461. *Alkenylation employing Lithium Alkenyls. Part V.* The Formation and Some Reactions of* cis-*Propenyl-lithium.*

By E. A. Braude and J. A. Coles.

cis-Propenyl bromide in ether reacts readily with lithium to give *cis*-propenyl- and propynyl-lithium in proportions of about 5 : 1. The composition of the mixture of lithium derivatives follows from that of their condensation products with carbonyl compounds and throws some light on the nature of the metalation reaction.

Treatment of the mixture of lithium derivatives with carbon dioxide yields mainly dipropenyl ketone and tetrolic acid, and reaction with benzaldehyde, acraldehyde, and crotonaldehyde affords 30—40% yields of the expected *cis*-propenylcarbinols, together with 5—10% yields of the corresponding propynylcarbinols. The structures of the *cis*-propenylcarbinols are established by catalytic hydrogenation, by their infra-red and ultra-violet light-absorption properties, and by synthesis by partial catalytic hydrogenation of the propynylcarbinols. The selective semi-hydrogenation of the propynyl group in propynylvinylcarbinol is, however, difficult to effect and the method of direct alkenylation is superior.

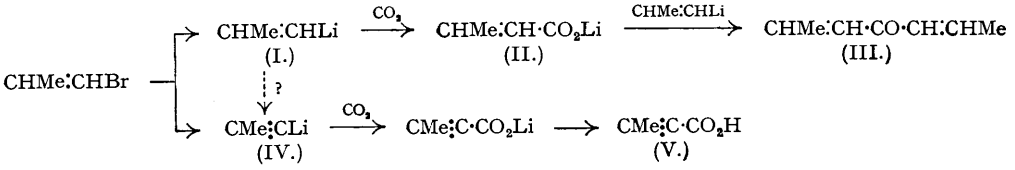
In previous papers (*J.*, 1950, 2000—2019; 1951, 1755) the preparation and some reactions of *iso*butenyl-, *cyclo*pentenyl-, and *cyclo*hexenyl-lithium have been described. The only other alkenyl-lithium at present known is styryl-lithium (Wright, *J. Org. Chem.*, 1936, **1**, 457). In order to establish the fact that formation of lithium derivatives is not limited to ββ-disubstituted and cyclic alkenyl halides which cannot easily undergo dehydrohalogenation, and to 2-arylvinyl halides which also yield Grignard derivatives, the preparation of propenyl-lithium, Me·CH:CHLi, was chosen as the next example for investigation.

Propenyl bromide can be prepared by the general method employed for *iso*butenyl bromide (Part III, *loc. cit.*), namely, simultaneous dehydrobromination and decarboxylation of the corresponding dibromocarboxylic acid, in this case 1 : 2-dibromobutyric acid, with sodium carbonate or pyridine. The propenyl bromide obtained by either procedure consists mainly of the isomer, b. p. 58—59°, together with a small proportion of the isomer, b. p. 63—64° (cf. Wislicenus and Langbein, *Annalen*, 1888, **248**, 325; Chavanne, *Compt. rend.*, 1914, **158**, 1698). Wislicenus and Langbein (*loc. cit.*) regarded the lower-boiling isomer as the *trans*-isomer, while Chavanne (*loc. cit.*) regarded it as the *cis*-isomer on the basis of its lower m. p. and b. p. and of its faster reaction with alcoholic potassium hydroxide. These assignments are clearly inconclusive, but the *cis*-configuration of the lower-boiling isomer can be inferred from dipole moment data. It has been shown by Hannay and Smyth (*J. Amer. Chem. Soc.*, 1946, **68**, 1005), from a consideration of contributing resonance structures, that the moment of a *cis*-propenyl halide would be expected to be similar to that of the *iso*propenyl halide, whereas the moment of the corresponding *trans*-propenyl halide should be higher, and that this expectation is fulfilled for the three propenyl chlorides. In the propenyl bromide series, only the moments of the propenyl bromide, b. p. 58°, and of *iso*propenyl bromide have been measured (Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 1243), but the closeness of the values (μ = 1·57 and 1·510 D., respectively) leaves no doubt that the lower-boiling propenyl bromide is the *cis*-isomer.

cis-Propenyl bromide, when carefully purified by fractionation, reacted rather more readily than *iso*butenyl bromide with lithium in ether, reaction being complete after 2—3 hours. Treatment of the resulting solution with excess of solid carbon dioxide yielded dipropenyl ketone (III) (20%) and tetrolic acid (V) (6%) as the main products. The ketone was characterised as the 2 : 4-dinitrophenylhydrazone and its skeletal structure was established by catalytic hydrogenation to di-*n*-propyl ketone and by its ultra-violet light absorption [maxima at 2450 (ε = 16,000) and 3360 A. (ε = 55)] which is typical of a dialkenyl ketone (cf. Part IV, *J.*, 1950, 2014). The predominant formation of ketones has previously been observed in the carboxylation of *iso*butenyl-, *cyclo*pentenyl-, and *cyclo*hexenyl-, but not of styryl-lithium, and must in this case proceed *via* the lithium salt (II) of *cis*-crotonic acid; the latter, though not isolated, was almost certainly present amongst the carboxylation products. The tetrolic acid must be derived from propynyl-lithium (IV); this may be formed either by the direct dehydro-

* Part IV, *J.*, 1950, 2014.

bromination of propenyl bromide or by the elimination of lithium hydride from propenyllithium (cf. Ziegler and Gellet, *Annalen*, 1950, **567**, 179), followed by further reaction of the resulting propyne with lithium.



In agreement with previous experience, the yields of carboxylation products are rather lower than those obtained in the reaction with other carbonyl compounds. The results obtained in the reaction with benzaldehyde (see below) indicate that, under optimum conditions, *cis*-propenyl bromide is converted into a mixture of propenyl- and propynyl-lithium in a proportion of 5 : 1 and in a total yield of not less than 50%. The proportion of ethylenic to acetylenic derivative is very similar to that observed by Wright (*loc. cit.*) for the corresponding reactions of β-bromostyrene but, in contrast to the behaviour of the latter bromide and of *iso*butenyl bromide (Part I, *loc. cit.*), direct metalation of propenyl bromide is not accompanied by the formation of the expected Wurtz reaction by-product, hexa-2 : 4-diene.

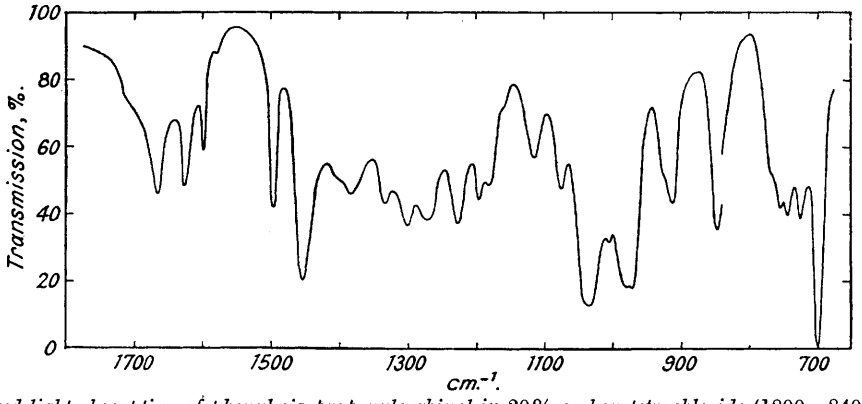
The reaction of the mixture of lithium derivatives obtained from *cis*-propenyl bromide with benzaldehyde afforded phenyl-*cis*-propenylcarbinol (VI) (35%) and phenylpropynylcarbinol (VII) (7%). The latter was also prepared by reaction of benzaldehyde with propynylmagnesium bromide (Iotsitch, *J. Russian Phys. Chem. Soc.*, 1909, **41**, 540) and was characterised by the *p*-nitrobenzoate. The structure of the ethylenic carbinol was established by catalytic hydrogenation (1 mol. of hydrogen) to 1-phenylbutanol and by the fact that it forms a nitrobenzoate (m. p. 57°) different from that (m. p. 99°) of the higher-boiling *trans*-isomer obtained by reaction of crotonaldehyde with phenylmagnesium bromide (Kenyon, Partridge, and Philipps, *J.*, 1937, 207; Braude, Jones, and Stern, *J.*, 1946, 396). The geometrical configuration of the higher-boiling isomer follows from the fact that the propenyl group in ordinary crotonaldehyde has a *trans*-configuration (Young, *J. Amer. Chem. Soc.*, 1932, **54**, 2498; Grédy and Piaux, *Compt. rend.*, 1934, **198**, 1235; Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957). The configuration of the lower-boiling isomer was confirmed by its synthesis by partial hydrogenation of phenylpropynylcarbinol in the presence of platinum oxide. It is well known that catalytic hydrogenation results in the *cis*-addition of two hydrogen atoms and that the semihydrogenation of an acetylenic derivative produces only the *cis*-olefinic derivatives unless the latter is unstable (cf. Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 148; Sondheimer, *J.*, 1950, 877; Raphael and Sondheimer, *J.*, 1950, 115). The catalyst usually preferred for semihydrogenation of an acetylenic linkage is palladium (cf. Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84) and the use of platinum oxide in the present case was accidental; however, on interruption of the hydrogenation after 1 molecular equivalent had been absorbed, an excellent yield of the *cis*-propenylcarbinol was obtained and platinum oxide thus appears to display the same selectivity as other catalysts.

(VI.) Ph·CH(OH)·CH:CHMe Ph·CH(OH)·C:CMe (VII.)

The configuration of the propenyl group in the stereoisomeric phenylpropenylcarbinols was confirmed by infra-red light absorption date, kindly determined by Mr. A. R. Philpotts and Mr. W. Thain (cf. *Nature*, 1950, **166**, 1028) and partly reproduced in Figs. 1*a* and 1*b*. The absorption curves of the two isomers show characteristic differences in the 500—2000-cm.$^{-1}$ range and contain two bands near 970 and 760 cm.$^{-1}$ which are much more intense with the *trans*- than with the *cis*-isomer. The 970-cm.$^{-1}$ band is probably to be ascribed to a deformation frequency of the C–O–H group (cf. Barnard *et al.*, *J.*, 1950, 915) which, in the *trans*-carbinols, overlaps with a deformation frequency of the *trans*-H–C≡C–H group; similar bands and intensity differences are shown by other pairs of stereoisomeric ethylenic carbinols (Crombie and Harper, *J.*, 1950, 873, 1707, 1714; Sondheimer, *loc. cit.*). The 760-cm.$^{-1}$ band has been assigned to an aromatic C–H deformation frequency (Philpotts and Thain, *loc. cit.*), but the difference between the intensity of this band in the phenyl-*cis*- and -*trans*-propenylcarbinols is rather unexpected on this basis. It can be estimated from the data that the samples of phenyl-*cis*-propenylcarbinol prepared by either of the two routes described above contained less than 3% of the *trans*-isomer.

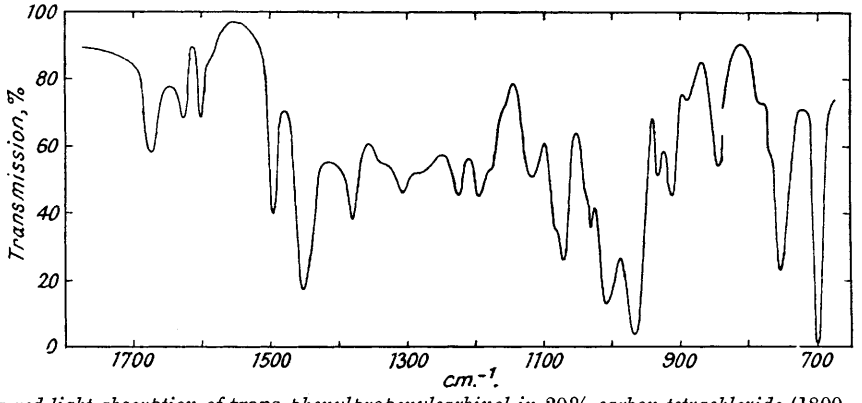
The reaction of the mixture of *cis*-propenyl- and propynyl-lithium obtained from *cis*-propenyl bromide with acraldehyde afforded *cis*-propenylvinylcarbinol (VIII) in 30% yield. None of the corresponding propynylcarbinol (IX) was isolated in this case and the reaction was attended by considerable polymerisation. This is in contrast to the condensation of acraldehyde with Grignard reagents which usually proceeds quite smoothly (cf. Braude, Jones, and Stern, *loc. cit.*), but it has previously been observed that vinyl compounds are polymerised more readily by

FIG. 1*a*.



Infra-red light absorption of phenyl-cis-*propenylcarbinol in* 20% *carbon tetrachloride* (1800—840 *cm.*$^{-1}$) *and* 10% cyclo*hexane* (840—600 *cm.*$^{-1}$) *solutions. Cell thickness* 0·013 *cm.*

FIG. 1*b*.



Infra-red light absorption of trans-*phenylpropenylcarbinol in* 20% *carbon tetrachloride* (1800—840 *cm.*$^{-1}$) *and* 10% cyclo*hexane* (840—600 *cm.*$^{-1}$) *solutions. Cell thickness* 0·013 *cm.*

lithium than by Grignard reagents (Ziegler *et al.*, *Annalen*, 1929, **473**, 57; 1934, **511**, 45). The structure of *cis*-propenylvinylcarbinol was proved by catalytic hydrogenation, which resulted

CHMe:CH·CH(OH)·CH:CH_2	CMe:C·CH(OH)·CH:CH_2	CHMe:CH·CHEt·OH
(VIII.)	(IX.)	(X.)

in the uptake of 2 moles of hydrogen to give *n*-hexan-3-ol and by the formation of an α-naphthylurethane (m. p. 86—88°) different from that (m. p. 96—98°) of *trans*-propenylvinylcarbinol obtained by the condensation of (*trans*-)crotonaldehyde with sodium acetylide and subsequent partial hydrogenation (Heilbron, Jones, McCombie, and Weedon, *loc. cit.*).

In an attempt to synthesise *cis*-propenylvinylcarbinol by an alternative route, propynylmagnesium bromide was condensed with acraldehyde to give propynylvinylcarbinol and the latter was subjected to partial catalytic hydrogenation (one mole of hydrogen). When a 0·3% palladium–calcium carbonate catalyst was used, the product consisted of about equal

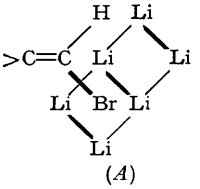
proportions of *cis*-propenylvinylcarbinol and ethyl-*cis*-propenylcarbinol (X) which are not readily separated by fractionation, while in the presence of 1·2% palladium-calcium carbonate or platinic oxide ethyl-*cis*-propenylcarbinol was the main product. The monoethylenic carbinol was characterised by an α-naphthylurethane, m. p. 75—76°, which is formed more readily than that of the diethylenic carbinol, and its structure was established by ozonisation, which afforded acetaldehyde but no formaldehyde. The structure was confirmed by an alternative synthesis in which propynylmagnesium bromide was condensed with propaldehyde to give ethylpropynylcarbinol, partial catalytic hydrogenation of which readily furnished ethyl-*cis*-propenylcarbinol, characterised by an α-naphthylurethane identical with that obtained before. The difficulty of achieving the selective hydrogenation of propynylvinylcarbinol shows that a vinyl group can effectively compete with a propynyl group under these conditions. No other examples of the semihydrogenation of a *di*-substituted acetylenic group in the presence of a vinyl group appear to have been described, but many cases of the selective semihydrogenation of a *mono*-substituted acetylenic (ethynyl) group in the presence of an alkenyl group are known. The ease of hydrogenation thus appears to decrease in the sequence R·C:CH > R·C:C·R > R·CH:CH_2 > R·CH:CH·R and it is possible to formulate the rule that in compounds containing two such groups selective hydrogenation can readily be effected only between non-adjacent members of the series. For this reason, as illustrated by the synthesis of *cis*-propenylvinylcarbinol, the method of direct alkenylation can offer considerable advantages even in the synthesis of ethylenic compounds which are structurally accessible through acetylenic intermediates.

The reaction of the mixture of lithium derivatives from *cis*-propenyl bromide with crotonaldehyde afforded a somewhat better yield of products than that with acraldehyde and gave *cis-trans*-dipropenylcarbinol (XI) (40%) and *trans*-propenylpropynylcarbinol (XII) (7%), which

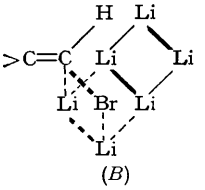
CHMe:CH·CH(OH)·CH:CHMe (XI.) CMe:C·CH(OH)·CH:CHMe (XII.)

were characterised by their α-naphthylurethanes. The skeletal structure of the dipropenylcarbinol was established by catalytic hydrogenation (two moles of hydrogen) to *n*-heptan-4-ol, which was oxidised to di-*n*-propyl ketone. The geometrical configuration of the ethylenic groups was not rigidly proved, but clearly follows from the work described above which shows that the propenyl group derived originally from *cis*-propenyl bromide will have the *cis*-configuration, whereas that derived from crotonaldehyde will have the *trans*-configuration.

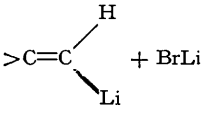
The fact that the only ethylenic products obtained by reaction of the lithium derivatives of *cis*-propenyl bromide with aldehydes are the *cis*-propenylcarbinols is of considerable interest in relation to the mechanism of the metalation reaction. Clearly the metalation and condensation reactions may either be both accompanied by partial or complete *cis-trans*-isomerisation, in which case the formation of the *cis*-propenylcarbinols would have to be ascribed to their superior stability as compared with the *trans*-isomers, or else both steps must be accompanied by complete retention. The first possibility may be dismissed since the *trans*-isomers do not undergo *cis-trans*-isomerisation under conditions resembling those of the condensation reaction, as well as for various other reasons which need not be detailed. It must be concluded that both steps are accompanied by complete retention of geometrical configuration and that the direct metalation reaction gives rise exclusively to *cis*-propenyl-lithium.* It has sometimes been suggested that metalation processes are homolytic and involve " free "-radical intermediates (cf. Waters, " The Chemistry of Free Radicals," Oxford, 1946) but conventional mechanisms of this type are rendered unlikely by the present observation since they would be



(*A*)



(*B*)



(*C*)

expected to give rise to mixtures of geometrical isomers. In the absence of other decisive evidence, it is suggested that the entire reaction takes place on the surface of the metal as

* Wright (*loc. cit.*) states that carboxylation of the lithium derivative of *cis*-β-bromostyrene yields only *trans*-cinnamic acid and phenylpropiolic acid, but details of this experiment are not given and the stabilities of the bromide, and of *cis*-cinnamic acid, under the reaction conditions were not examined.

indicated on p. 2081 ($A \longrightarrow C$). The distance between neighbouring atoms in the lithium-metal crystal is considerably greater (*ca.* 3 A.) than the length of the carbon–bromine bond (*ca.* 1·5 A.), but in view of the large size and polarisability of the halogen atom, the proposed four-centre, planar transition state (*B*) is quite feasible and obviously accounts for the retention of geometrical configuration. The superior efficacy of lithium in this type of reaction may well be due to the fact that it has the smallest interatomic spacing amongst the alkali metals.

Experimental.

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

cis-*Propenyl Bromide.*—The literature concerning the preparation and properties of propenyl bromide are somewhat conflicting. In our hands, all the methods of preparation used give mainly *cis*-propenyl bromide, as described below.

(*a*) Bromine (1600 g.) was added dropwise to crotonic acid (820 g.) in carbon disulphide (1300 ml.) at 0°. Next morning, the solvent was distilled off and the crude dibromobutyric acid (m. p. 84°; 2200 g.) was carefully treated with excess of sodium carbonate (1500 g.) in water (5 l.). The resulting solution was steam-distilled and the product extracted with ether, dried ($CaCl_2$), and fractionated, giving mainly *cis*-propenyl bromide (180 g., 16%), b. p. 58°/760 mm., n_D^{24} 1·4542, in agreement with the results of Wislicenus and Langbein (*Annalen*, 1888, **248**, 325) and contrary to those of Farrell and Bachmann (*J. Amer. Chem. Soc.*, 1935, **57**, 1281) who state that no propenyl bromide is formed under these conditions. Only a small yield of propenyl bromide was obtained on heating dibromobutyric acid with excess of 2N-sodium hydroxide.

(*b*) A solution of dibromobutyric acid (500 g.) in dry pyridine (1 l.) was heated under reflux for 5 hours and then poured into excess of ice-cold hydrochloric acid. Isolation of the product as before and fractionation gave *cis*-propenyl bromide (43 g., 20%), b. p. 58°/760 mm., n_D^{22} 1·4533, in agreement with Farrell and Bachmann's results (*loc. cit.*).

An attempt to convert *cis*-propenyl bromide, b. p. 58°, into the *trans*-isomer, b. p. 63°, by the dehydrobromination of 1 : 1 : 2-tribromopropane with zinc in ethanol, as described by Wislicenus and Langbein (*loc. cit.*), failed, the *cis*-bromide again being obtained in agreement with Chavanne's results (*Compt. rend.*, 1914, **158**, 1698). Commercial samples of propenyl bromide also consisted almost entirely of *cis*-propenyl bromide, as judged by the b. p., but considerable variations were observed in n_D^{24} (1·4450—1·4550). Similar unexplained variations have been noted in the case of *iso*butenyl bromide (Part I, *J.*, 1950, 2000) where no stereoisomerism is possible. According to Chavanne (*loc. cit.*), pure *cis*-propenyl bromide has b. p. 58°, n_D 1·4564 (temperature not stated), whereas ordinary propenyl bromide is a 4 : 1 equilibrium *cis–trans*-mixture, which can be separated by prolonged fractionation in the presence of ethanol, but rapidly reverts to the equilibrium mixture on storage. The transformations described below, in which the bromide, b. p. 58°, is converted into *cis*-propenyl derivatives containing less than 2% of the *trans*-isomers, provide no evidence for the presence of the *trans*-bromide. However, the yields in these transformations are only of the order of 50% and it is possible that the *trans*-bromide, though present, is less readily metalated than the *cis*-bromide.

cis-*Propenyl-lithium.*—When freshly distilled from a trace of sodium, *cis*-propenyl bromide in dry ether solution reacts readily with lithium, under conditions previously described for *iso*butenyl bromide (Part I, *loc. cit.*). About one-tenth of the bromide is added initially and reaction sets in after 10—20 minutes. The remainder of the bromide is then added at a rate sufficient to maintain gentle refluxing of the ether and stirring is continued until all the metal has been consumed, usually 1—2 hours.

Dipropenyl Ketone and Tetrolic Acid.—Excess of solid carbon dioxide (300 g.) was added to the solution obtained by reaction of *cis*-propenyl bromide (65 g., 0·54 mol.) in ether (1 l.) with a stirred suspension of finely cut lithium metal (6·9 g., 1 mol.) in ether (1 l.). Stirring was continued for 3 hours. Saturated aqueous ammonium chloride (500 ml.) was then added, followed by 2N-hydrochloric acid (100 ml.). The ethereal layer was separated and extracted with saturated sodium hydrogen carbonate solution. The alkaline extract was acidified and the oily product crystallised from light petroleum (b. p. 60—80°) to give tetrolic acid (2·5 g., 6%), m. p. 76°, undepressed by an authentic specimen. The ethereal layer was dried (K_2CO_3) and fractionated to give *dipropenyl ketone* (*hepta-2 : 5-dien-4-one*) (4 g., 15%), a pale yellow liquid, b. p. 67—70°/20 mm., n_D^{21} 1·4837 (Found: C, 76·5; H, 9·5. $C_7H_{10}O$ requires C, 76·3; H, 9·1%). Light absorption in ethanol: $\lambda_{max.}$ 2450, 2510, and 3360 A.; ε = 15,900, 15,500, and 55, respectively. The ketone gave a 2 : 4-*dinitrophenylhydrazone*, which was chromatographed on alumina from benzene solution and crystallised from aqueous methanol in red prisms, m. p. 152° (Found: C, 53·6; H, 4·8; N, 18·6. $C_{13}H_{14}O_4N_4$ requires C, 53·8; H, 4·8; N, 19·3%). Light absorption in chloroform: $\lambda_{max.}$ 2580 and 3870 A., ε = 17,000 and 31,000 respectively.

Hydrogenation of dipropenyl ketone (1·7 g.) in methanol (25 ml.) in the presence of platinic oxide resulted in the uptake of 760 ml. of hydrogen at 18°/768 mm. (Calc., 800 ml.) to give heptan-4-one, identified as the 2 : 4-dinitrophenylhydrazone, which after chromatography on alumina from benzene solution and crystallisation from methanol had m. p. 74—75°, undepressed on admixture with an authentic specimen.

Phenyl-cis-*propenylcarbinol* (1-*Phenylbut*-2-*en*-1-*ol*) (VI) *and Phenylpropynylcarbinol* (1-*Phenylbut*-2-*yn*-1-*ol*) (VII).—(*a*) Benzaldehyde (53 g.) in ether (50 ml.) was gradually added at 0° to the solution obtained by treating *cis*-propenyl bromide (65 g.) with lithium (6·9 g.) in ether (1 l.). Stirring was continued for 2 hours and ice-cold saturated aqueous ammonium chloride (500 ml.) was then added.

The ethereal layer was separated, dried (Na_2SO_4–K_2CO_3) and fractionated through an 8-inch Fenske column to give cis-1-*phenylbut*-2-*en*-1-*ol* (24 g., 35%), b. p. 81°/0·2 mm., n_D^{21} 1·5412 (Found: C, 80·8; H, 8·1. $C_{10}H_{12}O$ requires C, 80·9; H, 8·2%) and 1-phenylbut-2-yn-1-ol (5 g., 7%), b. p. 88°/0·2 mm., n_D^{20} 1·5496. The two carbinols exhibited light absorption properties identical with those of the samples obtained under (*b*) and formed *p*-nitrobenzoates in good yields, m. p.s 56—57° and 104—105°, respectively, undepressed on admixture with the authentic specimens described below.

Hydrogenation of *cis*-1-phenylbut-2-en-1-ol (1·6 g.) in methanol (30 ml.) in the presence of platinic oxide resulted in the uptake of 250 ml. of hydrogen at 27°/768 mm. (Calc., 250 ml.). After removal of the catalyst and solvent, the product was dissolved in ether (10 ml.) and oxidised to *n*-butyrophenone by shaking it with potassium dichromate (1·6 g.) in 2N-sulphuric acid. The ketone was identified as the semicarbazone, which was crystallised from aqueous ethanol and had m. p. 189·5—190·5° (Tiffeneau and Levy, *Compt. rend.*, 1926, **183**, 920, give m. p. 188—189°), and the 2 : 4-dinitrophenylhydrazone, which was chromatographed on alumina from benzene solution and crystallised from ethyl acetate in red plates, m. p. 192—193° (Evans, *J.*, 1936, 785, gives 190°) undepressed on admixture with an authentic specimen.

(*b*) Benzaldehyde (53 g.) in ether (50 ml.) was gradually added to a solution of propynylmagnesium bromide, obtained by passing propyne (Hurd, Meinert, and Spence, *J. Amer. Chem. Soc.*, 1930, **52**, 1138) into a solution of ethylmagnesium bromide (from Mg, 12·2 g.) in ether (500 ml.) at 0°. After overnight stirring, ice-cold saturated aqueous ammonium chloride (600 ml.) was added. The ethereal layer was separated, dried (Na_2SO_4–K_2CO_3) and fractionated, giving 1-phenylbut-2-yn-1-ol (20 g., 30%), b. p. 110°/0·8 mm., n_D^{26} 1·5519, which solidified on cooling in plates, m. p. 37° (Iotsitch, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 540, gives b. p. 128°/9 mm., m. p. 30°). Light absorption in ethanol: $\lambda_{max.}$ 2510, 2570, and 2640 A.; ε = 370, 440, and 390, respectively. The carbinol formed a p-*nitrobenzoate* which crystallised from aqueous methanol in long prisms, m. p. 107° (Found: C, 69·5; H, 4·5; N, 4·7. $C_{12}H_{13}O_4N$ requires C, 69·2; H, 4·4; N, 4·75%).

1-Phenylbut-2-yn-1-ol (5·5 g., 0·038 mol.) in methanol (100 ml.) was hydrogenated in the presence of platinic oxide (10 mg.) until 900 ml. of hydrogen at 21°/768 mm. (corresponding to one mol.) had been absorbed. Removal of the catalyst and fractionation afforded *cis*-1-phenylbut-2-en-1-ol (4·8 g.), b. p. 81°/0·2 mm., n_D^{22} 1·5350. Ultra-violet light absorption in ethanol: $\lambda_{max.}$ 2550 A.; ε = 2000. Infra-red light absorption: see Fig. 1*b*. Treatment of a solution of the carbinol in dry pyridine with the calculated amount of *p*-nitrobenzoyl chloride at 0° gave the *p*-nitrobenzoate which crystallised from aqueous methanol in microcrystalline plates, m. p. 57—58° (Found: C, 69·0; H, 5·2; N, 4·9. $C_{17}H_{13}O_4N$ requires C, 68·7; H, 5·05; N, 4·7%). Light absorption of the *p*-nitrobenzoate in ethanol: $\lambda_{max.}$ 2650 A.; ε = 16,500.

cis-*Propenylvinylcarbinol* (*Hexa*-1 : 4-*dien*-3-*ol*) (VIII).—Acraldehyde (35 g.) in ether (50 ml.) was gradually added at 0° to the solution obtained by treating *cis*-propenyl bromide (65 g.) with lithium (6·9 g.) in ether (1 l.). After the mixture had been stirred overnight, saturated aqueous ammonium chloride (500 ml.) was added. Solid polymeric products (10 g.) were filtered off and the ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated, to give cis-*hexa*-1 : 4-*dien*-3-*ol* (15 g., 30%), b. p. 86—87°/87 mm., n_D^{27} 1·4559 (Found: C, 73·6; H, 10·1. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Light absorption in ethanol: ε = <200 between 2200 and 3000 A. The carbinol formed an *α-naphthylurethane* which crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 86—88° (Found: N, 5·5. $C_{17}H_{17}O_2N$ requires N, 5·25%). A mixture of this derivative with *trans*-hexa-1 : 4-dien-3-ol α-naphthylurethane (m. p. 93·5—94·5; Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84) melted at 89—91·5°.

Hydrogenation of the *cis*-dienol (1·3 g.) in methanol (30 ml.) in the presence of platinic oxide resulted in the uptake of 650 ml. of hydrogen at 23°/761 mm. (Calc., 645 ml.). After removal of the catalyst and solvent, the residue was taken up in ether (10 ml.) and shaken with potassium dichromate (1·3 g.) in 2N-sulphuric acid (30 ml.), and the product converted into ethyl *n*-propyl ketone 2 : 4-dinitrophenylhydrazone, which after chromatography on alumina from benzene solution and crystallisation from ethyl acetate had m. p. 128—130°, undepressed on admixture with an authentic specimen.

Propynylvinylcarbinol (*Hexa*-1-*en*-4-*yn*-3-*ol*) (IX).—Acraldehyde (28 g.) in ether (35 ml.) was added dropwise to a solution prepared as above, of propynylmagnesium bromide (from Mg, 12·2 g.) in ether (500 ml.) at 0° and the whole stirred overnight. Ice-cold saturated aqueous ammonium chloride (600 ml.) was then added. The ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated, giving *hexa*-1-*en*-4-*yn*-3-*ol* (18 g., 37%), b. p. 73°/26 mm., n_D^{21} 1·4712 (Found: C, 75·1; H, 8·5. C_6H_8O requires C, 74·9; H, 8·4%). Light absorption in ethanol: ε = <100 in the region 2200—4000 A. The *α-naphthylurethane* crystallised from light petroleum (b. p. 80—100°) in white clusters, m. p. 97—99° (Found: N, 5·6. $C_{17}H_{15}O_2N$ requires N, 5·3%).

Ethylpropynylcarbinol (*Hex*-4-*yn*-3-*ol*) *and Ethyl*-cis-*propenylcarbinol* (cis-*Hex*-4-*en*-3-*ol*) (X).—Freshly distilled propaldehyde (29 g.) in ether (50 ml.) was added dropwise to a solution, prepared as above, of propynylmagnesium bromide (from Mg, 12·2 g.) in ether (500 ml.) at 0°. After being stirred overnight, the reaction mixture was added slowly, with stirring, to ice-cold, saturated aqueous ammonium chloride (400 ml.). The ethereal layer was separated, dried (Na_2SO_4), and fractionated, giving *hex*-4-*yn*-3-*ol* (20 g., 40%), b. p. 51—52°/13 mm., n_D^{21} 1·4490 (Found: C, 73·2; H, 10·5. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Light absorption in ethanol: ε = <200 in the region 2200—4000 A. The *α-naphthylurethane* crystallised from light petroleum (b. p. 80—100°) in white clusters, m. p. 82—83° (Found: C, 75·9; H, 6·2; N, 5·6. $C_{17}H_{17}O_2N$ requires C, 76·3; H, 6·4; N, 5·6%).

The hexynol (2·5 g.) in methanol (20 ml.) was hydrogenated in the presence of a 1·2% palladium–calcium carbonate catalyst until 600 ml. (one mol.) of hydrogen at 16°/759 mm. had been absorbed.

Distillation of the product gave cis-*hex*-4-*en*-3-*ol* (2·2 g.), b. p. 44—46°/14 mm., n_D^{21} 1·4342 (Found: C, 72·0; H, 12·0. $C_6H_{12}O$ requires C, 72·0; H, 11·1%) (Airs, Balfe, and Kenyon, *J.*, 1942, 18, give b. p. 135°/760 mm., n_D^{23} 1·4325, for the *trans*-isomer). The carbinol formed an *α-naphthylurethane*, which crystallised from light petroleum (b. p. 80—100°) in clusters, m. p. 74—75° (Found: C, 76·2; H, 7·6; N, 5·5. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·3%).

Partial Hydrogenation of Propynylvinylcarbinol (*Hex*-1-*en*-4-*yn*-3-*ol*).—Hex-1-en-4-yn-3-ol (3·4 g.) in methanol (20 ml.) was hydrogenated in the presence of a 0·3% palladium–calcium carbonate catalyst until 820 ml. of hydrogen at 17°/765 mm. (corresponding to one mol.) had been absorbed (about 8 hours). The product was fractionated through a 3″ Fenske column and yielded a continuous range of fractions (total, 2·6 g.), b. p. 44—47°/12 mm., n_D^{24} 1·4420—1·4530, containing varying proportions of *cis*-hexa-1 : 4-dien-3-ol and *cis*-hex-4-en-3-ol, which were not effectively separated under these conditions. On treatment with α-naphthyl *iso*cyanate and a trace of triethylamine, both the lowest and highest fractions yielded only the α-naphthylurethane of *cis*-hex-4-en-3-ol, which was crystallised from light petroleum (b. p. 80—100°) and had m. p. 75—76°, undepressed on admixture with the authentic sample described above. The presence of the other carbinol in about equal proportion was proved by acid treatment of the carbinol mixture, which results in the isomerisation of hexa-1 : 4-dien-3-ol into hexa-3 : 5-dien-2-ol which can be separated more easily from the unchanged hex-4-en-3-ol (Braude and Coles, *J.*, 1951, 2085).

When the partial hydrogenation (one mol. of hydrogen) was carried out in the presence of a 1·3% palladium–calcium carbonate catalyst or platinic oxide, the uptake of hydrogen was much more rapid and the main product was hex-4-en-3-ol, identified by the α-naphthylurethane, m. p. 76—77°, undepressed on admixture with the sample described above, and very little *cis*-hexa-1 : 4-dien-3-ol was obtained. Ozonisation of hex-4-en-3-ol (0·5 g.) in carbon tetrachloride (20 ml.) for 4 hours and decomposition of the ozonide by the method of Church *et al.* (*J. Amer. Chem. Soc.*, 1934, **56**, 176) afforded acetaldehyde, isolated as the 2 : 4-dinitrophenylhydrazone (0·4 g., 45%), m. p. 164°, undepressed on admixture with an authentic specimen.

cis-trans-*Dipropenylcarbinol* (*Hepta*-2 : 5-*dien*-4-*ol*) (XI) *and* trans-*Propenylpropynylcarbinol* (*Hept*-2-*en*-5-*yn*-4-*ol*) (XII).—Crotonaldehyde (35 g.) in ether (50 ml.) was added dropwise at 0° to the solution obtained by treating *cis*-propenyl bromide (65 g.) with lithium (6·9 g.) in ether (1 l.). Stirring was continued for 2 hours and the solution was then treated with saturated aqueous ammonium chloride (600 ml.). The ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated through a 12″ Fenske column, to give (i) cis-trans-*hepta*-2 : 5-*dien*-4-*ol* (21 g., 38%), b. p. 72°/16 mm., n_D^{24} 1·4617 (Found: C, 75·4; H, 11·0. $C_7H_{12}O$ requires C, 75·0; H, 10·8%), and (ii) cis-*hepta*-2-*en*-5-*yn*-4-*ol* (4 g., 7%), b. p. 78°/16 mm., n_D^{22} 1·4690. Neither carbinol showed any light absorption with ε = >500 in the 2200—3000-A. region. The dienol formed an *α-naphthylurethane* which crystallised from light petroleum (b. p. 80—100°) in plates, m. p. 108° (Found: C, 76·7; H, 6·7; N, 5·2. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0%). The heptenynol formed an *α-naphthylurethane* which crystallised from light petroleum (b. p. 100—120°) in plates, m. p. 132—133° (Found: C, 77·1; H, 6·2; N, 5·1. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; N, 5·0%).

Hydrogenation of *cis-trans*-hepta-2 : 5-dien-4-ol (1·5 g.) in methanol (50 ml.) in the presence of platinic oxide resulted in the uptake of 700 ml. of hydrogen at 27°/688 mm. (Calc., 650 ml.). After removal of the catalyst and solvent, the residue was taken up in ether and oxidised with potassium dichromate (1·4 g.) in 2N-sulphuric acid, giving di-*n*-propyl ketone, b. p. 145°, identified by the 2 : 4-dinitrophenylhydrazone which after chromatography on alumina from benzene solution and crystallisation from aqueous methanol had m. p. 74°, undepressed on admixture with an authentic specimen.

We thank Professor R. P. Linstead, C.B.E., F.R.S., for his interest in the work described in this and the following paper, and the Department of Scientific and Industrial Research for a grant (to J. A. C.).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, February 9th*, 1951.]