648. *Alkenylation with Lithium Alkenyls. Part XIII.** *1-Methylvinyl-lithium* (iso*Propenyl-lithium*).

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*iso*Propenyl bromide is readily converted into the lithium alkenyl, $CH_2{:}CMe{\cdot}Li$ by direct metallation. All five possible methyl-substituted vinyl-lithium derivatives $CR_2{:}CR{\cdot}Li$ (R = H or Me) are now known.

*iso*Propenyl-lithium reacts with carbon dioxide, to give α-methylacrylic acid, with aldehydes to give secondary alcohols (23—72%), and with ketones to give the expected tertiary alcohols (65—88%).

The acid-catalysed rearrangements of the alcohols $HO{\cdot}CRPh{\cdot}CMe{:}CH_2$ (R = H, Me or Ph) are described, and the spectral properties of the resulting substituted cinnamyl alcohols are discussed.

THIS paper describes the formation and some reactions of 1-methylvinyl-lithium (*iso*propenyl-lithium), $CH_2{:}CMe{\cdot}Li$. 2-Methylvinyl-lithium (propenyl-lithium),[1] as well as the three more highly methyl-substituted derivatives of the type $CR_2{:}CR{\cdot}Li$, have been described previously,[2,3] so that this series of lithium alkenyls, which are proving useful synthetical reagents,[4] is now completed. *iso*Propenyl-lithium is employed here for the preparation of a number of allylic alcohols required in connection with studies on anionotropic rearrangements.[5]

*iso*Propenyl bromide underwent direct metallation with ease under the usual conditions. Very little, if any, Wurtz-type coupling or other side reactions occurred, and no 2 : 3-dimethylbutadiene was isolated; yields as high as 88% were attained in subsequent reactions, *e.g.*, with acetophenone (see below). Carboxylation of *iso*propenyl-lithium afforded α-methylacrylic acid in low yield (about 20%), comparable to that obtained in other cases; as with 1 : 2-di- and 1 : 2 : 2-tri-methylvinyl-lithium, and in contrast to 2-methyl- and 2 : 2-dimethyl-vinyl-lithium, only traces of ketonic products were obtained. It is not clear at present whether this is due to a steric effect of the 1-methyl group or to some other cause. After the present investigation had been completed, the earlier work of Petrov[6a] and Nesmeyanov[6b] came to our notice. These authors carried out the carboxylation of *iso*propenyl-lithium, isolating, besides α-methylacrylic acid, a small amount of di*iso*propenyl ketone. They also effected metathetical reactions of *iso*propenyl-lithium with chlorotrimethylsilane and with several metal halides.

Reaction of *iso*propenyl-lithium with aldehydes and ketones gave the secondary or tertiary alcohols (see Table), the latter generally in higher yields.

Reactions of iso*propenyl-lithium with aldehydes and ketones.*

Carbonyl compound	Product	Yield (%)
Benzaldehyde	$HO{\cdot}CHPh{\cdot}CMe{:}CH_2$ (I)	72
Acetophenone	$HO{\cdot}CMePh{\cdot}CMe{:}CH_2$ (II)	88
Benzophenone	$HO{\cdot}CPh_2{\cdot}CMe{:}CH_2$ (III)	65
Acraldehyde	$CH_2{:}CH{\cdot}CH(OH){\cdot}CMe{:}CH_2$ (IV)	23
Crotonaldehyde	$CHMe{:}CH{\cdot}CH(OH){\cdot}CMe{:}CH_2$ (V)	38
Mesityl oxide	$CMe_2{:}CH{\cdot}CMe(OH){\cdot}CMe{:}CH_2$ (VI)	74

Treatment of the alcohols (I, II, and III) obtained from benzaldehyde, acetophenone, and benzophenone respectively with dilute mineral acid resulted in rearrangement to the corresponding substituted cinnamyl alcohols (VII, VIII, and IX); in the second case

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* Part XII, *J.*, 1955, 3337.

[1] Braude and Coles, *J.*, 1951, 2078; cf. Braude and Evans, *J.*, 1955, 3334.

[2] Braude and Evans, *J.*, 1955, 3324, 3331.

[3] Dreiding and Pratt, *J. Amer. Chem. Soc.*, 1954, **76**, 1902.

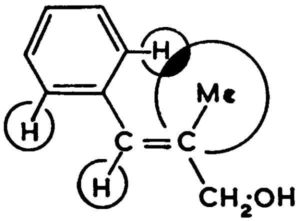
[4] Braude, in " Progress in Organic Chemistry," ed. J. W. Cook, 1955, Vol. III, chapter 4, p. 172.

[5] Cf. Braude, Coles, Evans, and Timmons, *Nature*, 1956, **177**, 1167.

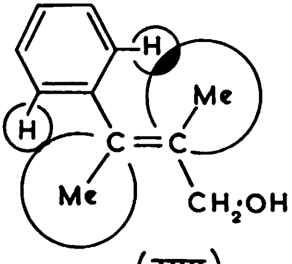
[6] (*a*) Petrov and Nikishin, *Doklady Akad. Nauk U.S.S.R.*, 1953, **93**, 1049; *Chem. Abs.*, 1955, **49**, 841; (*b*) Nesmeyanov, Borisov, and Novikova, *Doklady Akad. Nauk U.S.S.R.*, 1954, **96**, 289; *Chem. Abs.*, 1955, **49**, 5276.

simultaneous dehydration occurred, to yield 2-methyl-3-phenylbutadiene (X). α-Methylcinnamyl alcohol (VII) was characterised by oxidation to α-methylcinnamaldehyde; its geometrical configuration was not proved, but is almost certainly the less hindered form shown, in which the phenyl and hydroxymethyl groups are *trans*-oriented. Even so, the ultraviolet-light absorption ($\lambda_{max.}$ 2440 Å, ε 13,000) differs significantly from that of cinnamyl alcohol ($\lambda_{max.}$ 2510 Å, ε 19,000) undoubtedly owing to steric interference between the phenyl and the methyl groups which prevents the styryl chromophore from becoming uniplanar. This effect is more marked in the dimethyl derivative (VIII) ($\lambda_{max.}$ 2350 Å, ε 5000). Both these alcohols exhibit, not only a reduced absorption intensity, but also considerable hypsochromic shifts of the maxima, signifying appreciable hindrance to planarity.[7]

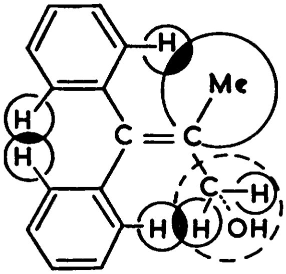
α-Methyl-β-phenylcinnamyl (2-methyl-3 : 3-diphenylallyl) alcohol (IX) has been obtained by Ziegler and Tiemann[8] from 1-methyl-2 : 2-diphenylvinylmagnesium bromide and formaldehyde. It shows an absorption maximum (λ 2420 Å, ε 14,000) practically identical with that of the monophenyl compound (VII); as with other compounds containing the 1 : 1-diphenylethylene unit,[9] the cross-conjugated phenyl group is entirely ineffective.



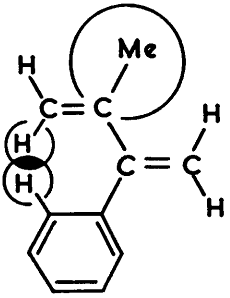
(VII)



(VIII)



(IX)



(X)

Similarly, the absorption of 2-methyl-3-phenylbuta-1 : 3-diene (X) ($\lambda_{max.}$ 2230 Å, ε 10,000) corresponds to that of the partial diene chromophore and is quite different from that of 1-phenylbuta-1 : 3-diene. The apparently almost complete lack of interaction in these cases must again be ascribed to steric hindrance * rather than (as has sometimes been suggested) to the cross-conjugated arrangement as such; less-hindered cross-conjugated systems, though they absorb at shorter wavelengths than their straight-conjugated analogues, show appreciable bathochromic displacement due to the crossed chromophore (*e.g.*, hexatriene,[10] $\lambda_{max.}$

* A non-planar *s-cis*-conformation for the diene (X) instead of the *s-trans*-conformation shown is equally compatible with the spectral data.

[7] Cf. Braude, *Experientia*, 1955, **11**, 457; Braude and Sondheimer, *J.*, 1955, 3773.
[8] Ziegler and Tiemann, *Ber.*, 1922, **55**, 3406.
[9] Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1820; Braude, Bruun, Weedon, and Woods, *J.*, 1952, 1419.
[10] Woods and Schwartzmann, *J. Amer. Chem. Soc.*, 1948, **70**, 3394.

2550 Å; 3-methylenepenta-1 : 4-diene,[11] $\lambda_{max.}$ 2310 Å; * butadiene,[12] $\lambda_{max.}$ 2170 Å; benzophenone, $\lambda_{max.}$ 2510 Å; benzaldehyde, $\lambda_{max.}$ 2420 Å). It is noteworthy that the overall effect of the β-methyl substituent in the alcohol (VIII) is larger than that of the β-phenyl substituent in the analogue (IX), although hindrance should be less severe in the former. This shows that the second phenyl group evidently does interact to some extent, thus compensating, in part, for the larger steric effect. It is probable that, in fact, both phenyl rings are tilted by about the same angle with respect to the plane of the double bond; similar observations have been made for di- and tri-phenylmethyl derivatives [13] and for diphenyl sulphones.[14]

Reaction of *iso*propenyl-lithium with dimethylformamide gave, instead of the expected α-methylacraldehyde, a low yield of a conjugated diene-aldehyde $C_7H_{10}O$, isolated as the 2 : 4-dinitrophenylhydrazone. A similar product was previously obtained [2] from propenyl-lithium.

EXPERIMENTAL

For general methods, see Part IX.[2]

1-*Methylvinyl-lithium* (iso*propenyl-lithium*).—Bromine (800 g.) was added dropwise to a stirred solution of α-methylacrylic acid (400 g.) in carbon disulphide (800 ml.) at 0°. After 15 hr., the solvent was distilled off, giving αβ-dibromo-α-methylpropionic acid, m. p. 46—48°. The dibromo-acid (500 g.) was refluxed for 6 hr. with anhydrous pyridine (1 l.). After cooling, a slight excess of ice-cold concentrated hydrochloric acid was added. Steam-distillation gave crude 2-bromopropene, which was washed with 2N-hydrochloric acid and water, dried ($CaCl_2$), and fractionated from a small piece of sodium. The pure bromide (130 g., 52%) had b. p. 48°, n_D^{20} 1·4438 (Farrell and Bachmann [15] give b. p. 48°, n_D^{20} 1·4426). No 2-bromopropene was obtained on reaction of the dibromo-acid with sodium carbonate.

2-Bromopropene (11 g.) was added in one lot to a stirred suspension of finely divided lithium (1 g.) in anhydrous ether (200 ml.). Reaction set in within 1 min. and the solvent refluxed without external heating. After 30 min., all the metal had been consumed.

α-*Methylacrylic Acid*.—*iso*Propenyl-lithium (from Li, 1 g.) in ether was added to a large excess of powdered carbon dioxide. The mixture was allowed to attain room temperature, water was added, and the solution was acidified with hydrochloric acid. The ether layer was separated and extracted with 2N-sodium carbonate. Evaporation of the ether gave only 0·2 g. of material which did not form a 2 : 4-dinitrophenylhydrazone and was not further investigated. The alkaline extract was acidified with concentrated hydrochloric acid and extracted with ether, and the ether extract was dried (Na_2SO_4) and distilled, giving α-methylacrylic acid (1·3 g., 17%), b. p. 65°/11 mm., n_D^{24} 1·4292 (lit.,[16] b. p. 72°/14 mm., n_D^{20} 1 4314). The acid was characterised as the *benzylamine salt* which crystallised from ethyl acetate in needles, m. p. 93—94°, undepressed on admixture with a sample from authentic acid (Found: C, 68·4; H, 8·0; N, 7·3. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8; N, 7·3%).

2-*Methyl*-1-*phenylallyl Alcohol* (2-*Methyl*-1-*phenylprop*-2-*en*-1-*ol*) (I).—Benzaldehyde (8 g.) in ether (25 ml.) was added dropwise to a stirred ethereal solution of *iso*propenyl-lithium (from Li, 1 g.) at room temperature. After 1 hr., excess of saturated aqueous ammonium chloride was added and the ether layer was separated, dried (Na_2SO_4–K_2CO_3), and distilled, giving the *alcohol* (8 g., 72%), b. p. 55°/0·1 mm., n_D^{20} 1·5349, $\lambda_{max.}$ 2510 (ε 500) and 2580 Å (ε 400) in EtOH (Found: C, 80·9; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%).

α-*Methylcinnamyl Alcohol* (2-*Methyl*-3-*phenylprop*-2-*en*-1-*ol*) (VII).—The foregoing alcohol (2 g.) was refluxed with 0·1M-hydrogen chloride in 60% aqueous acetone (100 ml.) for 20 hr. The solution was neutralised with potassium carbonate, and the acetone was distilled off. Isolation of the product with ether gave the alcohol (1 g., 50%), b. p. 77°/0·1 mm., n_D^{20} 1·5650,

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* The authors cited give severally $\lambda_{max.}$ 2230, 2310, and 2410 Å. These differences may perhaps be due to ring–chain tautomerism with 1-vinyl*cyclo*butene.

[11] Blomquist and Verdol, *J. Amer. Chem. Soc.*, 1955, **77**, 81; 1956, **78**, 109; Bailey and Economy. *ibid.*, p. 1133; Bailey, Cunov, and Nicholas, *ibid.*, p. 2787.

[12] Booker, Evans, and Gillam, *J.*, 1940, 1453.

[13] Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

[14] Koch, *J.*, 1949, 408.

[15] Farrell and Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 1281.

[16] Bruhl, *Annalen*, 1880, **200**, 181; Autenrieth and Pretzell, *Ber.*, 1903, **36**, 1272.

$\lambda_{max.}$ 2440 Å (ε 13,500) in EtOH (Found : C, 80·8; H, 8·4%) (Li and Eliott[17] give b. p. 96°/1·5 mm.).

Oxidation of the alcohol (0·5 g.) with tetrachloro-1 : 2-benzoquinone in chloroform at room temperature and treatment of the product with Brady's reagent gave α-methylcinnamaldehyde 2 : 4-dinitrophenylhydrazone (0·74 g., 67%), m. p. 209—210°, $\lambda_{max.}$ 3900 Å (ε 42,000) in $CHCl_3$.

1 : 2-*Dimethyl*-1-*phenylprop*-2-*en*-1-*ol* (II).—Acetophenone (8 g.) in ether (25 ml.) was allowed to react with *iso*propenyl-lithium (from Li, 1 g.), and the product was worked up as above, giving the *alcohol* (9·5 g., 88%), b. p. 58°/0·1 mm., n_D^{22} 1·5300, $\lambda_{max.}$ 2440 Å (ε 500) in EtOH (Found : C, 81·5; H, 8·8. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%).

αβ-*Dimethylcinnamyl Alcohol* (2 : 3-*Dimethyl*-3-*phenylprop*-2-*en*-1-*ol* (VIII) and 2-*Methyl*-3-*phenylbuta*-1 : 3-*diene* (X).—The foregoing alcohol (3·5 g.) was refluxed for 12 hr. with 0·005M-hydrogen chloride in 60% aqueous acetone (100 ml.). Isolation of the products as above and fractionation gave the *diene* (1·8 g., 60%), b. p. 39—41°/0·1 mm., n_D^{22} 1·5380, $\lambda_{max.}$ 2230 Å (ε 10,000) in EtOH [Found : C, 90·3; H, 8·4. $C_{11}H_{12}$ requires C, 91·7; H, 8·3% (low carbon values have been obtained [18] in analogous cases)], and the *alcohol* (0·8 g., 23%), b. p. 79—81°/0·1 mm., n_D^{22} 1·5450, $\lambda_{max.}$ 2350 Å (ε 5000) in EtOH (Found : C, 81·8; H, 8·8. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%).

When the alcohol (II) was refluxed with 0·1M-hydrogen chloride–60% aqueous acetone for 20 hr., only the diene (84%) was obtained.

2-*Methyl*-1 : 1-*diphenylallyl Alcohol* (2-*Methyl*-1 : 1-*diphenylprop*-2-*en*-1-*ol*) (III).—Benzophenone (10 g.) in ether (25 ml.) was allowed to react with *iso*propenyl-lithium (from Li, 0·8 g.) and the product worked up as above, giving the *alcohol* (8 g., 65%), b. p. 80—82° (bath-temp.)/10^{-3} mm., n_D^{23} 1·5849, $\lambda_{max.}$ 2580 Å (ε 400) in EtOH (Found : C, 86·1; H, 7·6. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

α-*Methyl*-β-*phenylcinnamyl Alcohol* (2-*Methyl*-3 : 3-*diphenylprop*-2-*en*-1-*ol*) (IX).—The foregoing alcohol (3 g.) was heated under reflux for 20 hr. with 0·1M-hydrogen chloride–60% aqueous acetone (100 ml.). Isolation of the product as above and fractionation gave the alcohol (2·5 g., 83%), m. p. 59—60°, b. p. 126°/10^{-2} mm., n_D^{24} 1·6067. After one recrystallisation from light petroleum (b.p. 40—60°), the alcohol had m. p. 69—70°, $\lambda_{max.}$ 2420 Å (ε 14,000) in EtOH (Found : C, 85·7; H, 7·3%). (Ziegler and Tiemann[8] give b. p. 184°/11 mm., m. p. 68—69°.) The α-*naphthylurethane* crystallised from light petroleum in needles, m. p. 99—100° (Found : C, 82·5; H, 6·3; N, 3·6. $C_{27}H_{23}O_2N$ requires C, 82·4; H, 5·9; N, 3·6%).

2-*Methylpenta*-1 : 4-*dien*-3-*ol* (IV).—Acraldehyde (5 g.) in ether (25 ml.) was added to *iso*propenyl-lithium (from Li, 1 g.) at 0°. After 1 hr. at 0°, excess of aqueous ammonium chloride was added and the product isolated with ether, giving the *alcohol* (2·0 g., 23%), b. p. 47°/12 mm., n_D^{22} 1·4505, ε <100 between 2000 and 4000 Å (Found : C, 72·9; H, 10·6. $C_6H_{10}O$ requires C, 73·4; H, 10·3%).

2-*Methylhexa*-1 : 4-*dien*-3-*ol* (V).—Crotonaldehyde (7 g.) was added to *iso*propenyl-lithium, and the product was worked up as above, giving the *alcohol* (4·2 g., 38%), b. p. 58—60°/12 mm., n_D^{20} 1·4575, ε <100 between 2000 and 4000 Å (Found : C, 74·7; H, 10·9. $C_7H_{12}O$ requires C, 74·95; H, 10·8%).

2 : 3 : 5-*Trimethylhexa*-1 : 4-*dien*-3-*ol* (VI).— Mesityl oxide (8 g.) in ether (25 ml.) was treated with *iso*propenyl-lithium, and the product was worked up as above, giving the *alcohol* (8·5 g., 74%), b. p. 63°/11 mm., n_D^{22} 1·4628, ε <100 between 2000 and 4000 Å (Found : C, 77·4; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·5%).

1 : 1-*Diethoxy*-2 : 3-*dimethylbut*-3-*en*-2-*ol*.—1 : 1-Diethoxyacetone (40 g.) in ether (50 ml.) was treated with *iso*propenyl-lithium (from Li, 5 g.) in ether (500 ml.) at room temperature. After 3 hr., excess of ammonium chloride was added and the ether layer was separated, dried, (Na_2SO_4–K_2CO_3), and distilled, giving the *acetal* (18 g., 35%), b. p. 89°/11 mm., n_D^{21} 1·4370 (Found : C, 64·1; H, 10·7. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·6%). Shaking the acetal (10 g.) with 2% aqueous tartaric acid for 14 hr. at room temperature gave unchanged acetal (3·2 g.) and 2-*hydroxy*-2 : 3-*dimethylbut*-3-*en*-1-*al* (2·7 g.), b. p. 69—72°/12 mm., n_D^{22} 1·4392, $\lambda_{max.}$ 3020 Å (ε 570) (Found : C, 63·2; H, 8·8. $C_6H_{10}O_2$ requires C, 63·1; H, 8·8%).

Reaction of iso*Propenyl-lithium with Dimethylformamide*.—Dimethylformamide (7 g.) in ether (25 ml.) was added dropwise to *iso*propenyl-lithium (from Li, 1 g.) in ether (200 ml.) at 0°. After 1 hr. at 0°, excess of ammonium chloride was added, the ether layer was dried (Na_2SO_4), and the solvent distilled off through an 8″ column. The residue (1 ml.) gave a positive

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[17] Li and Elliott, *J. Amer. Chem. Soc.*, 1952, **74**, 4089.

[18] Braude, Jones, and Stern, *J.*, 1947, 1087.

test with Schiff's reagent and on treatment with Brady's reagent furnished an unidentified 2 : 4-*dinitrophenylhydrazone* (0·4 g.) which crystallised from ethyl acetate in red needles, m. p. 198°, $\lambda_{max.}$ 3900 Å (ε 31,000) in $CHCl_3$ (Found : C, 53·5; H, 5·1; N, 19·3. $C_{13}H_{14}O_4N_4$ requires C, 53·8; H, 4·9; N, 19·3%).

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