}$	$[\alpha]_{5086}$	$[\alpha]_{4800}$	$[\alpha]_{4358}$
(+)-Alcohol	0·5	21°	+6·7°	+7·2	+8·4°	+10·9°	+13·4°	+19·8°
(−)-Alcohol	0·5	21°	−6·7	−7·3	−8·3	−10·8	−13·4	−19·6

(*b*) 1-*Phenylpent*-2-*en*-1-*ol* (d_4^{25} 0·9894)

	l	t	$[\alpha]_{5893}$	$[\alpha]_{5780}$	$[\alpha]_{5461}$	$[\alpha]_{5086}$	$[\alpha]_{4800}$	$[\alpha]_{4358}$
(−)-Alcohol	0·5	19°	−12·6	−13·0	−14·8	−19·8	−20·9	−26·0

From the evidence given later it seems probable that 1-phenylpent-1-en-3-ol in both its racemic and optically active forms has been obtained exclusively in the *trans*-modification.

A mixture of two stereoisomeric forms of 1 : 2-dibromo-1-phenylpentan-3-ol, m. p. 93—94° and m. p. 114—115°, in 60% and 40% yields, respectively, is obtained by the addition of bromine at room temperature to (+)-, (−)-, or (±)-1-phenylpent-1-en-3-ol. Oxidation of the resultant dibromo-alcohols gives 1 : 2-dibromo-1-phenylpentan-3-one, m. p. 109—110°, in about 90% yield. This single chemical species of dibromo-ketone is formed on oxidation of any of the stereoisomeric dibromo-alcohols, but it is produced as the (+)- or (−)- or (±)-variety according to which optical species of dibromo-alcohol has undergone oxidation. Somewhat unusually, the optically active and optically inactive forms of the dibromo-alcohols have the same m. p.: this is true also of the dibromo-ketones. Rotatory powers are given in Table 3.

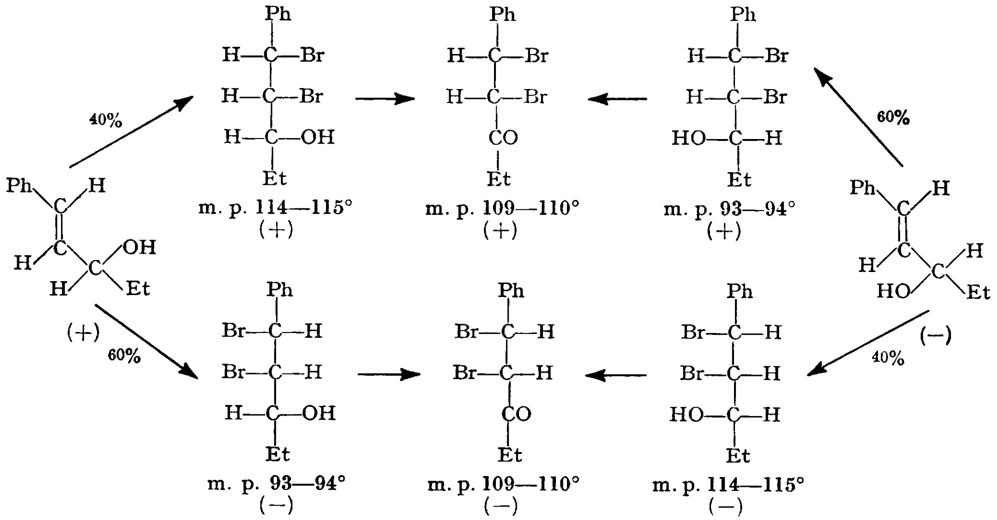
Since the formations of the dibromo-alcohols and dibromo-ketones are practically quantitative and since the two dibromo-ketones [the (+)- and the (−)-form] obtained from any one alcohol are homogeneous—for exhaustive fractional crystallisation of each effects no separation—it is improbable that a mixture of *cis*- and *trans*-dibromo-alcohols is formed by the addition of bromine to 2-phenylpent-1-en-3-ol; it is, in fact, currently accepted that such a reaction yields only the *trans*-dibromide. The reaction scheme is given in Table 4.

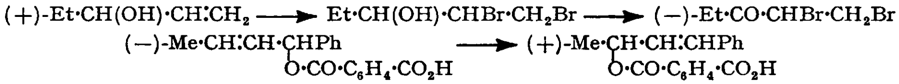
The two forms of the dibromo-alcohol are therefore diastereoisomerides, that of m. p. 114—115° containing a centre (or centres) of optical activity at $C_{(1)}$ or $C_{(2)}$ which has the same sign of rotatory power as the original centre of optical activity—namely $C_{(3)}$; while that of m. p. 93—94° has a contribution of rotatory power from $C_{(1)}$ or $C_{(2)}$ which is opposite in sign to that of the original centre at $C_{(3)}$. From the (±)-alcohol the isomeric dibromo-alcohols are formed in the same proportions as from the (+)- and the (—)-alcohol but each is racemic, being formed in equal proportions from (+)- and (—)-optical species in the (±)-alcohol. Although Kenyon and Partridge (*J.*, 1936, 1313) showed that 3 : 4-dibromo-4-phenylbutan-2-one obtained from (+)-4-phenylbut-3-en-2-ol is optically active they did not establish whether the optical activity is derived from $C_{(1)}$ or $C_{(2)}$ or from both $C_{(1)}$ and $C_{(2)}$. From the following considerations it is evident that both the $C_{(2)}$ and $C_{(3)}$ atoms in substituted allyl alcohols can become seats of optical activity when the 2 : 3-double bond becomes saturated: (—)-pent-1-en-3-ol yields, by similar reactions to those now described, (—)-1 : 2-dibromopentan-3-one (Partridge, Thesis, London, 1936) in which $C_{(2)}$ is the only possible seat of optical activity; whilst the rearrangement of the hydrogen phthalate of (—)-1-phenylbut-2-en-1-ol to that of (+)-1-phenylbut-1-en-3-ol (Kenyon, Partridge, and Phillips, *J.*, 1937, 207) similarly demonstrates that optical activity can arise when $C_{(3)}$ becomes asymmetrically saturated.

TABLE 3. *Specific rotatory powers of the dibromo-alcohols and dibromo-ketones* (in $CHCl_3$; *l*, 2).

	M. p.	*c*	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
(+)-1 : 2-Dibromo-1-phenylpentan-3-ol	114—115°	1·47	+107·7°	+128·1°	+239°
(—)- ,, ,, ...	93—94	2·01	—106·9	—130·8	—
(—)- ,, ,, ...	114—115	1·72	—104·4	—125·3	—241
(+)- ,, ,, ...	93—94	2·03	+104·4	+129·5	+236
(+)-1 : 2-Dibromo-1-phenylpentan-3-one ...	109—110	1·71	+ 25·4	+ 30·1	+ 41
(—)- ,, ,, ,, ...	109—110	2·05	— 25·8	— 30·6	— 40

TABLE 4.





$$(+)\text{-Et}\cdot\text{CH(OH)}\cdot\text{CH:CH}_2 \longrightarrow \text{Et}\cdot\text{CH(OH)}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br} \longrightarrow (-)\text{-Et}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$$

$$(-)\text{-Me}\cdot\text{CH:CH}\cdot\underset{\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}}{\text{CH}}\text{Ph} \longrightarrow (+)\text{-Me}\cdot\underset{\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}}{\text{CH}}\cdot\text{CH:CHPh}$$

The experiments now described afford evidence that *both* carbon atoms become optically active when an optically active 1 : 3-disubstituted allyl alcohol combines with bromine; this evidence being the homogeneity of the derived dibromo-ketone. The ketone contains two asymmetric carbon atoms, at least one of which is optically active in the ketones derived from the (+)- or (—)-alcohol. If the second asymmetric carbon atom were not giving rise to optical activity, *i.e.* were present in its (+)-form in half the ketone molecules and in its (—)-form in the other half, the ketone would be a mixture of diastereoisomerides which could be separated by fractional crystallisation. Since such a separation cannot be effected it follows that the second carbon atom of the $C_{(2)}$—$C_{(3)}$ pair in the (+)- or (—)-dibromo-ketone is also optically active and both must therefore have become optically active during the combination of the unsaturated alcohol with bromine.

The course of the addition of bromine to 1-phenylpent-1-en-3-ol, like that to 1-phenylbut-1-en-2-ol (Kenyon and Partridge, *loc. cit.*), is sensitive to temperature. The mixture of dibromo-ketones obtained (by subsequent oxidation) when the (+)-alcohol combines with bromine at —10° has —9·0°; when combination takes place at +60° the rotatory power of the mixed ketones falls to zero and at intermediate temperatures the rotatory power becomes lower as the temperature of reaction rises.

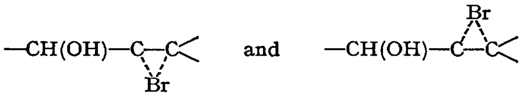
The lack of rotatory power in the mixture of dibromo-ketones obtained *via* combination at 60° (cf. Table 5) cannot be due to the racemisation of an initially active dibromo-alcohol since the dibromo-alcohol (of $[\alpha]_D$ —3·89° in chloroform) was recovered with unchanged rotatory power after its solution in chloroform has been heated under reflux for 2 hours; furthermore the (±)-mixture of dibromo-alcohols formed from the (+)-alcohol at 60° can be separated into the (+)-dibromo-alcohol of m. p. 114—115° and the (—)-dibromo-alcohol of m. p. 93—94° [these two dibromo-alcohols are diastereoisomerides, containing a (+)-centre of optical activity at $C_{(3)}$ and either a (+)- or (—)-centre at $C_{(1)}$—$C_{(2)}$].

TABLE 5. *Specific rotatory powers of the* 1 : 2-*dibromo*-1-*phenylpentan*-3-*ones obtained by oxidation of the unseparated* 1 : 2-*dibromo*-1-*phenylpentan*-3-*ols prepared at temperature* t° (in $CHCl_3$; *l*, 2).

t	Medium	*c*	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
—10°	$CHCl_3$	1·55	—8·34°	—10·30°	—16·7°
+ 5	,,	2·90	5·20	6·11	8·4
22	,,	2·01	4·91	5·84	7·7
60	CCl_4	1·95	0	0	0
72	,,	1·80	0	0	0

The differences in rotatory power between the dibromo-ketones derived from the dibromo-alcohols produced at different temperatures must therefore be due to variations in the proportions of the two dibromo-alcohols (m. p. 93—94° and 114—115°, respectively) formed on addition of bromine to the alcohol.

It would appear that the equilibrium between the two stereoisomerides of the intermediate in the addition of bromine to the alcohol, which may be written :



is dependent on the temperature at which combination with bromine occurs: this equilibrium controls the relative proportions in which the diastereoisomeric dibromo-alcohols are formed when addition of the second atom of bromine ensues.

1-Phenylpent-2-en-1-ol rearranges very easily in the presence of acid to 1-phenylpent-1-en-3-ol. The (+)- and the (—)-alcohol, after some 3 days, yield products of changed sign of rotation which contain no optically active species of the original alcohol and yield the racemic diphenylylurethane and dibromo-derivatives of 1-phenylpent-1-en-3-ol. It therefore appears that the rearrangement occurs with complete racemisation, and that there is a concomitant formation of an optically active unidentified substance (or substances) in small amount (see below). The alcohol also rearranges with complete racemisation on reaction with diphenylyl *iso*cyanate or pyridine hydrogen bromide perbromide in acetic acid solution forming the (±)-urethane of 1-phenylpent-1-en-3-ol and the acetate of (±)-1 : 2-dibromo-1-phenylpentan-3-ol, respectively: the racemisations do not occur after the formation of these derivatives, which are themselves optically stable under the conditions of the experiment. 1-Phenylpent-1-en-3-ol does not rearrange in the presence of acid, but undergoes mutarotation, probably due to the formation of an unidentified optically active substance, the alcohol recovered after the racemisation being substantially racemic.

The hydrogen phthalate of 1-phenylpent-2-en-1-ol rearranges very readily to that of 1-phenylpent-1-en-3-ol; if, during the preparation, the temperature exceeds 40°, only the rearranged product can be isolated. The homogeneous hydrogen phthalate racemises more rapidly than it rearranges and the product of rearrangement is the hydrogen phthalate of 1-phenylpent-1-en-3-ol possessing 39% of the maximum optical rotatory power. In solution (+)- or the (−)-1-phenylpent-2-en-1-yl hydrogen phthalate rearranges to the (−)- or the (+)-ester of 1-phenylpent-1-en-3-ol with varying degrees of racemisation according to the nature of the solvent. These rearrangements of 1-phenylpent-2-en-1-ol and its esters are analogous to those of 1-phenylbut-2-en-1-ol and its ester, which have been discussed by Kenyon, Partridge, and Phillips (*loc. cit.*), by Catchpole, Hughes, and Ingold (*J.*, 1948, 8), and by Braude *et al.* (*J.*, 1946, 396; 1947, 1096; 1948, 1982).

EXPERIMENTAL

(+)-1-Phenylpent-1-en-3-ol (126 g.), prepared by the addition of an ethereal solution of cinnamaldehyde (125 g.) to the Grignard reagent obtained from magnesium (24 g.) and ethyl chloride (68 g.), had b. p. 104—108°/2·5 mm. and n_D^{25} 1·5548 (cf. Levene and Stevens, *J. Biol. Chem.*, 1930, **87**, 375). An attempt to separate the alcohol into *cis*- and *trans*-isomerides by fractional distillation was unsuccessful. Its p-*diphenylylurethane* separates from benzene in needles, m. p. 150—151° (Found: N, 4·1. $C_{24}H_{23}O_2N$ requires N, 3·9%).

(±)-1-*Ethyl*-3-*phenylprop*-2-*enyl Hydrogen Phthalate*.—A mixture of the (±)-1-phenylpent-1-en-3-ol (162 g.), phthalic anhydride (148 g.), and pyridine (100 g.), heated for 1·5 hr. on the steam-bath, became a homogeneous, viscous liquid. Next day the product was diluted with ether and decomposed with dilute hydrochloric acid; the washed and dried (Na_2SO_4) solution, after dilution with light petroleum, deposited the *hydrogen phthalate* (284 g.) in irregular, glassy, rhombs (likewise from carbon disulphide), m. p. 109—110° (Found, by titration: *M*, 311. $C_{19}H_{18}O_4$ requires *M*, 310).

(+)-1-*Ethyl*-3-*phenylprop*-2-*enyl Hydrogen Phthalate*.—Cinchonidine (114 g.) was dissolved in a solution of the (±)-hydrogen phthalate (120 g.) in hot ethyl acetate (350 c.c.). After cooling, the *cinchonidine salt* of (+)-1-ethyl-3-phenylprop-2-enyl hydrogen phthalate separated and, after one recrystallisation from ethyl acetate, was obtained optically pure as bulky fibrous needles (96·5 g.), m. p. 175° (decomp.), $[\alpha]_{5893}$ −52·6°, $[\alpha]_{5461}$ −62·5°, $[\alpha]_{4358}$ −106° (*c*, 2·580 in $CHCl_3$; *l*, 2). On decomposition, by being covered with acetone and treated with dilute hydrochloric acid, it yielded the (−)-hydrogen phthalate as prismatic needles from carbon disulphide–light petroleum; it had m. p. 83—84° (decomp.). Rotatory powers are in Table 1.

(−)-1-*Ethyl*-3-*phenylprop*-2-*enyl Hydrogen Phthalate*.—The first filtrate from the crystallisation of the cinchonidine salt yielded a hydrogen phthalate (45·5 g.), with $[\alpha]_D$ −40·5° (in CS_2). To a portion (4·9 g.) of this in methyl acetate (15 c.c.) was added brucine (6·3 g.); the crystals, which slowly separated, after one recrystallisation from methyl acetate yielded optically pure *brucine salt* of the (−)-hydrogen phthalate; this formed needles, m. p. 118° (decomp.) $[\alpha]_{5983}$ −32·1°, $[\alpha]_{5461}$ −40·5°, $[\alpha]_{4358}$ −88° (*c*, 2·380 in $CHCl_3$; *l*, 2). The brucine salt (3·5 g.) when decomposed with acid yielded optically pure (−)-hydrogen phthalate (1·31 g.) as prismatic needles (from carbon disulphide–petroleum), m. p. 84° (decomp.).

Alternatively, and more conveniently, the optically impure (−)-hydrogen phthalate, by fractional crystallisation from carbon disulphide, yielded the optically pure ester, m. p. 83—84° (decomp.). Rotatory powers are in Table 1.

(+)-1-*Phenylpent*-1-*en*-3-*ol*—Sodium hydroxide (5N; 50 c.c.) was added to a solution of the (+)-hydrogen phthalate (30 g.) in ethanol (100 c.c.), the whole heated on the steam-bath for 1 hr. and then in a current of steam. The steam-distillate yielded the (+)-alcohol (14 g.), b. p. 110—112°/2·5 mm., n_D^{25} 1·5549, d_4^{25} 0·9980: rotatory powers are in Table 2. Its p-*diphenyl*-

ylurethane separates from benzene in bulky fine needles, m. p. 163—164° (Found: N, 4·2%), $[\alpha]_{5893}$ +144°, $[\alpha]_{5461}$ +180°, $[\alpha]_{4358}$ +402° (*c*, 0·671 in $CHCl_3$; *l*, 2).

(−)-1-Phenylpent-1-en-3-ol (5·45 g.), similarly prepared from the (−)-hydrogen phthalate (12·8 g.), had b. p. 113—115°/3 mm., n_D^{25} 1·5549. Rotatory powers are in Table 2.

(+)-1-*Ethyl-3-phenylprop-2-enyl Acetate*.—This was prepared from the (+)-alcohol, acetic anhydride, and pyridine at 100°, and had b. p. 158—159°/22 mm., n_D^{25} 1·5218, d_4^{25} 0·9720, d_4^{20} 0·9742, $[\alpha]_{5893}^{20}$ +120·1°, $[\alpha]_{5461}^{20}$ +146·8°, $[\alpha]_{4800}^{20}$ +211° (homogeneous; l, 0·5).

The corresponding (±)-*acetate* had b. p. 156—156·5°/21 mm., n_D^{25} 1·5249 (Found: C, 76·6; H, 7·8. $C_{12}H_{16}O_2$ requires C, 76·5; H, 7·9%).

(±)-1 : 2-*Dibromo-1-phenylpentan-3-ols*.—(*a*) A solution of bromine (40 g.) in chloroform (30 c.c.) was added to a stirred solution of the (±)-alcohol (40·5 g.) in chloroform (50 c.c.) maintained at 15°. Evaporation of the solvent and several crystallisations of the residue from light petroleum yielded the first *dibromo-alcohol*, fine needles (25·6 g.), m. p. 114—115° (Found: Br, 49·6. $C_{11}H_{14}OBr_2$ requires Br, 49·6%).

The original mother-liquor deposited both fine needles and hexagonal prisms, the latter being rather more soluble in light petroleum. Fractional crystallisation yielded the second *dibromo-alcohol*, hexagonal plates (39·9 g.), m. p. 93—94° (Found: Br, 49·85%).

(*b*) Pyridine bromide perbromide (9·35 g.) was added in portions to a solution of the (±)-alcohol (5 g.) in acetic acid (25 c.c.), and the mixture poured into ice–water and extracted with ether. By fractional crystallisation of the reaction product the two forms of the dibromo-alcohol were isolated with m. p. 92—93° and m. p. 114—115°, respectively: these values were unchanged when the compounds were mixed with the corresponding products obtained as in (*a*).

(*c*) *N*-Bromoacetamide (2 mols.) was added to a solution of the (±)-alcohol (2·5 g.) in chloroform (15 c.c.) under the light from a mercury arc. After several hours' illumination the solution was washed, dried, and evaporated: in this case also both forms of the (±)-dibromo-alcohol were obtained but in very poor yield.

By similar procedure the (+)-alcohol (8·0 g.) yielded (+)-1 : 2-dibromo-1-phenylpentan-3-ol as needles, m. p. 114—115° (5·8 g.), and (−)-1 : 2-dibromo-1-phenylpentan-3-ol as plates, m. p. 93—94° (9·15 g.), and the (−)-alcohol (5·0 g.) yielded (−)-1 : 2-dibromo-1-phenylpentan-3-ol as needles, m. p. 114—115° (2·80 g.), and (+)-1 : 2-dibromo-1-phenylpentan-3-ol as hexagonal plates, m. p. 93—94° (4·31 g.). Rotatory powers are in Table 3. (±)-2 : 3-Dibromo-1-ethyl-3-phenylpropyl acetate, obtained by addition of pyridine hydrobromide perbromide (1·9 g.) to a solution of the (±)-acetate (1·4 g.) in acetic acid (20 c.c.), was separated by fractional crystallisation from light petroleum into its two isomers, which formed fine rods, m. p. 164—165°, and short needles, m. p. 127—128° (see below).

TABLE 6. *Oxidation of the isomeric* 1 : 2-*dibromo*-1-*phenylpentan*-3-*ols to the isomeric pentan*-3-*ones.*

(i) (±)-Alcohol, m. p. 93—94°. Chromic anhydride (0·26 g.) was added in portions to a solution of the alcohol (0·5 g.) in acetic acid (2 c.c.) at 60°. Dilution with water followed by recrystallisation from ethanol yielded the ketone as needles (0·44 g.), m. p. 109—110°.

(ii) (±)-Alcohol, m. p. 114—115°, treated similarly, yielded the same ketone, m. p. 109—110°.
(iii) (+)-Alcohol, m. p. 114—115°, gave the (+)-ketone, m. p. 109—110°.
(iv) (−)-Alcohol, m. p. 93—94°, gave the (−)-ketone, m. p. 109—110°.
(v) (+)-Alcohol, m. p. 93—94°, gave the (+)-ketone, m. p. 109—110°.
(vi) (−)-Alcohol, m. p. 114—115°, gave the (−)-ketone, m. p. 109—110°.
Yields were about 90% in each case.

Determinations of mixed m. p.s were made where appropriate (Found: C, 41·3; H, 3·8; Br, 49·7. Calc. for $C_{11}H_{14}OBr_2$: C, 41·3; H, 3·7; Br, 49·9%).

(±)-1-*Phenylpent-2-en-1-ol*.—Prepared by the dropwise addition of a solution of pent-2-en-1-al (27 g.; b. p. 123—124°) in ether (100 c.c.) to a Grignard reagent [obtained from magnesium (8·76 g.) and bromobenzene (57·5 g.)] and maintained at 5—10°, the (±)-*alcohol* (37 g.) had b. p. 93—94°/0·7 mm., $n_D^{25°}$ 1·5270 (Found: C, 81·2; H, 8·6. $C_{11}H_{14}O$ requires C, 81·4; H, 8·6%). Its *p*-diphenylylurethane separated from ether–light petroleum in fine needles, m. p. 115—116° (Found: N, 3·7. $C_{24}H_{23}O_2N$ requires N, 3·9%). On admixture with the *p*-diphenylylurethane m. p. 150—151°, of the isomeric 1-phenylpent-1-en-3-ol it melted at 102—126°.

(±)-1-*Phenylpent-2-en-1-yl Hydrogen Phthalate*.—The (±)-alcohol (10 g.) was added to a solution of phthalic anhydride (9·2 g.) in warm pyridine (16 g.), and the mixture maintained at 40° during 2 hr. with occasional shaking in order to obtain a homogeneous solution as soon as possible. (These conditions are critical if isomeric change is to be avoided; at 95° isomeric change is complete.) After being worked up as previously described, the *hydrogen phthalate* (18·9 g.) separated from ether–light petroleum in prismatic needles, m. p. 112—113° (when freshly prepared) (Found: C, 73·1; H, 5·9. $C_{19}H_{18}O_4$ requires C, 73·2; H, 5·8%). A mixture with the isomeric 1-ethyl-3-phenylprop-2-enyl hydrogen phthalate, of m. p. 109—110°, melted at 85—108°.

(−)-1-*Phenylpent-2-en-1-yl Hydrogen Phthalate.*—Quinidine (19·8 g.) was dissolved in a warm solution of the (±)-hydrogen phthalate (19 g.) in acetone (100 c.c.). The *quinidine salt* (20·5 g.) of the (−)-ester rapidly separated, and on recrystallisation from acetone (1500 c.c.) yielded the optically pure compound (17 g.) in cotton-wool-like needles, m. p. 150—151° (decomp.), $[\alpha]_{5893}$ +127°, $[\alpha]_{5461}$ +150·5°, $[\alpha]_{4358}$ +278° (*c*, 2·190 in $CHCl_3$; *l*, 2). A suspension of this salt (8·5 g.) in acetone (350 c.c.) was decomposed with ice-cold hydrochloric acid and yielded the (−)-hydrogen phthalate as an uncrystallisable oil, $[\alpha]_{5893}$ −4·35°, $[\alpha]_{5461}$ −6·45°, $[\alpha]_{4358}$ −13·6° (*c*, 5·50 in Et_2O; *l*, 2).

(−)-1-*Phenylpent-2-en-1-ol.*—The freshly prepared (−)-hydrogen phthalate (4·5 g.) was added to a solution of sodium ethoxide [from sodium (1·4 g.) in absolute ethanol (65 c.c.)] and heated on the steam-bath for 5 min. The liberated alcohol (1·9 g.), removed in a current of steam, had b. p. 94°/0·7 mm., n_D^{25} 1·5299, d_4^{25} 0·9894. Rotatory powers are in Table 2.

Its p-*diphenylylurethane* formed needles (from ether–light petroleum), m. p. 124—125°, $[\alpha]_D^{15}$ +14·1° (*c*, 1·277 in $CHCl_3$; *l*, 2). From the more soluble fractions of the quinidine salt there was obtained optically impure (+)-1-phenylpent-2-en-1-ol, b. p. 94—95°/0·7 mm., n_D^{25} 1·5290, $[\alpha]_D^{20}$ +3·64° (*l*, 0·5).

(±)-1-*Phenylpent-2-enyl Acetate.*—Prepared by interaction of the (±)-alcohol, pyridine, and *purified* acetic anhydride at 35° during 1½ hr., the (±)-acetate had b. p. 93—95°/1 mm., n_D^{25} 1·5069 (Found: C, 79·8; H, 7·9. Calc. for $C_{13}H_{16}O_2$: C, 76·5; H, 7·8%). When this acetate (2 g.) was heated with glacial acetic acid (3 g.) on the steam-bath for 4 hr. it was completely converted into the isomeric 1-ethyl-3-phenylprop-2-enyl acetate (confirmed by hydrolysis and formation of *p*-diphenylylurethane, m. p. and mixed m. p. 150—151°).

Rearrangement of 1-*Phenylpent*-2-*en*-1-*yl Hydrogen Phthalate to* 1-*Ethyl*-3-*phenylprop*-2-*enyl Hydrogen Phthalate.*—(i) A solution of the (±)-hydrogen phthalate (0·5 g.) in pyridine (0·5 c.c.) was heated on the steam-bath for 1·5 hr., cooled, and decomposed with hydrochloric acid. The product separated from carbon disulphide–light petroleum in glassy rhombs (0·25 g.), m. p. 109—110° alone or when mixed with authentic (±)-1-ethyl-3-phenylprop-2-enyl hydrogen phthalate.

(ii) A similar result was obtained when the (±)-hydrogen phthalate was kept in an evacuated desiccator at room temperature: the crystals become coated with a viscous oil within 30 min. and eventually turned pasty. Within 10 days the mass had re-solidified (m. p. 108—110°) and then separated from carbon disulphide–light petroleum in rhombs, m. p. 111—112°.

(iii) Optically pure (—)-hydrogen phthalate (0·5 g.) after 72 hr. at room temperature was hydrolysed by being heated with a solution of sodium ethoxide [from sodium (0·3 g.) and absolute ethanol (20 c.c.)], and the resultant alcohols (0·27 g.) were converted into their *p*-diphenylylurethanes. These, by fractional crystallisation from methylene chloride–light petroleum, were separated into the *p*-diphenylylurethanes of (−)-1-phenylpent-2-en-1-ol (0·14 g.), $[\alpha]_D$ +11·8° (*c*, 0·59 in $CHCl_3$; *l*, 2), and of a mixture of (±)- and (+)-1-phenylpent-1-en-3-ols having $[\alpha]_D$ +59·4° (*c*, 0·454 in $CHCl_3$; *l*, 2). This mixture was separated by crystallisation from benzene into its (+)-component (0·068 g.), m. p. 162—164°, $[\alpha]_D$ +144° (*c*, 0·67 in $CHCl_3$; *l*, 2) and the (±)-component (0·097 g.), m. p. 115—116°. The extent of racemisation in the recovered 1-phenylpent-2-en-1-ol was thus 16·4% whilst the retention of optical activity in the isomeric (+)-1-phenylpent-1-en-3-ol was 41%.

(iv) A solution of optically pure (−)-hydrogen phthalate (1·1932 g.) in chloroform (20 c.c.) had, when freshly prepared, α_D +0·18°; after 10 min., α_D +0·25°; after 24 hr., α_D +0·40° (unchanged after 3 days). During this period the chloroform solution deposited phthalic acid (0·11 g.); the recovered hydrogen phthalate {0·71 g.; $[\alpha]_D$ +7·6° (*c*, 1·365 in CS_2; *l*, 2)} was separated by crystallisation from carbon disulphide–light petroleum into optically pure (+)-1-ethyl-3-phenylprop-2-enyl hydrogen phthalate, m. p. 83°, $[\alpha]_D$ +53·3° (*c*, 1·400 in CS_2; *l*, 2), and the corresponding (±)-compound, m. p. 109—110°. The retention of optical activity is thus 14·2% (a duplicate experiment gave 13·8%).

(v) Duplication in benzene solution of experiment (iv) resulted in a retention of optical activity of 23·0%.

(vi) A specimen of the (−)-hydrogen phthalate (0·9 g.) after 15 days at room temperature was completely converted into the isomeric 1-ethyl-3-phenylprop-2-enyl hydrogen phthalate,

$[\alpha]_{\rm D}$ +20·66° (*c*, 1·548; *l*, 1), which fractional crystallisation separated into the (±)- and the optically pure (+)-isomeride. The retention of optical activity in this reaction is 38·7%.

In another experiment the reaction was stopped before isomeric change was complete: the recovered 1-phenylpent-2-en-1-yl hydrogen phthalate had racemised to the extent of 16·4%.

Conversion of (+)-1-*Phenylpent*-2-*en*-1-*yl Hydrogen Phthalate*.—(a) *Into* (±)-1-*ethyl*-3-*phenylprop*-2-*enyl acetate*. A solution of the (+)-hydrogen phthalate (1·722 g.) in glacial acetic acid (20 c.c.) showed $\alpha_{\rm D}$ +0·48° (*l*, 2) when freshly prepared and $\alpha_{\rm D}$ +0·75° next day. This solution yielded phthalic acid (0·81 g.) and 1-ethyl-3-phenylprop-2-enyl acetate, b. p. 90—92°/0·9 mm., $\alpha_{\rm D}^{20°}$ −0·15° (*l*, 0·5). The retention of optical activity is 0·25%.

(b) *Into* (−)-1-*ethyl*-3-*phenylprop*-2-*enyl methyl ether*. A solution of the (+)-hydrogen phthalate (1·70 g.; freshly prepared) in anhydrous methanol (20 c.c.) showed $\alpha_{\rm D}^{20}$ +0·68° (*l*, 2), a value which gradually decreased:

hr.	0·5	1	1·5	2	3	4	22	30	170
$\alpha_{\rm D}$	+0·62°	0·57°	0·50°	0·45°	0·39°	0·33°	0·15°	0·12°	0·06°

After removal of the solvent, 1-*ethyl*-3-*phenylprop*-2-*enyl methyl ether*, b. p. 120°/22 mm., $\alpha_{\rm D}^{20}$ −0·25° (*l*, 0·5), was recovered (Found: C, 81·7; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

Rearrangement of (−)-1-*Phenylpent*-2-*en*-1-*ol to* (+)-1-*Phenylpent*-1-*en*-3-*ol in Acid Solution*.—To a solution of the (−)-alcohol (0·6482 g.) in dioxan (12 c.c.) was added hydrochloric acid (0·36 c.c.; constant b. p.) followed by distilled water to 20 c.c. The observed rotatory power oft he freshly prepared solution, $\alpha_{\rm D}$ −0·54° (*l*, 2), changed steadily to +0·14° during 16 hr. and to +0·20° after 3 days. The recovered (+)-1-phenylpent-1-en-3-ol had $n_{\rm D}^{25}$ 1·5137, $\alpha_{\rm D}^{14°}$ +2·05° (*l*, 0·5); the retention of optical activity thus being 59% (see next paragraph).

Racemisation of (+)-1-*Phenylpent*-1-*en*-3-*ol in Acid Solution*.—To a solution of the (+)-alcohol [0·9875 g.; $\alpha_{\rm D}^{21°}$ +3·36° (*l*, 0·5)] in dioxan (12 c.c.) was added hydrochloric acid (0·36 c.c.) followed by distilled water to 20 c.c. The observed rotatory power, $\alpha_{\rm D}$ −2·00° (*l*, 2), changed steadily to −0·75° after 65 hr., to −0·30° after 94 hr., to ±0° after 144 hr., to +0·16° after 234 hr., and to +0·23° after 20 days. The recovered alcohol had $n_{\rm D}^{25}$ 1·5182, $\alpha_{\rm D}^{15°}$ +0·72° (*l*, 0·5), the loss in rotatory power being 79%. It thus follows that the isomeric (+)-1-phenylpent-1-en-3-ol produced in the preceding experiment would undergo partial racemisation after rearrangement. This implies that the rearrangement occurs with retention of optical activity considerably greater than 59%.

Conversion of (+)-1-*Phenyl-pent*-2-*en*-1-*ol*.—(a) *Into* (−)-1-*ethyl*-3-*phenylprop*-2-*enyl acetate*. A solution of the (+)-alcohol (*c*, 4·621; *l*, 2) in pure acetic acid had, when freshly prepared, $\alpha_{\rm D}$ +0·49°: this fell after 6 hr. to +0·15° and after 60 hr. to −0·27° (constant). The recovered 1-ethyl-3-phenylprop-2-enyl acetate had b. p. 90—91°/0·7 mm., $n_{\rm D}^{25}$ 1·5221, $\alpha_{\rm D}^{20}$ −1·30° (*l*, 0·5). The retention of optical activity is 3·7%.

(b) *Into* (−)-1-*ethyl*-3-*phenylprop*-2-*enyl* p-*diphenylylurethane*. A mixture of the (+)-alcohol (0·4 g.) and *p*-diphenylyl *iso*cyanate (0·5 g.) was heated on the steam-bath for 1 hr. The product, after crystallisation from benzene, had m. p. 147—160°, $[\alpha]_{\rm D}$ −13·2° (*c*, 1·513 in $CHCl_3$; *l*, 2). By fractional crystallisation from benzene it was separated into the *p*-diphenylylurethanes of (i) (±)-1-phenylpent-1-en-3-ol, m. p. 152°, and (ii) (−)-1-phenylpent-1-en-3-ol, m. p. 163°, $[\alpha]_{\rm D}$ −145° (*c*, 0·67 in $CHCl_3$; *l*, 2).

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