260. *Alkenylation employing Lithium Alkenyls. Part VII.* The Reaction of* iso*Butenyl-lithium with Ethylenic Ketones.*

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*iso*Butenyl-lithium, previously obtained from *iso*butenyl bromide, is also readily formed from the chloride. Its reactions with methyl vinyl ketone, methyl propenyl ketone, and mesityl oxide have been examined and compared with those of the corresponding ethylenic aldehydes.

Di*iso*butenylcarbinol and di*iso*butenylmethylcarbinol, obtained from the reactions of *iso*butenyl-lithium with β-methylcrotonaldehyde and mesityl oxide, respectively, undergo rearrangement with extreme ease in the presence of dilute acids to the isomers (IV) and (VII), and represent the most mobile oxotropic systems yet known. The isomer (IV) has been synthesised by an alternative route.

IN previous papers (Parts I—III, *J.*, 1950, 2000—2014) the conversion of *iso*butenyl bromide into *iso*butenyl-lithium and the addition reactions of the latter with a variety of carbonyl compounds were described. We have now examined the direct metalation of *iso*butenyl chloride and the alkenylation of αβ-ethylenic ketones as well as of β-methylcrotonaldehyde. The object of the work was threefold : (*a*) to establish to what extent the coupling reaction which accompanies alkenylation with *iso*butenyl bromide, but which is not observed in the case of propenyl bromide (Part V, *J.*, 1951, 2078) or *cyclo*alkenyl chlorides (Part IV, *J.*, 1950, 2014; Part VI;* Braude and Forbes, *J.*, 1951, 1755), is caused by the alkenyl moiety or by the halogen or the carbonyl compound, severally, (*b*) to confirm that the alkenylation of αβ-ethylenic ketones, like those of αβ-ethylenic aldehydes previously studied, proceeds normally and is not accompanied by 1 : 4-addition (1 : 4-addition of lithium derivatives to unsaturated ketones had been noted in certain cases, cf. Tucker and Whalley, *J.*, 1949, 50), and (*c*) to synthesise some missing members in the series of dialkenylcarbinols required in investigations on anionotropic systems.

*iso*Butenyl chloride, conveniently prepared from *iso*butaldehyde by treatment with phosphorus pentachloride, followed by dehydrochlorination (Kirrman, *Bull. Soc. chim.*, 1948, 15, 163), reacts somewhat less readily than the corresponding bromide with lithium in ether. The difference in reactivity of the two halogen derivatives appears to be smaller than is usual in other reactions of this type, but is to be expected in terms of the mechanism previously suggested for the metalation process (Part V, *loc. cit.*) since the carbon–chlorine bond is stronger than the carbon–bromine bond and since its dimensions are less favourable for accommodation on the metal lattice.

The reaction of *iso*butenyl-lithium with methyl vinyl ketone yielded mainly polymeric material together with 2 : 5-dimethylhexa-2 : 4-diene (*ca.* 35%), but none of the expected

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* Part VI, preceding paper.

carbinol could be isolated. This is in contrast to the reaction of *iso*butenyl-lithium with acraldehyde (Part II, *loc. cit.*) as well as those of methyl vinyl ketone with Grignard reagents (Cymerman, Heilbron, and Jones, *J.*, 1944, 144; Lebedeva and Shlyakova, *J. Gen. Chem. Russia*, 1949, **19**, 1290), which gave the expected carbinols, although failure has been reported in one instance (Smith and Sprung, *J. Amer. Chem. Soc.*, 1943, **65**, 1276). Moreover, the extent of the coupling reaction, while of the same order as in alkenylations employing *iso*butenyl bromide, is much larger than in the other three cases described in the sequel, in which no diene was isolated, though small amounts may also be formed. From these facts, it may be inferred (*a*) that the extent of coupling, presumably by the reaction RHal + RLi ⟶ RR + LiHal, during the actual metalation is much less in the case of the chloride than of the bromide, as would be expected by analogy with other cases (Ziegler and Colonius, *Annalen*, 1930, **479**, 135), (*b*) that coupling of the lithium alkenyl, once formed, can be induced by methyl vinyl ketone and is concomitant with the polymerisation reaction. Somewhat similar observations have been made with *tert.*-butylmagnesium halides which yield appreciable proportions of hexamethylethane when reacting with carbonyl compounds, although none of the hydrocarbon is obtained by the interaction of the halides and Grignard reagents alone (Whitmore, Stehman, and Herndon, *J. Amer. Chem. Soc.*, 1933, **55**, 3807; Shine, *J.*, 1951, 11). Evidence has been adduced that the coupling does *not* involve a free-radical process, and although no certain conclusions can be drawn, it seems likely that the same applies in the present case, and that the coupling may arise as a side reaction of the polymerisation of the methyl vinyl ketone by the lithium alkenyl. Other instances of such polymerisation have been investigated in detail by Ziegler and his co-workers (cf *Annalen*, 1929, **473**, 1; 1934, **511**, 13 *et seq.*).

The reactions of *iso*butenyl-lithium with methyl propyl ketone and with mesityl oxide afforded low yields of the carbinols (I) and (III), together with higher-boiling products, but no dimethylhexadiene was isolated. The low yields (10—15%) of the carbinols contrast with those obtained from the corresponding ethylenic aldehydes (cf. Part II, *loc. cit.*, and below). The carbinol (III), a low-melting solid, has previously been prepared by Fellenberg (*Ber.*, 1904, **37**, 3578) in 2·5% yield from phorone and methylmagnesium iodide; a greatly improved yield (60%) has now been obtained by employing methylmagnesium bromide.

$$\mathrm{CHMe{:}CH{\cdot}COMe} \xrightarrow{\mathrm{CMe_2{:}CHLi}} \underset{\text{(I)}}{\mathrm{CHMe{:}CH{\cdot}CMe(OH){\cdot}CH{:}CMe_2}} \xrightarrow{\mathrm{H^+}} \underset{\text{(II)}}{\mathrm{CHMe{:}CH{\cdot}CMe{:}CH{\cdot}CMe_2{\cdot}OH}}$$

Both the carbinols (I) and (III) readily undergo the usual oxotropic rearrangement in the presence of dilute acids. The rearrangement of (I) was not examined in detail, but by analogy with earlier work on unsymmetrical systems (Part II, *loc. cit.*), the initial product is expected to be the tertiary isomer (II). The rearrangement of the symmetrical carbinol (III) can only give one product (IV). The constitution of (IV) was confirmed by catalytic hydrogenation to 2 : 4 : 6-trimethylheptan-2-ol, characterised as the 3 : 5-dinitrobenzoate, and by an alternative synthesis from methylmagnesium bromide and methyl 3 : 5-dimethylhexa-2 : 4-dienoate (V), obtained by the Reformatski reaction of mesityl oxide and methyl bromoacetate. The carbinol (IV) exhibits anomalous ultra-violet light absorption; the maximum is at somewhat shorter wave-length (2290 Å) than expected for a trialkylated diene and the extinction coefficient (ε, 8000) is less than half the usual value. Similar anomalies are shown by 1 : 1 : 3-trimethylbutadiene (Lunt and Sondheimer, *J.*, 1950, 2957) and by the ester (V); they undoubtedly arise from steric hindrance to a coplanar all-*trans*-configuration of the conjugated systems and will be discussed in more detail in another series (cf. *J.*, 1949, 1890; Part I, *loc. cit.*).

$$\begin{tikzcd}
\mathrm{CMe_2{:}CH{\cdot}COMe} \arrow[r, "\mathrm{CMe_2{:}CHLi}"] & \underset{\text{(III)}}{\mathrm{CMe_2{:}CH{\cdot}CMe(OH){\cdot}CH{:}CMe_2}} \arrow[d, "\mathrm{H^+}"] & \mathrm{CMe_2{:}CH{\cdot}CO{\cdot}CH{:}CMe_2} \arrow[l, "\mathrm{MeMgBr}"'] \\
 & \underset{\text{(IV)}}{\mathrm{CMe_2{:}CH{\cdot}CMe{:}CH{\cdot}CMe_2{\cdot}OH}} & \underset{\text{(V)}}{\mathrm{CMe_2{:}CH{\cdot}CMe{:}CH{\cdot}CO_2Me}} \arrow[l, "\mathrm{MeMgBr}"']
\end{tikzcd}$$

In contrast to its reaction with the ethylenic ketones, the addition of *iso*butenyl-lithium to β-methylcrotonaldehyde gives a 50% yield of the expected di*iso*butenylcarbinol (VI). This is extremely sensitive to acids and probably represents the most mobile oxotropic system yet described. Although it contains one methyl substituent less than the homologue (III), it rearranges even more readily and is completely isomerised to (VII) by 0·001N-hydrochloric acid at room temperature in a few minutes. The great sensitivity of di*iso*butenylcarbinol to traces of acidic impurities and the ease of dehydration of its isomer to the triene (VIII) render the isolation of both carbinols difficult except under very carefully controlled conditions. An attempt to prepare di*iso*butenyl carbinol by the reduction of phorone with lithium aluminium hydride yielded mainly the triene (VIII).

$$\mathrm{CMe_2{:}CH{\cdot}CHO} \xrightarrow{\mathrm{CMe_2{:}CHLi}} \underset{\text{(VI)}}{\mathrm{CMe_2{:}CH{\cdot}CH(OH){\cdot}CH{:}CMe_2}} \xrightarrow{\mathrm{H^+}}$$

$$\underset{\text{(VII)}}{\mathrm{CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH}} \xrightarrow{-\mathrm{H_2O}} \underset{\text{(VIII)}}{\mathrm{CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH_2}}$$

EXPERIMENTAL

(All reactions were carried out under purified nitrogen. M. p.s were taken on a Kofler block and are corrected.)

iso*But*-1-*enyl-lithium.*—The preparation of *iso*butenyl chloride was adapted from Kirrman (*Bull. Soc. chim.*, 1948, **15**, 163). *iso*Butaldehyde (170 g.) was added to phosphorus pentachloride (500 g.) at 0°. After the vigorous initial reaction, the mixture was kept for 2 hours with occasional shaking and then added dropwise to ice-water (3 l.). The product was extracted with ether (1 l.), and the ethereal solution was dried ($CaCl_2$) and fractionated, giving 1 : 1-dichloro-3-methylpropane (135 g.), b. p. 107—108°. The latter was added in small portions to potassium hydroxide (65 g.) in ethylene glycol (300 ml.). The mixture was kept at 120° for 6 hours and then slowly distilled, giving *iso*butenyl chloride (50 g.) which after refractionation from a trace of sodium had b. p. 63°/740 mm., n_D^{20} 1·4192. A sample kindly given to us by Dr. S. H. Harper had b. p. 67°/750 mm., n_D^{19} 1·4212. Kirrman (*loc. cit.*) gives b. p. 67—69°, n_D^{20} 1·422; Frank and Blackham (*J. Amer. Chem. Soc.*, 1950, **72**, 3283) give b. p. 76°/740 mm., n_D^{20} 1·4224.

For the formation of *iso*butenyl-lithium, the chloride (46 g., 0·5 mole) is slowly added to a stirred suspension of finely-cut lithium (6·9 g., 1 mole) in sodium-dried ether (1 l.) (cf. Part I, *J.*, 1950, 2000). Reaction sets in after approx. ½ hour and is completed by gentle refluxing overnight. Less than 0·5 g. of unchanged metal then remains and is conveniently removed by means of a wire-gauze spoon.

Reaction with Methyl Vinyl Ketone.—Anhydrous methyl vinyl ketone (40 g.) in ether (50 ml.) was added slowly to a stirred ethereal solution of *iso*butenyl-lithium (from Li, 6·9 g.) at 0°. After 2 hours, saturated aqueous ammonium chloride solution (500 ml.) was added. Insoluble polymeric material (20 g.) was filtered off and the ethereal layer was separated, dried, and fractionated, giving 2 : 5-dimethylhexa-2 : 4-diene (9 g., 33%), b. p. 60—65°/135 mm., n_D^{23} 1·4752, $\lambda_{max.}$ 2420 Å, ε 21 500 (in EtOH), which solidified on cooling to 0° and formed crystals, m. p. 10° (Braude and Timmons, Part I, *loc. cit.*, give m. p. 11°, n_D^{18} 1·4780, and $\lambda_{max.}$ 2410 Å, ε 22 500).

Reaction with Methyl Propenyl Ketone.—Fractionation of a commercial sample of the ketone gave material boiling over the range 122—124°/770 mm., but of constant refractive index (n_D^{20} 1·4340) which contained about 15% of mesityl oxide as indicated by the intensity of an absorption band at 1660 cm.$^{-1}$ in the infra-red spectrum, kindly determined by Dr. E. S. Waight. The ketone (42 g.) in ether (50 ml.) was added dropwise to a stirred ethereal solution of *iso*butenyl-lithium (from Li, 6·9 g.) at 0°. Stirring was continued for 2 hours, excess of aqueous ammonium chloride was then added, and the ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated, giving the following products : (i) unchanged methyl propenyl ketone (8 g.), b. p. 65°/130 mm., identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158°; (ii) unchanged mesityl oxide (6·5 g., 13%), b. p. 70°/130 mm., identified as the 2 : 4-dinitrophenylhydrazone which was chromatographed (alumina–benzene) and had m. p. and mixed m. p. 202—203° (Found : C, 51·5; H, 5·2; N, 19·7. Calc. for $C_{12}H_{14}O_4N_4$: C, 51·9; H, 5·1; N, 20·1%); (iii) iso*butenylmethylpropenylcarbinol* (2 : 4-*dimethylhepta*-2 : 5-*dien*-4-*ol*)

(10·4 g., 15%), which after refractionation had b. p. 77—79°/17 mm., $n_{\rm D}^{22}$ 1·4667 (Found : C, 77·3; H, 11·3. $C_9H_{16}O$ requires C, 77·1; H, 11·5%), and exhibited no light absorption with $\varepsilon > 1000$ in the 2200—4000-Å range in ethanol containing 0·1% of sodium ethoxide; (iv) a higher-boiling product (13 g.), b. p. 140°/0·5 mm., $n_{\rm D}^{23}$ 1·4922 (Found : C, 73·3; H, 9·1%), which exhibited no light absorption with $E_{1\,\text{cm.}}^{1\%} > 100$ in the 2200—4000-Å range. It did not form a 2 : 4-dinitrophenylhydrazone and was not further investigated.

On treatment with 0·002M-hydrochloric acid in 60% acetone for 1 hour at room temperature, the above dienol was converted into a conjugated isomer, formulated as 2 : 4-*dimethylhepta*-3 : 5-*dien*-2-*ol*, b. p. 95°/16 mm., $n_{\rm D}^{22}$ 1·4802 (Found : C, 77·8; H, 11·1. $C_9H_{16}O$ requires C, 77·1; H, 11·5%). Light absorption in ethanol : maximum, 2280 Å (ε 13 000), inflexion, 2350 Å (ε 12 000).

Reaction with Mesityl Oxide.—Mesityl oxide (25 g.) in ether (50 ml.) was added during 1 hour to an ethereal solution of *iso*butenyl-lithium (from Li, 3 g.) at 0°. Stirring was continued for 1 hour and then excess of aqueous ammonium chloride was added. The products were isolated as above and fractionated through a 12″ Fenske column, giving (i) unchanged mesityl oxide (4 g.), b. p. 65°/110 mm., identified as the 2 : 4-dinitrophenylhydrazone, m. p. 203°; (ii) di*iso*butenylmethylcarbinol (2 : 4 : 6-trimethylhepta-2 : 5-dien-4-ol) (2 g., 8%), b. p. 36°/0·2 mm., which solidified on being kept and after recrystallisation from pentane had m. p. 56°, undepressed on admixture with the authentic sample described below, (iii) a higher-boiling product (14·4 g.), b. p. 81°/0·2 mm., $n_{\rm D}^{19}$ 1·4722, which solidified on being kept and crystallised from pentane in needles, m. p. 73—74°, and showed no light absorption with $E_{1\,\text{cm.}}^{1\%} > 100$ in the 2200—4000-Å range (Found : C, 74·0; H, 10·3%; *M*, in camphor, 196). It did not form a 2 : 4-dinitrophenylhydrazone and was not further investigated.

2 : 4 : 6-*Trimethylhepta*-2 : 5-*dien*-4-*ol* (III).—Phorone (30 g., m. p. 28°; prepared by the method of Cologne and Dumont, *Bull. Soc. chim.*, 1947, **14**, 38) in ether (40 ml.) was added dropwise to a stirred solution of methylmagnesium bromide (from Mg, 6 g.) in ether (250 ml.) at 0°. Stirring was continued for 2 hours and saturated aqueous ammonium chloride (500 g.) was then added. The ethereal layer was separated, the aqueous layer was extracted with ether (3 × 150 ml.), and the united ether solutions were dried (Na_2SO_4–K_2CO_2) and fractionated, giving the carbinol (20 g., 60%), b. p. 41°/0·2 mm., $n_{\rm D}^{21}$ 1·4638, which crystallised from pentane in needles, m. p. 56° (Found : C, 77·9; H, 11·9. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). Fellenberg (*Ber.*, 1904, **37**, 3578) gives b. p. 43—46°/0·25 mm., m. p. 57·5°, and states that no satisfactory analytical data could be obtained owing to rapid aerial oxidation. We find that the carbinol is reasonably stable when pure. It reacted vigorously with methylmagnesium iodide in ether and exhibited no light absorption with $\varepsilon > 1000$ in the range 2200—4000-Å in ethanol containing 0·1% of sodium ethoxide.

2 : 4 : 6-*Trimethylhepta*-3 : 5-*dien*-2-*ol* (IV) and 2 : 4 : 6-*Trimethylheptan*-2-*ol*.—(*a*) 2 : 4 : 6-Trimethylhepta-2 : 5-dien-4-ol (4·0 g.) was dissolved in 0·001M-solution of hydrochloric acid in 60% aqueous acetone (100 ml.) at room temperature. After 10 minutes, potassium carbonate (200 mg.) was added and most of the acetone removed under reduced pressure (100 mm.). The remaining solution was extracted with ether, and the ethereal extract was dried (Na_2SO_4–K_2CO_3) and fractionated, giving 2 : 4 : 6-*trimethylhepta*-3 : 5-*dien*-2-*ol* (3·4 g.), b. p. 41°/0·2 mm., $n_{\rm D}^{21}$ 1·4715 (Found : C, 77·8; H, 12·0. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). Light absorption in ethanol : maximum, 2280 Å (ε 8000), inflexion, 2360 Å (ε 7400).

The above dienol (3 g.) in methanol (30 ml.) was shaken with platinic oxide (10 mg.) in hydrogen until 880 ml. of hydrogen at 20°/765 mm. (Calc., 930 ml.) had been absorbed. Isolation of the product gave 2 : 4 : 6-*trimethylheptan*-2-*ol* (2·6 g.), b. p. 85—88°/25 mm., $n_{\rm D}^{23}$ 1·4352 (Found : C, 75·7; H, 13·9. $C_{10}H_{22}O$ requires C, 75·9; H, 14·0%). The 3 : 5-*dinitrobenzoate* crystallised from aqueous methanol in needles, m. p. 81—83° (Found : N, 8·1. $C_{17}H_{24}O_6N_2$ requires N, 7·95%).

(*b*) A mixture of mesityl oxide (66 g.) and methyl bromoacetate (102 g.) was added to zinc turnings (44 g.) in boiling benzene (300 ml.) during ½ hour (cf. Rupe and Lotz, *Ber.*, 1903, **36**, 15; Auwers and Eisenlohr, *J. pr. Chem.*, 1911, **84**, 93). When the vigorous reaction had subsided, the mixture was refluxed for a further 3 hours and then allowed to cool. Sulphuric acid (50 ml.) in water (300 ml.) was added and, after ½ hour, the benzene layer was separated. The aqueous layer was extracted with ether (3 × 100 ml.) and the combined extracts were fractionated, giving *methyl* 3 : 5-*dimethylhexa*-2 : 4-*dienoate* (50 g., 48%), b. p. 74°/0·5 mm., $n_{\rm D}^{22}$ 1·4761, $\lambda_{\text{max.}}$ 2700 and 2800 Å (ε 6500 and 6300, respectively) in ethanol (Found : C, 69·6; H, 9·1. $C_9H_{14}O_3$ requires C, 70·1; H, 9·2%). The ester failed to give an adduct on treatment with maleic anhydride in benzene.

The ester (13 g.) in ether (25 ml.) was added dropwise to a stirred solution of methylmagnesium bromide (from Mg, 5 g.) in ether (150 ml.) at 0°. Next day, excess of aqueous ammonium chloride was added and the products were worked up as above, giving 2 : 4 : 6-trimethylhepta-3 : 5-dien-2-ol (11·5 g., 82%), b. p. 40°/0·2 mm., n_D^{21} 1·4680, $\lambda_{max.}$ 2290 Å (ε 8000), $\lambda_{infl.}$ 2360 Å (ε 7400) in ethanol.

The dienol (2·5 g.) in methanol (30 ml.) in the presence of platinic oxide (10 mg.) absorbed 740 ml. of hydrogen at 760 mm./20° (Calc., 780 ml.), giving 2 : 4 : 6-trimethylheptan-2-ol (2 g.), b. p. 82°/23 mm., n_D^{23} 1·4345. It formed a 3 : 5-dinitrobenzoate, m. p. 79—83°, undepressed on admixture with the sample described above.

2 : 6-*Dimethylhepta*-2 : 5-*dien*-4-*ol* (VI).—β-Methylcrotonaldehyde (6·5 g.), b. p. 79—81°/116 mm. (prepared by the method of Young and Linden, *J. Amer. Chem. Soc.*, 1947, **69**, 2912), in ether (20 ml.) was added dropwise to an ethereal solution of *iso*butenyl-lithium (from Li, 2·3 g.) at 0°. After 2 hours, excess of aqueous ammonium chloride was added and the products were worked up as above, giving 2 : 6-*dimethylhepta*-2 : 5-*dien*-4-*ol* (4·6 g., 48%), b. p. 43—44°/0·4 mm., n_D^{23} 1·4833 (Found : C, 76·8, H, 11·2. $C_9H_{16}O$ requires C, 77·1; H, 11·5%). A solution of the dienol in ethanol containing 0·1% of sodium ethoxide showed no light absorption with $\varepsilon > 1000$ in the range 2200—4000 Å. The dienol is very unstable in air and repetitions of this preparation under apparently identical conditions often gave partly rearranged and dehydrated material.

2 : 6-*Dimethylhepta*-3 : 5-*dien*-2-*ol* (VII) *and* 2 : 6-*Dimethylhepta*-1 : 3 : 5-*triene* (VIII).—The above dienol (3 g.) was dissolved in an 0·001M-solution of hydrochloric acid in 60% aqueous acetone (50 ml.) at room temperature. After 10 minutes, potassium carbonate (100 mg.) was added and the product worked up as above, giving 2 : 6-*dimethylhepta*-3 : 5-*dien*-2-*ol* (2·1 g.), b. p. 42°/0·05 mm., n_D^{16} 1·4983 (Found : C, 77·2; H, 11·2. $C_9H_{16}O$ requires C, 77·1; H, 11·5%). Light absorption in ethanol : maximum, 2370 Å; ε 20 000.

On being kept, or on treatment with more concentrated mineral acid, the carbinol slowly underwent dehydration, and distillation from a trace of potassium hydrogen sulphate afforded 2 : 6-*dimethylhepta*-1 : 3 : 5-*triene*, b. p. 54°/15 mm., 32°/0·1 mm., n_D^{21} 1·5130—1·5190, which was not obtained completely pure (Found : C, 86·2; H, 11·5. C_9H_{14} requires C, 88·4; H, 11·5%). Light absorption in ethanol : maxima, 2610, 2700, and 2880 Å; ε 22 000, 32 000, and 24 000, respectively. The triene (5 g.) was also the main product obtained by the action of lithium aluminium hydride (2 g.) on phorone (9 g.) in ether at −10°.

Reaction of iso*Butenyl Phenyl Ketone with Methyl-lithium*.—The ketone (15 g.; prepared by Darzens's method, *Compt. rend.*, 1929, **189**, 767) in ether (50 ml.) was added to a solution of methyl-lithium (from Li, 1·4 g.; methyl bromide, 9 g.) in ether (300 ml.). After 2 hours, excess of aqueous ammonium chloride was added. The products were isolated in the usual way and fractionated from a trace of potassium carbonate, giving 4-methyl-2-phenylpent-3-en-2-ol (13 g., 80%), b. p. 64°/0·3 mm., n_D^{21} 1·5286 (Braude and Coles, Part III, *loc. cit.*, give n_D^{20} 1·5289). The first fractions, on treatment with Brady's reagent, gave a small quantity (30 mg.) of a red 2 : 4-*dinitrophenylhydrazone* which crystallised from dioxan in plates, m. p. 277—278°, $\lambda_{max.}$ 3850 Å ($E_{1\,cm.}^{1\%}$ 900, in chloroform) (Found : N, 15·9. $C_{18}H_{20}O_4N_4$ requires N, 15·7%). The analytical data correspond to the derivative of *neo*pentyl phenyl ketone.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to J. A. C.) and Dr. E. S. Waight, British Rubber Producers Research Association, Welwyn Garden City, for the infra-red data.

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[*Received, November* 30*th*, 1951.]