410. *Alkenylation by Use of Lithium Alkenyls. Part I. The Condensation of* iso*Butenyl-lithium with Benzaldehyde and Acetophenone, and the Oxotropic Rearrangement of the Resulting Carbinols.* (*Studies in Molecular Rearrangement. Part III.*) *

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This series of papers describes the preparation and some of the reactions and synthetic applications of a hitherto almost unknown class of reagents, the alk-1-enyl-lithium derivatives (cf. Braude, Coles, and Timmons, *Nature*, 1950, **166**, 58).

Highly purified *iso*butenyl bromide (I) with lithium in ether readily gives iso*butenyl-lithium* (II) and 2 : 5-dimethylhexa-2 : 4-diene (III). Carboxylation of *iso*butenyl-lithium affords β-methylcrotonic acid and phorone. Condensation of *iso*butenyl-lithium with benzaldehyde and acetophenone yields the *iso*butenylcarbinols (VI and VIII), which on treatment with dilute acids readily undergo the expected oxotropic rearrangements to the conjugated styryl derivatives (VII and IX).

α-Methylstyryldimethylcarbinol (IX) exhibits anomalous ultra-violet light absorption properties which are explained in terms of steric interference between the α- and γ-substituents.

ONE of the limitations to the manifold synthetic applications of Grignard reagents arises from the well-known fact that alkenyl halides containing a halogen atom adjacent to an ethylenic

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* Patent applications cover the subject matter of this and the following three papers.

bond are very unreactive towards magnesium and give the organo-magnesium derivatives only with great difficulty. The sole known exceptions to this rule are 2-arylvinyl bromides such as β-bromostyrene (Tiffeneau, *Compt. rend.*, 1902, **135**, 1346; Rupe and Proske, *Ber.*, 1910, **43**, 1231; Meyer, *Ber.*, 1922, **55**, 817; Ziegler *et al.*, *Ber.*, 1924, **57**, 1986; 1925, **58**, 359; *Annalen*, 1923, **434**, 75; 1925, **443**, 167; Hurd and Webb, *J. Amer. Chem. Soc.*, 1927, **49**, 546; Lüttringhaus, *Ber.*, 1934, **67**, 1602; Wright, *J. Org. Chem.*, 1936, **1**, 457; Koelsch and Rosewald, *J. Amer. Chem. Soc.*, 1937, **59**, 2166; Willstaedt, *Svensk Kem. Tidskr.*, 1941, **53**, 416; Bergmann *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2968). Vinyl bromide has been claimed to react with 2-chloroprop-1-ene in the presence of magnesium to give isoprene and butadiene (Austerweil, G.P. 245,180; *Chem. Zentr.*, 1912, I, 1267), a reaction which presumably involves an alkenylmagnesium halide as intermediate, but according to Krestinsky (*Ber.*, 1922, **55**, 2773) vinyl bromide itself undergoes dehydrobromination to acetylene on treatment with activated magnesium. The only successful attempts to employ aliphatic-substituted vinyl bromides in Grignard condensations are those reported by Krestinsky (*ibid.*, pp. 2754, 2762, 2770) who treated *iso*butenyl (2 : 2-dimethylvinyl) bromide (I) and 1 : 2 : 2-trimethylvinyl bromide with benzaldehyde and other aldehydes in the presence of activated magnesium and obtained, amongst other products, small yields of the expected unsaturated carbinols. In our hands, appreciable reaction between *iso*butenyl bromide and magnesium could only be induced in the presence of methyl bromide, and the yields of condensation products with aldehydes or ketones were only of the order of 10%. Mousseron and his co-workers (*Bull. Soc. chim.*, 1947, [v], **14**, 81) have reported the formation and the carboxylation in " poor " yields of the magnesium derivative of 1-chloro-2-methyl*cyclo*hexene, but neither 1-chloro*cyclo*hexene (Braude and Coles, *J.*, 1950, 2014) nor a number of other methyl-substituted homologues (Braude, Bruun, and Weedon, forthcoming paper) react appreciably with magnesium under the usual conditions. Very recently, van Dorp and Arens (Dutch P. 62,738; *Chem. Abstr.*, 1949, 5417) have described the condensation, in unstated yields, of 2-ethoxyvinyl bromide with a C_{18} ketone in the presence of activated magnesium.

It thus appears that, whereas the use of Grignard reagents provides general methods of alkylation, arylation, and alkynylation (the Grignard derivative being prepared in the last case from the acetylenic component containing a free ethynyl grouping and an alkylmagnesium halide), alkenylation cannot generally be effected in this way, or only with great difficulty. To some extent this limitation can be overcome by alkynylation followed by semihydrogenation to give the ethylenic derivative, a method which has been extensively developed within recent years in this and other laboratories (cf. Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77; Heilbron, Jones, *et al.*, *J.*, 1945, 84 and later papers; Nazarov *et al.*, *Bull. Acad. Sci. U.R.S.S.*, *Cl. Sci. chim.*, 1946, 305, and later papers). However, semihydrogenation of the acetylenic intermediate is not always easy to achieve, especially with polyfunctional compounds, and its application is limited to the introduction of vinyl and mono-2-substituted vinyl groups.

Morton and his collaborators (*J. Amer. Chem. Soc.*, 1947, **69**, 160, 1675; U.S.P. 2,454,082) have studied the metalation of olefins with amylsodium. With propene and the butenes, mono-metalation was found to take place almost exclusively in the allyl position, but in the case of pent-1-ene a mixture of about 20% of pent-1-enyl- and 60% of pent-3-enylsodium appeared to be formed, as judged by the proportion of αβ- and βγ-ethylenic acids obtained on carboxylation. The applicability of this method to α-alkenylation is thus evidently rather limited.

The present work originated in the desire to employ α-alkenyl organo-metallic derivatives for the synthesis of various ethylenic systems not easily accessible by the conventional routes. The difficulty of preparing Grignard reagents of this type, together with certain additional complicating factors subsequently encountered in some of their reactions (Braude and Timmons, forthcoming paper), directed our attention to the possibility of obtaining the corresponding lithium derivatives, since lithium often reacts more readily than magnesium with alkyl and aryl halides (cf. Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1932, **54**, 1957; 1933, **55**, 1252). The literature concerning lithium alkenyls was not encouraging; the only example previously described, styryl-lithium, is formed in no better yield than the corresponding Grignard derivative (Wright, *loc. cit.*), and attempts to metalate vinyl bromide with phenyl- or butyl-lithium result in complete dehydrohalogenation (Wittig and Harborth, *Ber.*, 1944, **77**, *B*, 306; Gilman and Haubein, *J. Amer. Chem. Soc.*, 1945, **67**, 1420). *cyclo*Hex-1-enyl-lithium has been postulated as an intermediate in the formation of 1-phenyl*cyclo*hexene from 1-chloro*cyclo*hexene and phenyl-lithium (Wittig and Harborth, *loc. cit.*), but it appears at least equally likely that a direct coupling reaction is involved (cf. Kharasch, Lewis, and Reynolds, *J. Amer. Chem. Soc.*, 1943, **65**, 498).

We have found that lithium derivatives can readily be obtained in good yields from a variety of alk-1-enyl halides by direct reaction with metallic lithium in an anhydrous solvent, preferably ether, provided that the necessary attention is paid to the purity of the reagents employed. The preparation and some reactions of *iso*butenyl- and *cyclo*hexenyl-lithium are described in this and the following three papers. Studies of other lithium alkenyls and their synthetic applications will be reported subsequently.

Formation and Carboxylation of iso*Butenyl-lithium.*—*iso*Butenyl bromide was chosen as a test case in the present work because it gives at least small yields of the Grignard derivative under suitable conditions and cannot easily undergo dehydrobromination. The bromide was prepared by treating 1 : 2-dibromo*iso*butane with aqueous-alcoholic potassium hydroxide (Krestinsky, *loc. cit.*); the yield could not be improved beyond 30%, but various other dehydrobrominating agents were even less satisfactory. The twice-fractionated bromide reacted readily with lithium in dry ether. Treating the resulting solution with an excess of solid carbon dioxide gave 2 : 5-dimethylhexa-2 : 4-diene (III), β-methylcrotonic acid (IV), and phorone (V), in an overall yield of nearly 60%. None of the corresponding unconjugated derivatives was isolated, showing that the formation of the lithium alkenyl is not accompanied by migration of the ethylenic double bond.

There is considerable evidence that Wurtz reactions with alkali metals involve the organometallic derivatives as intermediates (cf. Ziegler and Colonius, *Annalen*, 1930, **479**, 135; Morton and Richardson, *J. Amer. Chem. Soc.*, 1940, **62**, 123). It is thus very probable that the 2 : 5-dimethylhexa-2 : 4-diene is formed by reaction of *iso*butenyl-lithium with unchanged *iso*butenyl bromide; this assumption finds some support in the fact that the yield of other condensation products derived from *iso*butenyl-lithium is increased if the bromide and lithium are allowed to interact in the presence of a secondary component, such as benzaldehyde (see below). It is of interest that little or no 2 : 5-dimethylhexa-2 : 4-diene is produced in the reaction between *iso*butenyl bromide and magnesium (Krestinsky, *loc. cit.*), whereas the bromide reacts with sodium in benzene (Prévost, *Compt. rend.*, 1927, **184**, 1460; *Ann. Chim.*, 1928, **10**, 422) or, more rapidly, in ether to give the diene as the main product. This implies, in agreement with general experience, that the reactivity of the organo-metallic derivatives towards the bromide increases in the sequence $\mathrm{RMgBr} < \mathrm{RLi} < \mathrm{RNa}$.

The formation of phorone must be due to the reaction of lithium β-methylcrotonate, the first carboxylation product, with a second molecule of *iso*butenyl-lithium; the proportion of β-methylcrotonic acid obtained is increased, and that of phorone reduced, if the effective concentration of carbon dioxide is increased by adding the alkenyl-lithium solution to solid carbon dioxide instead of *vice versa.* The formation of ketones in the carboxylation of both magnesium and lithium organic compounds has previously been observed in a number of cases (Gilman and van Ess, *J. Amer. Chem. Soc.*, 1933, **55**, 1258; Meals, *J. Org. Chem.*, 1944, **9**, 211; Denisenko, *J. Gen. Chem. Russia*, 1948, **18**, 219).

$$\begin{tikzcd}
 & \underset{\text{(I.)}}{\mathrm{Me_2C{:}CHBr}} \arrow[r] & \underset{\text{(II.)}}{\mathrm{Me_2C{:}CHLi}} \arrow[r, "\mathrm{Me_2C{:}CHBr}"] \arrow[d, "\mathrm{CO_2}"] & \underset{\text{(III.)}}{\mathrm{Me_2C{:}CH{\cdot}CH{:}CMe_2}} \\
\underset{\text{(V.)}}{\mathrm{Me_2C{:}CH{\cdot}CO{\cdot}CH{:}CMe_2}} & & \mathrm{Me_2C{:}CH{\cdot}CO_2Li} \arrow[ll, "\mathrm{Me_2C{:}CHLi}"'] \arrow[r] & \underset{\text{(IV.)}}{\mathrm{Me_2C{:}CH{\cdot}CO_2H}}
\end{tikzcd}$$

Condensation of iso*Butenyl-lithium with Benzaldehyde or Acetophenone.*—The reaction of benzaldehyde or acetophenone with ethereal *iso*butenyl-lithium furnished the expected carbinols (VI and VIII) in about 30% yield (based on *iso*butenyl bromide), together with 2 : 5-dimethylhexa-2 : 4-diene as before. In one experiment, the formation of *iso*butenyl-lithium was allowed to proceed in the presence of benzaldehyde; the yield of phenyl*iso*butenylcarbinol (VI) was substantially the same, but a 20% yield of 1-phenyl-3-methylbuta-1 : 3-diene, a dehydration product of the carbinol, was also obtained.

The structure of phenyl*iso*butenylcarbinol (VI) was proved by hydrogenation, with platinum oxide as catalyst, to give phenyl*iso*butylcarbinol which was oxidised to *iso*valerophenone. The carbinol obtained from *iso*butenyl-lithium and acetophenone was identical in physical properties with phenylmethyl*iso*butenylcarbinol (VIII) prepared by the condensation of phenylmagnesium bromide with mesityl oxide (Ravier, *Compt. rend.*, 1934, **198**, 1786) and absorbed 1 mole of hydrogen on hydrogenation over platinum oxide to give phenylmethyl*iso*butylcarbinol.

*Oxotropic Rearrangements of Phenyl*iso*butenyl- and Phenylmethyl*iso*butenyl-carbinol.*—On treatment with dilute hydrochloric acid in aqueous dioxan, phenyl*iso*butenylcarbinol was readily isomerised to styryldimethylcarbinol (VII), identical with a sample prepared from benzylideneacetone and methylmagnesium bromide (Klages, *Ber.*, 1906, **39**, 2592). This

$$\mathrm{Ph{\cdot}CHO} \xrightarrow{\mathrm{Me_2C{:}CHLi}} \underset{\text{(VI.)}}{\mathrm{Ph{\cdot}CH(OH){\cdot}CH{:}CMe_2}} \xrightarrow{\mathrm{H^+}} \underset{\text{(VII.)}}{\mathrm{Ph{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH}}$$

oxotropic rearrangement is in all respects analogous to the isomerisation of the lower homologues, phenylvinylcarbinol and phenylpropenylcarbinol, to cinnamyl alcohol and styrylmethylcarbinol, respectively (Braude, Jones, and Stern, *J.*, 1946, 396).

The corresponding rearrangement of phenylmethyl*iso*butenylcarbinol presents some unusual features. Whereas side-chain methyl substituents usually increase the ease of isomerisation (Braude and Jones, *J.*, 1946, 122, 128; Braude, Jones, and Stern, *loc. cit.*), phenylmethyl*iso*butenylcarbinol was found to rearrange considerably more slowly than phenyl*iso*butenylcarbinol under the same conditions, in aqueous dioxan containing hydrochloric acid. (Detailed kinetic studies of the rearrangement are in progress and will be reported in due course.) The rearranged isomer, 4-phenyl-2-methylpent-3-en-2-ol (IX), was also obtained on shaking (VIII) with 5% aqueous sulphuric acid, but the rearrangement under heterogeneous conditions was accompanied by some dehydration to 4-phenyl-2-methylpenta-1 : 3-diene (X), which was also obtained, though in an impure state, by distilling the rearranged carbinol (IX) from potassium hydrogen sulphate. It is of interest that Klages (*Ber.*, 1904, **37**, 2301), on decomposing the Grignard

$$\mathrm{Ph{\cdot}CO\,Me} \xrightarrow{\mathrm{Me_2C{:}CHLi}} \underset{\text{(VIII.)}}{\mathrm{Ph{\cdot}CMe(OH){\cdot}CH{:}CMe_2}} \xrightarrow{\mathrm{H^+}} \underset{\text{(IX.)}}{\mathrm{Ph{\cdot}CMe{:}CH{\cdot}CMe_2{\cdot}OH}} \longrightarrow \underset{\text{(X.)}}{\mathrm{Ph{\cdot}CMe{:}CH{\cdot}CMe{:}CH_2}}$$

complex from phenylmagnesium bromide and mesityl oxide with sulphuric acid, obtained, instead of (IX) or (X), an isomeric hydrocarbon, $C_{12}H_{14}$, which, owing to its low refractive index (n_D^{20} 1·5236), was formulated as 1-phenyl-1 : 3 : 3-trimethylallene. No product of this nature was isolated in the present work.

The structure of (IX) was established by an alternative synthesis from ethyl β-methylcinnamate and methylmagnesium bromide and by the catalytic hydrogenation of both samples to 4-phenyl-2-methylpentan-2-ol, characterised as the 3 : 5-dinitrobenzoate.

The alcohol (IX) exhibits somewhat anomalous physical properties. Whereas the three lower homologues, cinnamyl alcohol, styrylmethyl- and styryldimethyl-carbinol all have melting points above 30°, α-methylstyryldimethylcarbinol (IX) could not be obtained solid at room temperature. Moreover, its ultra-violet light absorption properties differ considerably from those of its lower homologues (see Table). The other styrylmethylcarbinols uniformly show a main band with a maximum at 2510 A. (ε *ca.* 20,000), which is attributed to the conjugated styryl chromophore (Braude, Jones, and Stern, *J.*, 1947, 1087) but is considerably displaced

Ultra-violet light absorption properties of styryl and α-methylated styryl derivatives.

	$\lambda_{max.}$, A.*	$\varepsilon_{max.}$			$\lambda_{max.}$, A.*	$\varepsilon_{max.}$	
Ph·CH═CH$_2$	2440	12,000	[1]	Ph·CH═CH·CO$_2$Me	2710	26,000	[2]
Ph·CMe═CH$_2$	2440	12,400	[2]		2800	26,000	
	2500	11,200		Ph·CMe═CH·CO$_2$Et	2650	17,000	[2]
Ph·CH═CHMe	2460	12,000	[1]				
Ph·CH═CH·CH$_2$·OH	2480	19,000	[3]	Ph·CH═CH·CMe═CH$_2$...	2730	20,200 †	[2]
	2510	19,500			2790	20,200	
Ph·CH═CH·CHMe·OH ...	2480	19,000	[3]		*2910*	13,000	
	2510	19,500					
Ph·CH═CH·CMe$_2$·OH ...	2510	17,300	[2]	Ph·CMe═CH·CMe═CH$_2$	2510	11,000 †	[2]
	2560	16,300			2580	12,000	
Ph·CMe═CH·CMe$_2$·OH ...	2420	11,500	[2]		2660	11,000	
	2480	11,500			2760	9,000	

* Principal bands, in ethanol solution. Figures in *italics* refer to inflections.

† These values are probably low, as the dienes were not completely pure.

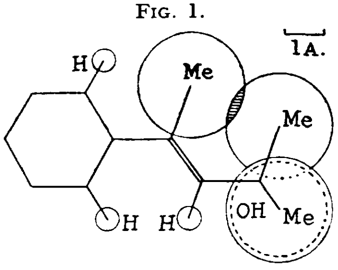
[1] Ramart-Lucas and Amagat, *Bull. Soc. chim.*, 1932, **51**, 108, 965; 1934, **1**, 719.

[2] This paper.

[3] Braude, Jones, and Stern, *J.*, 1946, 396; 1947, 1087.

towards higher wave-lengths and intensified in comparison with that of styrene. The bathochromic and hyperchromic effects must clearly be ascribed to the $-CR_2{\cdot}OH$ substituents and are practically independent of whether R is hydrogen or methyl; moreover, since the ultraviolet absorption of α- as well as β-methylstyrene and other alkylated styrenes is practically identical with that of styrene (Ramart-Lucas and Amagat, *Bull. Soc. chim.*, **1932**, **51**, 108, 965), the variochromic effects in the styrylcarbinols must be associated specifically with the $-C{=}CH{-}C(OH)-$ grouping and with electronic interaction (hyperconjugation) between the ethylenic bond and the hydroxyl group *via* the saturated carbon atom. Analogous effects are observed in benzyl alcohol, benzyl halides, and other hyperconjugated systems (Braude, *J.*, **1949**, 1902), though the increase in intensity in the styrylcarbinols is unusually large. α-Methylstyryldimethylcarbinol (IX), on the other hand, exhibits absorption almost identical with that of styrene and α-methylstyrene; evidently in this case the α-methyl substituent almost completely inhibits hyperconjugation between the styryl system and the hydroxymethyl group. It is now well known that electronic interaction in conjugated systems requires the co-planarity of the different groups concerned and that appreciable deviations from co-planarity are strikingly manifested in the ultra-violet light absorption properties (for a recent discussion, see Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, **1949**, 1890). A scale projection of α-methylstyryldimethylcarbinol (Fig. 1) using covalent radii which are a minimum measure of interference properties, shows that there is appreciable overlap between the α- and γ-methyl groups in a planar *trans*-configuration. (A *cis*-configuration can be ruled out in view of the very considerable steric interference which it would involve.) The steric interference in the *trans*-configuration can be relieved by twisting either end of the molecule, but the light-absorption data are best explained by assuming that it is the $-CMe_2{\cdot}OH$ group and the β-hydrogen atom which are displaced out of the plane of the ethylenic bond, and it can easily be seen that this is the accommodation which will result in the smallest loss of resonance energy. Several cases of steric inhibition of resonance in related first-order conjugated systems, *e.g.*, α-methylstilbene (Jones, *J. Amer. Chem. Soc.*, **1943**, **65**, 1818; cf. Braude, *J.*, **1949**, 1902), have been described, but as far as we are aware the present observations constitute the first recorded example of steric inhibition of hyperconjugation.

FIG. 1.



Anomalous ultra-violet light absorption properties are also exhibited by the other α-methylstyryl derivatives, ethyl β-methylcinnamate and 4-phenyl-2-methylpenta-1 : 3-diene (see Table). Here again, steric inhibition of resonance due to the α-methyl substituent clearly comes into play, but, as would be expected, the effects are rather larger than in the example discussed above, because the terminal groups undergoing steric displacement are unsaturated.

EXPERIMENTAL.

(M. p.s were determined on a Kofler block and are corrected.)

iso*Butenyl Bromide* (I).—*iso*Butene, generated by heating *tert.*-butanol with oxalic acid (Hurd and Spence, *J. Amer. Chem. Soc.*, **1929**, **51**, 3562), was passed into an excess of bromine. The crude product, obtained in 85% yield in 2-kg. batches, was distilled to give 1 : 2-dibromo*iso*butane as a colourless oil, b. p. 152°, n_D^{20} 1·5078 (Dojarenko, *Ber.*, **1926**, **59**, 2946, gives b. p. 147°/742 mm., n_D^{17} 1·5103; Winstein and Grunwald, *J. Amer. Chem. Soc.*, **1948**, **70**, 836, give n_D^{17} 1·5095).

The dibromide (1800 g.) was added to a stirred, hot solution of potassium hydroxide (520 g.) in ethanol (2·5 l.) and water (200 ml.) at a rate sufficient to maintain gentle refluxing. The mixture was then heated under reflux for a further 7 hours and allowed to cool overnight. The upper layer was separated by suction through a filter-stick and added to water (15 l.). Next morning the lower layer was separated and dried ($CaCl_2$). On careful fractionation, through a 14-inch Fenski column, a middle fraction (470 g.), b. p. 91·0—91·5°, was obtained which was refractionated from a small piece of sodium to give *iso*butenyl bromide (360 g., 27%) as a colourless liquid, b. p. 91·0—91·3°, n_D^{21} 1·4603 (Farrell and Bachman, *ibid.*, **1935**, **57**, 1281, give b. p. 90—91°, n_D^{20} 1·4625). On one occasion a sample of the same b. p. but with n_D^{22} 1·4490 was obtained, which gave identical derivatives on lithium condensation. Prototropic isomerism is thus unlikely, and since geometical isomerism is excluded, the difference in refractive indices remains unexplained.

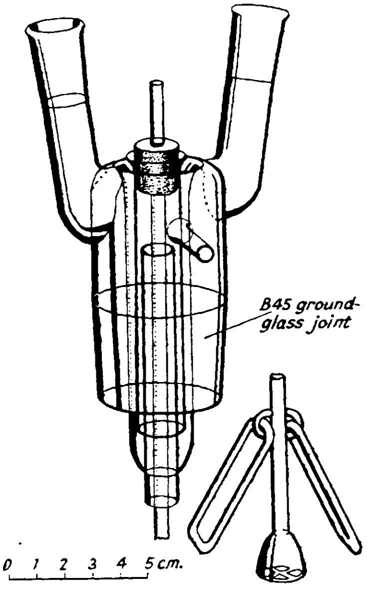
Alternatively, 1 : 2-dibromo*iso*butane (890 g.) was added dropwise, with stirring, to potassium hydroxide (250 g.) and ethylene glycol (1 l.) in a three-necked copper flask immersed in an oil-bath at 120—130°. The *iso*butenyl bromide, which distilled, was collected, dried, and fractionated as above, 100 g. (30%) of pure product being obtained.

No significant yield of *iso*butenyl bromide was obtained from the attempted dehydrobromination of 1 : 2-dibromo*iso*butane with sodamide in liquid ammonia, with diethylamine or with potassium acetate in glacial acetic acid, although Bainbridge (*J.*, 1914, 2294) claims to have obtained a theoretical yield of the bromide by the last method.

iso*Butenyl-lithium* (II).—The preparation of the lithium alkenyl and subsequent reactions were carried out in wide-necked flasks fitted with the special adaptor illustrated in Fig. 2 (kindly drawn by Mr. E. S. Waight). A hollow stirrer provided with a glass wool plug at the lower end passes through the central neck which is also provided with a mercury seal. One side-neck carries an efficient reflux condenser and drying-tube; the other serves for the addition of reagents. Metallic lithium (6·9 g., 1 mol.) was cut into small pieces in a rapid stream of oxygen-free nitrogen and dropped through the side-arm into the flask, which contained sodium-dried ether (2 l., 20 mols.) and *iso*butenyl bromide (15 g.). The mixture was stirred in a slow stream of nitrogen until the reaction commenced as indicated by the appearance of a white turbidity, usually after about 45 minutes. The remainder of the bromide (total: 73 g., 0·5 mol.) in ether (150 ml.) was then added drop-wise at such a rate that the solution refluxed gently, and stirring was continued for a short time until nearly all the metal had dissolved.

For reactions in which other components are added *to* the lithium alkenyl solution, the special adaptor illustrated in Fig. 2, though convenient, is unnecessary and an ordinary three-necked flask or adaptor can be employed. For " reverse " condensations, a separating funnel was connected to the top of the stirrer by a short piece of rubber tubing, the two side-necks were closed with glass stoppers, and the lithium alkenyl solution was forced through the stirrer-tube into the funnel by applying excess nitrogen pressure; the compact design of the adaptor and short length of the stirrer-tube ensure that only a small pressure is required.

FIG. 2.



Carboxylation.—Solid carbon dioxide (200 g.) was added in small pieces to a solution of *iso*butenyl-lithium (from Li, 4·2 g.) in ether (500 ml.). When the contents of the flask had attained room temperature, water (200 ml.) was added, and the aqueous layer was acidified with hydrochloric acid. The ethereal layer was separated and extracted with aqueous sodium carbonate. On acidification of the alkaline extract, β-methylcrotonic acid (IV) (2·4 g., 7%) separated; after one crystallisation from light petroleum (b. p. 40—60°) it had m. p. 69—70°, undepressed by an authentic specimen. Distillation of the ethereal layer afforded 2 : 5-dimethylhexa-2 : 4-diene (III) (8 g., 36%), b. p. 78°/110 mm., and phorone (V) (3·2 g., 14%), b. p. 88°/17 mm., n_D^{21} 1·4968. The diene, on redistillation, had b. p. 132—133°/760 mm., m. p. 11°, n_D^{19} 1·4780 [Krestinsky (*J. Russ. Phys. Chem.*, 1920, **52**, 84; *Ber.*, 1922, **55**, 2769) gives b. p. 136°, m. p. 14·5°, n_D^{19} 1·4796]. Light absorption in ethanol: Max., 2410 A., ε = 22,500; inflections 2450 and 2500 A., ε = 21,500 and 16,500 respectively. The dihydrobromide was prepared by heating, the diene with hydrogen bromide in a sealed tube at 100° for 17 hours and crystallised from light petroleum (b. p. 40—60°) in colourless needles, which sublimed to give colourless plates, m. p. 68—69° (Pogorzelsky, *Chem. Zentr.*, 1899, I, 773, gives m. p. 68·5—69°; Krestinsky, *loc. cit.*, gives m. p. 65°). Phorone was identified as the 2 : 4-*dinitrophenylhydrazone*, which was chromatographed on alumina from benzene solution and crystallised from methanol in red needles, m. p. 115—116°, undepressed by an authentic sample (Found: C, 56·6; H, 5·5; N, 18·3. $C_{15}H_{18}O_4N_4$ requires C, 56·6; H, 5·7; N, 17·6%); Connolly (*J.*, 1944, 339) gives m. p. 118°, and Braude and Jones (*J.*, 1945, 498) give m. p. 108°, but no analytical data are recorded.

In another experiment, in which the ethereal solution of *iso*butenyl-lithium was slowly added to excess of solid carbon dioxide, an increased yield of β-methylcrotonic acid (4·8 g., 14%) was obtained.

*Phenyl*iso*butenylcarbinol* (*1-Phenyl-3-methylbut-2-en-1-ol*) (VI).—(*a*) Benzaldehyde (35 g.) in ether (50 ml.) was added dropwise to a stirred ethereal solution of *iso*butenyl-lithium (from Li, 4·2 g.) at 0°. After a further hour's stirring at room temperature, an ice-cold saturated aqueous solution of ammonium chloride (35 g.) was added. The ethereal layer was separated and dried (Na_2SO_4 + a little K_2CO_3) and fractionated from a trace of potassium carbonate. A mixture of 2 : 5-dimethylhexa-2 : 4-diene and unchanged benzaldehyde distilled first, followed by phenyl*iso*butenylcarbinol (18 g., 33%), b. p. 79°/10^{-2} mm., n_D^{18} 1·5373 (Found: C, 81·3; H, 8·8. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·7%) (Krestinsky, *Ber.*, 1922, **55**, 2770, gives b. p. 122—125°/7 mm., n_D^{20} 1·5352). Light absorption in ethanol: Max. 2590, 2640, and 2780 A., ε = 710, 670, and 360, respectively.

(*b*) A mixture of *iso*butenyl bromide (total, 58 g.) and benzaldehyde (35 g.) was added during 1 hour to lithium (4·2 g.) in ether (600 ml.) containing some *iso*butenyl bromide, after reaction had commenced as described above. Stirring was continued for a further 2 hours and the products were worked up in the usual manner to give impure 1-phenyl-3-methylbuta-1 : 3-diene (9 g., 18%), b. p. 73—76°/1 mm., n_D^{19} 1·5757 (light absorption: see Table), and phenyl*iso*butenylcarbinol (18 g., 33%), b. p. 95°/1 mm., n_D^{18} 1·5366.

Hydrogenation of phenyl*iso*butenylcarbinol (3·1 g.) in ethyl acetate (30 ml.) in the presence of platinic oxide resulted in the uptake of 1 mole of hydrogen and gave phenyl*iso*butylcarbinol (2·7 g.), b. p. 74—76°/0·05 mm., n_D^{15} 1·5072 (Grignard, *Compt. rend.*, 1900, **130**, 1323, gives b. p. 122°/9 mm., n_D^{17} 1·5080).

Oxidation of the product with potassium dichromate in sulphuric acid afforded *iso*valerophenone, identified as the 2 : 4-dinitrophenylhydrazone, m. p. 134—136°, undepressed on admixture with an authentic specimen.

Styryldimethylcarbinol (*4-Phenyl-2-methylbut-3-en-2-ol*) (VII).—A solution of phenyl*iso*butenylcarbinol (1·0 g.) in 60% aqueous dioxan containing hydrochloric acid (0·01M.) was set aside for 2 hours at room temperature. The solution was then diluted with water and extracted with ether. The ethereal extract was dried ($Na_2SO_4 + K_2CO_3$) and distilled, to give styryldimethylcarbinol (0·6 g.) which solidified on cooling and crystallised from pentane in needles, m. p. 36—37°, undepressed on admixture with an authentic specimen (Klages, *Ber.*, 1906, **39**, 2592). Light absorption in ethanol: Max. 2510, 2820, and 2910 A., ε = 17,300, 1200, and 800, respectively; inflection 2560 A., ε = 16,300.

*Phenylmethyl*iso*butenylcarbinol* (*2-Phenyl-4-methylpent-3-en-2-ol*) (VIII).—An ethereal solution of *iso*butenyl-lithium (from Li, 5·6 g.) was slowly added to a stirred solution of acetophenone (35 g.) in ether (200 ml.). Stirring was continued overnight and saturated ammonium chloride solution (400 g.) was added. The products were worked up in the usual manner to give a low-boiling fraction of 2 : 5-dimethylhexa-2 : 4-diene (ca. 10 g.) and phenylmethyl*iso*butenylcarbinol (13 g., 25%), b. p. 63—64°/7 × 10^{-4} mm., n_D^{17} 1·5283 (Found: C, 81·6; H, 9·2. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%). A sample prepared from mesityl oxide and phenylmagnesium bromide had b. p. 56°/2 × 10^{-4} mm., n_D^{18} 1·5287 (Ravier, *Compt. rend.*, 1934, **198**, 1786, gives b. p. 95—96°/9 mm., n_D^{20} 1·534. The high refractive index recorded by this author is probably due to some rearranged or dehydrated material). Light absorption in ethanol: Max. 2510 A., ε = 245; inflection 2580 A., ε = 235.

Hydrogenation of the carbinol (1·3 g.) in ethyl acetate (20 ml.) in the presence of platinic oxide resulted in the uptake of 1 mole of hydrogen to give phenylmethyl*iso*butylcarbinol (0·8 g.), b. p. 64°/10^{-3} mm., n_D^{19} 1·5058; Bodroux and Taboury (*Compt. rend.*, 1909, **148**, 1676; *Bull. Soc. chim.*, 1909, **5**, 813) give b. p. 125—128°/18 mm., n_D^{16} 1·5157.

α-Methylstyryldimethylcarbinol (*4-Phenyl-2-methylpent-3-en-2-ol*) (IX) *and 4-Phenyl-2-methylpenta-1 : 3-diene* (X).—(*a*) A solution of phenylmethyl*iso*butenylcarbinol (8 g.) in 60% aqueous acetone (200 ml.) containing hydrochloric acid (0·02M.) was set aside for 3 hours at room temperature, and the solution was then made just alkaline with aqueous 2N-sodium hydroxide. Isolation of the products in the usual manner afforded *α-methylstyryldimethylcarbinol* (6·5 g.), b. p. 85—88°/10^{-2} mm., n_D^{22} 1·5430 (Found: C, 82·0, 81·6; H, 8·9, 9·2. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). Active hydrogen, determined by the method of Braude and Stern, (*J.*, 1946, 404): 1·01, 0·99. Light absorption: see Table.

Hydrogenation of the carbinol (3 g.) in methanol (30 ml.) resulted in the uptake of 1 mole of hydrogen, to give *4-phenyl-2-methylpentan-2-ol* (2·5 g.), b. p. 66—68°/10^{-2} mm., n_D^{19} 1·5061 (Found: C, 80·8; H, 10·1. $C_{12}H_{18}O$ requires C, 80·8; H, 10·2%). The 3 : 5-*dinitrobenzoate* crystallised from *n*-hexane–benzene in plates, m. p. 97—98°, undepressed on admixture with the specimen described below (*c*) (Found: C, 61·4; H, 5·6; N, 7·7. $C_{19}H_{20}O_6N_2$ requires C, 61·3; H, 5·4; N, 7·5%).

(*b*) Phenylmethyl*iso*butenylcarbinol (27 g.) was shaken with 2N-sulphuric acid (100 ml.) for 24 hours. The upper layer was separated and dried (Na_2SO_4–K_2CO_3). Fractionation from a trace of potassium carbonate afforded α-methylstyryldimethylcarbinol (12 g.), b. p. 72—75°/10^{-3} mm., n_D^{20} 1·5412, and impure 2-phenyl-4-methylpenta-2 : 4-diene, b. p. 63—66°/0·1 mm., n_D^{20} 1·5537 (Found: C, 89·9; H, 9·4. Calc. for $C_{12}H_{14}$: C, 91·1; H, 8·9%). Light absorption in ethanol: Max. 2510, 2580, 2660, and 2760 A., ε = 11,000, 12,000, 11,000, and 9,000, respectively.

(*c*) Ethyl β-methylcinnamate (9·5 g.) [prepared by the method of Lindenbaum (*Ber.*, 1917, **50**, 1270) but without isolation of the intermediate hydroxy-ester], b. p. 83—85°/0·2 mm., n_D^{23} 1·5438 (Kon and Johnson, *J.*, 1926, 2752, give b. p. 142—145°/16 mm., n_D^{19} 1·5451), was treated with methylmagnesium bromide (from Mg, 3 g.), to give α-methylstyryldimethylcarbinol (5 g.), b. p. 86—87°/0·05 mm., n_D^{20} 1·5423 (Found: C, 82·3; H, 9·2%). Light absorption: identical with that of the sample obtained under (*a*). Catalytic hydrogenation as above gave 2-methyl-4-phenylpentan-2-ol [3 : 5-dinitrobenzoate, m. p. 97—98°, undepressed on admixture with the specimen prepared as in (*a*)].

α-Methylstyrene.—Phenyldimethylcarbinol (Tissier and Grignard, *Compt. rend.*, 1901, **132**, 1184) [p-*nitrobenzoate*, m. p. 134—135° (Found: C, 67·2; H, 5·5; N, 4·8. $C_{16}H_{15}O_4N$ requires C, 67·4; H, 5·3; N, 4·9%)] was dehydrated, by distillation from potassium hydrogen sulphate (Perkin and Matsubara, *J.*, 1905, **87**, 671), to α-methylstyrene, b. p. 165°, n_D^{16} 1·5407. Light absorption: see Table. In one experiment, a *dimer* of α-methylstyrene, b. p. 147—152°/1 mm., n_D^{29} 1·5667 [Found: C, 91·6; H, 8·8%; *M* (in camphor), 232. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%; *M*, 236], was obtained as sole product. Light absorption in ethanol: Max. 2420 A., ε = 13,500. An analogous dimer from *p*-methyl-α-methylstyrene is described by Hukki (*Acta Chem. Scand.*, 1949, **3**, 279).

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