

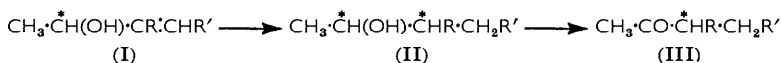
**243. Olefinic Additions with Asymmetric Reactants. Part V.\* The Asymmetric Hydrogenation of (–)-3-Methyl-4-phenylbut-3-en-2-ol and of (+)- $\alpha$ -Pinene.**

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(–)-3-Methyl-4-phenylbut-3-en-2-ol on hydrogenation gave (+)-3-methyl-4-phenylbutan-2-ol, which on oxidation yielded (–)-3-methyl-4-phenylbutan-2-one. A partial asymmetric synthesis is effected by these reactions: a new centre of asymmetry is formed at the 3-position with preponderance of one configuration, and the original centre at the 2-position is rendered symmetrical. Substantial separation of the diastereoisomeric methylphenylbutanols has been effected by vapour-phase chromatography, whence 22 and 17% asymmetric syntheses are deduced for the two sets of reactions.

By the use of vapour-phase chromatography, the hydrogenation of (+)- $\alpha$ -pinene is shown to give predominantly one form [(+)-*cis*] of pinane.

THERE has been described<sup>1</sup> a partial asymmetric synthesis in which (–)-3-ethylhept-3-en-2-ol on hydrogenation with Raney nickel catalyst gave (–)-3-ethylheptan-2-ol, which on oxidation yielded (+)-3-ethylheptan-2-one (I, II, III; R = Et, R' = Pr<sup>n</sup>); a new centre of asymmetry is formed at C<sub>(3)</sub> with preponderance of one configuration, and the original centre at C<sub>(2)</sub> is rendered symmetrical. A second example of an asymmetric synthesis of this type (where, in I, II, III, R = Me and R' = Ph) is now reported.



3-Methyl-4-phenylbut-3-en-2-one was prepared by the condensation of benzaldehyde with butan-2-one in the presence of hydrogen chloride.<sup>2</sup> In this ketone the phenyl group is *trans* to the carbonyl group, since oxidation with sodium hypochlorite yields  $\alpha$ -methyl-*trans*-cinnamic acid.<sup>3,4</sup> The present material, which behaved as a single entity when subjected to purification by zone-melting and by recrystallisation, on reduction with aluminium isopropoxide gave ( $\pm$ )-3-methyl-4-phenylbut-3-en-2-ol, which was resolved by fractional crystallisation of the brucine salt of its hydrogen phthalate. The (+)-hydrogen

TABLE I. Rotatory powers at 25°; l, 0.5.

Compound	$\alpha_{4358}$	$\alpha_{5088}$	$\alpha_{5461}$	$\alpha_{5893}$	$\alpha_{6438}$
CHPh·CMe·CHMe·OH (i) .....	–6.54°	–6.02°	–5.45°	–4.88°	–4.23°
(ii) .....	–6.41	–6.09	–5.47	–4.91	–4.28
CH <sub>2</sub> Ph·CHMe·CHMe·OH (i) .....	+11.63	+7.97	+6.67	+5.56	+4.39
(ii) .....	+10.94	+7.75	+6.41	+5.35	+4.32
CH <sub>2</sub> Ph·CHMe·COMe (i) .....	—	–2.58	–2.10	–1.76	–1.31
(ii) .....	—	–2.16	–1.76	–1.42	–1.07

phthalate, which gave the less soluble salt, was obtained from two resolutions as an oil of constant maximum rotatory power, which yielded the specimens of (–)-alcohol whose rotatory powers are recorded in Table I. Each was hydrogenated (in solution in ethanol, with W-3 Raney nickel catalyst,<sup>5</sup> the maximum temperature and pressure being 36° and 95 atm.) to (+)-3-methyl-4-phenylbutan-2-ol. Oxidation of this alcohol with chromic anhydride in acetic acid yielded (–)-3-methyl-4-phenylbutan-2-one, which was converted

\* Part IV, *J.*, 1957, 3407.

<sup>1</sup> Arcus and Smyth, *J.*, 1955, 34.

<sup>2</sup> Harries and Müller, *Ber.*, 1902, **35**, 966.

<sup>3</sup> Stoermer and Wehln, *Ber.*, 1902, **35**, 3552.

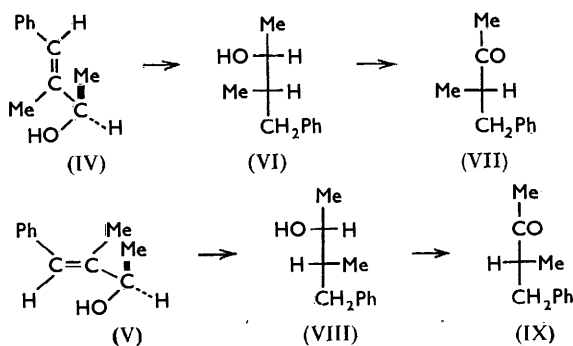
<sup>4</sup> Stoermer and Voht, *Annalen*, 1915, **409**, 49.

<sup>5</sup> Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471.

into the (–)-semicarbazone and the (–)-4-phenylsemicarbazone. Rotatory powers of the butanols and butanones are recorded in Table 1.

The stereochemistry of the hydrogenation of (–)-3-ethylhept-3-en-2-ol is discussed, together with the relevant literature, in Part III,<sup>1</sup> the following conclusions, applicable to the present hydrogenations, being reached: (a) The addition of hydrogen is *cis* to that surface of the molecule which is adjacent to the nickel surface. (b) No asymmetric synthesis can result if adsorption, and hence hydrogenation, were to occur with equal ease at either side of the double bond; hence the asymmetric carbon atom must determine the conformation in which the molecule is adsorbed, *i.e.*, asymmetric adsorption precedes, and leads to, asymmetric addition of hydrogen.

The present asymmetric synthesis demonstrates the (–)-3-methyl-4-phenylbut-3-en-2-ol to have been adsorbed asymmetrically on the nickel surface. In the deduction of the conformation so taken up, there are two main considerations: that the side of the molecule which becomes adjacent to the nickel surface is the one conforming most closely to a plane,<sup>6,7</sup> and that lone pairs and  $\pi$ -electrons interact with the nickel surface. Two conformations (IV) and V\*) are available which, equally, place the styryl portion of the molecule and the oxygen atom close to the plane of the paper. It is found, however, from examination of C.R.L.-Catalin models, that there is closer crowding of the two methyl groups in (V) than in (IV); hence the latter is the more probable conformation. Hydrogenation of conformation (IV), from below the plane of the paper, yields the methylphenylbutanol (VI) which on oxidation forms the methylphenylbutanone (VII). On the other hand, insofar as the (–)-alcohol is adsorbed in conformation (V), there result the diastereoisomeric methylphenylbutanol (VIII) and the enantiomeric ketone (IX).



The percentage asymmetric synthesis cannot be estimated from the rotatory power of specimens of (–)-3-methyl-4-phenylbutan-2-one because the rotation of the optically pure ketone is unknown, and, although the rotations of the semicarbazone and 4-phenylsemicarbazone remained substantially constant on recrystallisation, this (from data below) is probably because the ratio of active to racemic compound remains nearly constant.

Towards the end of this investigation we were fortunate in having carried out for us, by Dr. J. N. Haresnape and Mr. W. T. Swanton, at The British Petroleum Company Research Centre, Sunbury-on-Thames, a vapour-phase chromatographic examination of the hydrogenated alcohols and the corresponding ketones, and of two pinanes (see below). The chromatogram of (+)-3-methyl-4-phenylbutan-2-ol in each instance showed two substantially separate, but overlapping peaks, the less volatile component forming

\* The absolute configuration of the asymmetric centre in the alcohol (IV) being unknown, a configuration has been arbitrarily selected.

<sup>6</sup> Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

<sup>7</sup> Prelog, *Bull. Soc. chim. France*, 1956, 987.

the larger peak. The (–)-3-methyl-4-phenylbutan-2-one in each instance gave a single peak.

The chromatograms of the ketone showed there to be present about 1% of a low-boiling impurity and traces of, probably, the original alcohol.

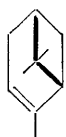
The two peaks observed with the (+)-methylphenylbutanols are identified as the diastereoisomeric alcohols (VI, or its enantiomer) and (VIII, or its enantiomer). The single peak found for the ketone accords with the latter's being an (unequal) mixture of the enantiomers (VII and IX). (Optical isomers would not be expected to separate on a symmetrical chromatographic medium.) The molecular ratio of the diastereoisomeric methylphenylbutanols is equal to that of the areas under the two peaks of the chromatogram. These, as stated, overlap; they have been approximately separated by the ordinate through the minimum between them and the areas measured. The ratios so found were: (i) 1.55 : 1; (ii) 1.42 : 1.

Where  $a$  and  $b$  are the areas under the two peaks, the percentage asymmetric synthesis is given by  $100(a - b)/(a + b)$ ; the values so obtained are (i) 21.5 and (ii) 17.3%.

Further, the ratio of the percentages of asymmetric synthesis for the two sets of experiments is 1.24 : 1; this accords with the ratio of the values of  $\alpha_{5893}$  for the respective specimens of (–)-3-methyl-4-phenylbutan-2-one, 1.24 : 1, a result tending to confirm that the percentage of asymmetric synthesis can be determined by vapour-phase chromatography.

(+)- $\alpha$ -Pinene.—The separation of the 3-methyl-4-phenylbutan-2-ols appears to be the first instance of the vapour-phase chromatographic separation of diastereoisomers which are not also geometrical isomers, separation of the *cis*- and *trans*-isomers of 2-, 3-, and 4-methylcyclohexanol having been reported by Komers, Kochloeff, and Bazant.<sup>8</sup> These separations point to considerable simplification in the investigation of product ratios in asymmetric reactions of the type:  $dA - \text{sym}X \longrightarrow dA - dY + dA - lY$ . Hitherto it has been necessary either to work with optically active material, remove the original centre of asymmetry, and determine the optical purity of the product, or to rely on the separation of mixtures of diastereoisomers by fractional crystallisation. (Fractional distillation and chromatography on a solid phase have also found limited application.) Where practicable, the direct separation and quantitative estimation of diastereoisomers by vapour-phase chromatography is clearly more satisfactory.

The assistance given by this method in studies of the kind above is further exemplified by the following. (+)- $\alpha$ -Pinene (X), in ether, was hydrogenated with W-3 Raney nickel catalyst (maximum temperature and pressure 107° and 103 atm.). The greater part of



(X)

the product appeared to be a single entity having refractive index and density in good agreement with those of *cis*-pinane.\* (The values for *trans*-pinane are a little lower; however, *cis*-pinane is the major product from hydrogenation of  $\alpha$ - and  $\beta$ -pinene under mild conditions.<sup>9</sup>)

On vapour-phase chromatography of the main and the immediately preceding fractions of pinane, each gave a single sharp major peak having a small shoulder on the more volatile side. It appears reasonable to ascribe the main peak to *cis*-pinane and the shoulder to an isomer, presumably *trans*-pinane, estimated to form 1% of the specimens. (There were also two small low-boiling impurities totalling  $\approx$ 1% of the specimens.)

Hydrogenation of (+)- $\alpha$ -pinene would be expected to proceed preferentially through the adsorption-conformation which presents the double bond most closely to a plane, *i.e.*, that having the isopropylidene bridge remote from the surface. On hydrogenation this yields *cis*-pinane, a result in accordance with the experimental finding.

\* The *cis*-compound is that having the methyl group and the isopropylidene bridge in the *cis*-relationship.

<sup>8</sup> Komers, Kochloeff, and Bazant, *Chem. and Ind.*, 1958, 1405.

<sup>9</sup> Lipp, *Ber.*, 1923, 56, 2098; 1930, 63, 411; Fisher, Stinson, and Goldblatt, *J. Amer. Chem. Soc.*, 1953, 75, 3675.

## EXPERIMENTAL

M. p.s are corrected. Unless otherwise stated, heating was on a steam-bath, ethanol refers to the 96% alcohol, and the rotations of undiluted liquid compounds were determined at  $l$  1.0, and those of solutions at  $l$  1.0.

3-Methyl-4-phenylbut-3-en-2-one,<sup>2</sup> b. p. 131—132°/12 mm., m. p. (by the conventional method) 38° (100 g.), was melted in a 45 cm. tube, which was then lowered at 2 cm./hr. through an annular copper jacket, through which water at 50° was circulating, into a constant-level bath of ice and water. When nine-tenths of the ketone had solidified, the remainder was removed by suction. The f. p. of the ketone was determined by plotting the cooling curve of a stirred specimen placed in a bath at 33°. After two passages the ketone had f. p. 36.25°, unchanged by further treatment; the original ketone, after recrystallisation from light petroleum (b. p. 60—80°) also had f. p. 36.25°.

To a solution of aluminium isopropoxide (from aluminium 85 g., propan-2-ol 1500 ml., and mercuric chloride 1 g.) was added 3-methyl-4-phenylbut-3-en-2-one (230 g.); the whole was boiled under reflux for 45 min. and acetone then removed by distillation at slightly reduced pressure. The product was cooled and added to excess of 6N-sulphuric acid and ice. The whole was extracted with ether, the aqueous layer having been saturated with sodium chloride. The extract was washed with 2N-sulphuric acid, with 2N-sodium hydroxide, and with water, then dried ( $K_2CO_3$ ). It yielded ( $\pm$ )-3-methyl-4-phenylbut-3-en-2-ol (166 g.), having on redistillation, b. p. 92°/0.2 mm.,  $n_D^{25}$  1.5600 (Found: C, 81.7; H, 8.8.  $C_{11}H_{14}O$  requires C, 81.45; H, 8.7%).

This alcohol (7.8 g.), pyridine (6.2 g.), and acetic anhydride (6.5 g.) were kept at room temperature for 2½ days, thus yielding the acetate (7.7 g.), b. p. 88—88.5°/0.2 mm.,  $n_D^{25}$  1.5250 (Found: C, 76.9; H, 8.15.  $C_{13}H_{16}O_2$  requires C, 76.4; H, 7.9%).

The ( $\pm$ )-alcohol (11.7 g.) was allowed to react with finely divided potassium (3.0 g.) in benzene (40 ml.), the whole being refluxed for ½ hr. Methyl iodide (13.2 g.) in benzene (10 ml.) was added portionwise, the mixture being finally refluxed for ¾ hr. After being washed with dilute hydrochloric acid and water, the benzene solution was dried ( $Na_2SO_4$ ) and distilled. It gave the methyl ether (3.6 g.), b. p. 64—66°/0.5 mm.,  $n_D^{25}$  1.5195 (Found: C, 81.75; H, 9.5.  $C_{12}H_{16}O$  requires C, 81.8; H, 9.15%).

The following were prepared by the methods described below for the corresponding optically active compounds.

( $\pm$ )-3-Methyl-4-phenylbut-3-en-2-ol yielded ( $\pm$ )-3-methyl-4-phenylbutan-2-ol, b. p. 80—81°/0.3 mm.,  $n_D^{25}$  1.5138 (Colonge and Pichat<sup>10</sup> record b. p. 124°/11 mm.,  $n_D^{10}$  1.5190). This alcohol (1.64 g.) was heated (oil-bath) under reflux for 2 hr. with 1-isocyanatonaphthalene (1.86 g.) in light petroleum (b. p. 100—120°; 10 ml.). After two weeks the crystalline product (3.50 g.) was collected; it yielded, after 5 recrystallisations from the above solvent, one diastereoisomeric racemate of the ( $\pm$ )-N- $\alpha$ -naphthylcarbamate (0.80 g.), needles, m. p. 73.5—74.5° (Found: C, 79.05; H, 7.05; N, 4.0.  $C_{22}H_{23}O_2N$  requires C, 79.1; H, 6.95; N, 4.2%).

Oxidation of the methylphenylbutanol gave ( $\pm$ )-3-methyl-4-phenylbutan-2-one, b. p. 72—73.5°/0.5 mm.,  $n_D^{25}$  1.5041,  $n_D^{18}$  1.5066 (semicarbazone, needles, m. p. 116.5°). Its 4-phenylsemicarbazone, which separated having m. p. 85.5—86.5°, had after successive recrystallisations from aqueous ethanol, m. p. 120—121°, 88.5—89°, 120—121° (needles); it is presumed to be dimorphic (Found: C, 73.35; H, 6.65; N, 14.3. Calc. for  $C_{18}H_{21}ON_3$ : C, 73.2; H, 7.15; N, 14.2%) (Colonge and Pichat<sup>11</sup> record b. p. 106°/9 mm. and  $n_D^{18}$  1.5065 for the ketone, and m. p. 114° for the semicarbazone).

Phthalic anhydride (148 g.) was partly dissolved in hot pyridine (84 g.); the mixture was cooled, the ( $\pm$ )-butenol (162 g.) was added and the whole heated under reflux for 3 hr. The resultant solution was cooled, diluted with an equal volume of acetone, and added with stirring to excess of 3N-hydrochloric acid and ice. The oil which separated was stirred with 2N-hydrochloric acid, then dissolved in ether; the solution was extracted with aqueous sodium hydrogen carbonate, and the latter was acidified with hydrochloric acid. The oil which separated solidified; the ( $\pm$ )-hydrogen phthalate was ground, washed with water, and dried. It (227 g.) had m. p. 73.5—76.5° (Found: equiv., 338.  $C_{18}H_{17}O_2CO_2H$  requires equiv., 310).

<sup>10</sup> Colonge and Pichat, *Bull. Soc. chim. France*, 1949, 177.

(a) All specimens of this phthalate had an equivalent in excess of the theoretical. It is possible that a hydrate is formed. For calculation of the quantity of ethruine required for the salt, the equivalent determined by titration was used. (b) Traces of ether were removed from specimens to be used for rotation measurements by pumping at 40°, for 5 min. at 15 mm., and for 15 min. at 1 mm. The phthalate then formed a colourless oil. (c) Chloroform containing 1% of ethanol as stabiliser was necessary for use in the determination of rotations. (d) More drastic drying or solvent-removal, and the use of non-stabilised chloroform containing carbonyl chloride, resulted in the separation of phthalic acid.

To a solution of the ( $\pm$ )-hydrogen phthalate (200 g.) in acetone (400 ml.) anhydrous ethruine (233.5 g.) was added, and the whole was boiled under reflux until a homogeneous solution was obtained. On cooling, the alkaloidal salt (274 g.) separated. The specific rotation of the hydrogen phthalate derived from a portion of the salt after seven recrystallisations from acetone ( $[\alpha]_{5893}^{25} + 53^\circ$ ; *l* 2; *c* 2) was unaltered after four further recrystallisations. [The same value was attained in resolution (ii).] The optically pure salt (90 g.) was suspended in acetone (200 ml.) and shaken with 3*N*-hydrochloric acid and ice; the whole was extracted with ether; the extract was washed with 2*N*-hydrochloric acid, then with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure, yielding the (+)-hydrogen phthalate as a colourless oil (35 g.; equiv., 336). It was dissolved in ethanol (128 ml.), and potassium hydroxide (33.7 g.) in water (117 ml.) was added. The whole was heated under reflux for 1 hr., then steam-distilled. The distillate was saturated with sodium chloride and extracted with ether; the latter was dried ( $\text{K}_2\text{CO}_3$ ), and yielded the (–)-*alcohol* (14.0 g.), b. p. 90.5–91°/0.3 mm.,  $n_D^{25}$  1.5576,  $d_4^{25}$  0.998 (Found: C, 81.2; H, 8.35.  $\text{C}_{11}\text{H}_{14}\text{O}$  requires C, 81.45; H, 8.7%).

The (–)-*alcohol* (i; 12.7 g.) in ethanol (75 ml.) was hydrogenated in the presence of W-3 Raney nickel<sup>5</sup> (1 g.) with stirring for 1½ hr., then kept overnight without stirring, and stirred for a further 3 hr.; the maximum temperature and pressure attained were 36° and 90 atm. The solution was filtered and evaporated; the product was diluted with ether and dried for 5 days with two portions of potassium carbonate; it yielded (+)-3-*methyl-4-phenylbutan-2-ol* (i; 10.75 g.), b. p. 88°/1.1 mm.,  $n_D^{25}$  1.5141,  $d_4^{25}$  0.968 (Found: C, 79.8; H, 9.65.  $\text{C}_{11}\text{H}_{16}\text{O}$  requires C, 80.45; H, 9.8%).

A solution of this alcohol (5.32 g.) in acetic acid (10 ml.) was placed in a bath at 80°. A suspension of powdered chromic anhydride (3.85 g.) in acetic acid (20 ml.) was added during 17 min., with stirring which was continued for a further 17 min. The mixture was cooled and poured into water (50 ml.); the whole was extracted with light petroleum (b. p. 40–60°); the extract was washed with aqueous sodium hydrogen carbonate and water, dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure. The product yielded, on redistillation, (–)-3-*methyl-4-phenylbutan-2-one* (i; 1.52 g.), b. p. 71–73°/1.1 mm.,  $n_D^{25}$  1.5042 (Found: C, 81.25; H, 8.55.  $\text{C}_{11}\text{H}_{14}\text{O}$  requires C, 81.45; H, 8.7%). Closely similar adjacent fractions totalled 1.21 g. This ketone (1.02 g.) gave a 4-*phenylsemicarbazone* (1.60 g.), (after two recrystallisations from ethanol, 1.19 g.; needles), m. p. 119.5–120.5°,  $[\alpha]_{5893}^{25} - 1.4^\circ$  (*c* 5.032) (Found: C, 72.8; H, 6.65; N, 14.4%).

The butenol (ii; 13.6 g.) was hydrogenated as above except that the stirring times were 3 hr. on the first day and 1½ hr. on the second (max. 29°, 95 atm.); there was obtained (+)-3-*methyl-4-phenylbutan-2-ol* (ii; 12.0 g.), b. p. 84–85.5°/0.4 mm.,  $n_D^{25}$  1.5145,  $d_4^{25}$  0.970 (Found: C, 80.2; H, 9.6%). This alcohol was oxidised as above in three portions of 3.3 g.; the combined products on redistillation yielded the (–)-ketone (ii; 2.16 g.), b. p. 69.5–71°/0.3 mm.,  $n_D^{25}$  1.5039,  $d_4^{25}$  0.967 (Found: C, 80.85; H, 8.45%), and closely similar adjacent fractions totalling 1.83 g. This ketone (1.43 g.) gave a *semicarbazone* (1.53 g.), m. p. (after two recrystallisations from aqueous ethanol; needles), 116.5°,  $[\alpha]_{5893}^{25} - 2.3^\circ$  (*c* 3.035) (Found: C, 65.5; H, 7.4; N, 19.25.  $\text{C}_{12}\text{H}_{17}\text{ON}_3$  requires C, 65.7; H, 7.8; N, 19.15%). The combined fractions (1.67 g.;  $\alpha_{5893}^{25} - 1.28^\circ$ ) adjacent to ketone (ii) gave a 4-*phenylsemicarbazone* (2.44 g.), m. p. 114.5–115.5°,  $[\alpha]_{5893}^{25} - 1.9^\circ$  (*c* 5.350 in  $\text{CHCl}_3$ ); after two recrystallisations it had m. p. 119–120°,  $[\alpha]_{5893}^{25} - 1.7^\circ$  (*c* 5.447) (Found: C, 73.3; H, 6.75; N, 14.5%).

(+)- $\alpha$ -*Pinene*.—Repeated fractionation of pinene from *Pinus halipensis* through a heated 20 cm. column, packed with glass helices, gave (+)- $\alpha$ -pinene, b. p. 156°,  $n_D^{20}$  1.4661,  $n_D^{25}$  1.4636,  $d_4^{20}$  0.859,  $d_4^{25}$  0.856,  $\alpha_{5893}^{25} + 81.75^\circ$  (*l* 2), whence  $[\alpha]_{5893}^{25} + 47.78^\circ$ .

It (100 g.) was hydrogenated in ether (200 ml.), in the presence of W-3 Raney nickel catalyst (3 g.); the pressure was initially 99 atm. at 16°, and during 4 hr. the temperature was raised to 107° (max. pressure 103 atm.). The product was thrice distilled; in order to minimise heating, no column was used in these distillations. The fractions obtained are tabulated.

	(i)			(ii)			
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
B. p. ....	166—169	166—168	169	166	166	166—167	167—168°
$n_D^{25}$ .....	—	1.4603	1.4603	1.4579	1.4600	1.4602	1.4602
Wt. (g.) ...	95.4	67.2	21.5	2.4	5.3	42.8	10.1

The following further measurements were made:

Fraction	$n_D^{20}$	$d_4^{20}$	$d_4^{25}$	$\alpha_{5893}^{25}$		$[\alpha]_{5893}^{25}$
(v)	1.4623	0.857	0.854	+9.65°	0.5	+22.61°
(vi)	1.4626	0.857	0.854	+39.33	2	+23.03
(vii)	—	—	—	+39.76	2	—

Confirmed comparable b. p.s for *cis*- and *trans*-pinane are lacking; on refractive indices and densities there is agreement as follows: *cis*-pinane,  $n_D^{20}$  1.4624,  $d_4^{20}$  0.857,  $d_4^{25}$  0.853;<sup>9</sup> and for *trans*-pinane,  $n_D^{20}$  1.4619,  $d_4^{20}$  0.856,  $d_4^{25}$  0.852.<sup>9,11</sup> The final main fraction (vi) and its preceding fraction (v) were subjected to vapour-phase chromatography.

The conditions for chromatography of the methylphenylbutan-ols and -ones were: Column: 120 × 0.4 cm. Temp., 150°. Packing: 20% tritolyl phosphate on 100—120 mesh Celite 545. Carrier gas: argon, with Lovelock ionisation detector. Inlet pressure: 110 cm. Hg. Outlet pressure: atmospheric. Rate of flow: 33 ml./min. For the pinanes, conditions were as above except that measurements were made at 75° and 50°, the rate of flow being 41 ml./min; measurements were also made with squalane as packing, at 75°.

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<sup>11</sup> Schmidt, *Chem. Ber.*, 1947, **80**, 520.