# *Alkenylation with Lithium Alkenyls. Part X.* Some Reactions of Trimethylvinyl-lithium* (1 : 2-*Dimethylpropenyl-lithium*).

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The formation of trimethylvinyl-lithium (1 : 2-dimethylpropenyl-lithium) by direct metallation of the bromide, its carboxylation to give αβ-dimethylcrotonic acid, and its reactions with a number of aldehydes and ketones are described.

In previous papers, the formation and reactions of propenyl (2-methylvinyl-) (*J.*, 1951, 2078) and *iso*butenyl-lithium (2 : 2-dimethylvinyl-lithium) (*J.*, 1950, 2007, 2012; 1952, 1425; 1953, 3131; 1955, 3324) have been described. In the meantime, 1-methylpropenyl-lithium (1 : 2-dimethylvinyl-lithium) has been reported by Dreiding and Pratt (*J. Amer. Chem. Soc.*, 1954, **76**, 1902), so that apart from the parent vinyl-lithium, only the 1-methyl and the 1 : 2 : 2-trimethyl derivative are still unknown amongst the methylated vinyl-lithium derivatives. Vinyl-lithium is not formed from either vinyl chloride or vinyl bromide under the usual conditions of direct metallation (unpublished experiments by Dr. K. R. H. Wooldridge) and it is not of great synthetical interest since the desired products are usually accessible through semi-hydrogenation of the corresponding ethynyl compounds obtained from sodium acetylide, and since, moreover, vinylsodium (Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Amer. Chem Soc.*, 1950, **72**, 3785) as well as vinylmagnesium halides [Yushchenko, *Zhur. obshchei Khim.*, 1951, **21**, 1244; *Chem. Abs.*, 1952, **46**, 1957; Akiyoshi and Okuno, *J. Chem. Soc. Japan*, 1953, **74**, 467; Normant, *Compt. rend.*, 1954, **239**, 1510, 1811; 1955, **240**, 314, 631] can be utilised. In this paper,

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* Part IX, preceding paper.

the formation and some reactions of the fully substituted trimethylvinyl-lithium (1 : 2-dimethylpropenyl-lithium) are detailed.

Trimethylvinyl bromide was conveniently prepared by the direct action of bromine on *tert.*-pentyl alcohol and was readily metallated by metallic lithium in ether. Carboxylation afforded αβ-dimethylcrotonic acid but, in contrast to the corresponding reactions with dimethylvinyl halides, only a small amount of diene formed by a coupling reaction was obtained and there was no trace of ketonic products. αβ-Dimethylcrotonic acid was characterised by a benzylamine salt and exhibits spectral properties typical of an αβ-ethylenic acid (see Table). Progressive alkylation of acrylic acid results in the usual bathochromic displacement of the ultraviolet maxima, as well as in a regular shift of the infrared frequencies associated with C=C and C=O stretching vibrations, which can be interpreted as arising from a decrease in the strength of the C=C and C=O bonds, due to the increasing importance of resonance of the type $C{=}C{-}C{=}O \longleftrightarrow C^{+}{-}C{=}C{-}O^{-}$. A simultaneous decrease in the intensities of the ultraviolet bands may be associated with weak steric interference between the carboxyl and *cis*-β-methyl groups (cf. Braude and Waight in " Progress in Stereochemistry," ed. W. Klyne, Vol. I, Chapter 4, Butterworths, London, 1954; Part IX, *J.*, 1955, 3324), but since the ε values for the lower homologues are not very accurate (cf. Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564; 1952, **74**, 6313; Jones, Whitham, and Whiting, *J.*, 1954, 1865) detailed consideration of these data is deferred.

Trimethylvinyl-lithium reacted normally with the following aldehydes and ketones, giving the secondary or tertiary allylic alcohols in good to moderate yields: from acraldehyde, (I; $R = CH{:}CH_2$; 27%); from crotonaldehyde, (I; $R = CH{:}CHMe$; 29%); from benzaldehyde, (I; R = Ph; 41%); from mesityl oxide, (II; $R = CH{:}CMe_2$; 67%); from acetophenone, (II; R = Ph; 36%); and from benzophenone, (III; 56%). The structures of the products were confirmed by their spectral properties and by microhydrogenation. The secondary alcohols obtained from acraldehyde and crotonaldehyde were also oxidised by chromium trioxide to the diethylenic ketones (IV; R = H and Me). Other reactions of the alcohols will be described later.

(I) $CMe_2{:}CMe{\cdot}CHR{\cdot}OH$
$CMe_2{:}CMe{\cdot}CMeR{\cdot}OH$ (II)
(III) $CMe_2{:}CMe{\cdot}CPh_2{\cdot}OH$
$CMe_2{:}CMe{\cdot}COR$ (IV)

*Light absorption of αβ-ethylenic acids.*

| | Ultraviolet * | | Infrared † | | | Ultraviolet * | | Infrared † | |
|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max.}$ (Å) | ε | $\nu_{C=O}$ | $\nu_{C=C}$ | | $\lambda_{max.}$ (Å) | ε | $\nu_{C=O}$ | $\nu_{C=C}$ |
| $CH_2{:}CH{\cdot}CO_2H$ ... | <2100 | — [1] | 1705 | ? | $CHMe{:}CMe{\cdot}CO_2H$ | 2155 | 9400 [4] | 1689 | 1645 |
| $CH_2{:}CMe{\cdot}CO_2H$... | <2100 | — | 1700 | ? | $CMe_2{:}CH{\cdot}CO_2H$ ... | 2160 | 12,000 [5] | 1689 | 1637 |
| $CHMe{:}CH{\cdot}CO_2H$ | 2060 | 15,000 [2] | 1698 | 1653 | $CMe_2{:}CMe{\cdot}CO_2H$ ... | 2210 | 9700 [5] | 1675 | 1621 |
| $CHMe{:}CMe{\cdot}CO_2H$ | 2125 | 12,500 [3] | 1684 | 1647 | | | | | |

* In ethanol. † Stretching frequencies in $cm.^{-1}$ (paraffin mulls).

[1] Ungnade and Ortega, *loc. cit.* [2] *trans*-Crotonic acid (measurement by Dr. C. J. Timmons). [3] Tiglic acid (Dreiding and Pratt, *loc. cit.*). [4] Angelic acid (*idem, loc. cit.*). [5] This paper. [6] Flett, *J.*, 1951, 962.

## EXPERIMENTAL

For general methods, see Part IX, *loc. cit.*

1 : 2-*Dimethylpropenyl Bromide*.—Bromine (1 kg.) was added dropwise to *tert.*-pentyl alcohol (550 g.) which was heated under reflux on the steam-bath. There was immediate decolorisation and the alcohol refluxed vigorously. When all the bromine had been added, the mixture was allowed to cool. The lower dibromide layer was separated, washed with water (3 × 250 ml.), and dried ($CaCl_2$). Distillation through an 8" Dufton column gave a fraction (645 g.) of 2 : 3-dibromo-3-methylbutane, b. p. 58—63°/14 mm., $n_D^{24}$ 1·5001 [Pansevich-Kolyada and Prilezhaev, *Zhur. obshchei Khim.*, 1951, **21**, 517, give b. p. 56—58°/12 mm., $n_D^{20}$ 1·5112], which was sufficiently pure for the next stage.

The dibromide (645 g.) was added dropwise with vigorous stirring to potassium hydroxide (250 g.) in ethylene glycol (800 ml.) in a three-necked copper flask at 165—170° and the alkenyl bromide was allowed to distil as it was formed. The distillate was washed with 5% aqueous potassium hydroxide (100 ml.) and water (4 × 250 ml.), dried ($CaCl_2$), and fractionated through an 8″ Dufton column from a small piece of sodium, giving 1 : 2-dimethylpropenyl bromide (115 g., 12% overall yield from *tert*.-pentyl alcohol), b. p. 120—121°/750 mm., $n_D^{22}$ 1·4700 (Farrell and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 1281, give b. p. 118—120°, $n_D^{20}$ 1·4738).

αβ-*Dimethylcrotonic Acid*.—The foregoing bromide (10 g.) was added to a well-stirred suspension of finely-cut lithium (1 g.) in anhydrous ether (200 ml.) under nitrogen. Reaction set in after a few minutes and metallation was complete after 2—3 hr. under reflux. The green-grey mixture was cooled, added to powdered carbon dioxide (300 g,), and allowed to attain room temperature. Water (100 ml.) was then added and the solution acidified dropwise with concentrated hydrochloric acid. The ether layer was separated, extracted with 2N-sodium carbonate (2 × 100 ml.), dried ($Na_2SO_4$), and evaporated, giving a small amount of neutral products (0·3 g.) which showed no absorption with $E_{1\,cm.}^{1\%}$ >50 between 2200 and 4000 Å and gave no 2 : 4-dinitrophenylhydrazone, but rapidly decolorised a solution of bromine in carbon tetrachloride. This was probably impure 2 : 3 : 4 : 5-tetramethylhexa-2 : 4-diene, which, like hexachlorobutadiene (cf. Szasz and Sheppard, *Trans. Faraday Soc.*, 1953, **49**, 358; Braude and Waight, *loc. cit.*), would not be expected to show a typical diene band, owing to steric hindrance. Microfractionation gave a middle cut, b. p. 80°/20 mm., $n_D^{20}$ 1·4485 (Found: C, 86·4; H, 12·4. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%. Hydrogenation no., 106. Calc. for 2 double bonds, 69). The sodium carbonate extract was acidified at 0° with concentrated hydrochloric acid and extracted with ether. The ethereal solution was dried ($Na_2SO_4$) and evaporated, and the residue crystallised from light petroleum (b. p. 40—60°), giving αβ-dimethylcrotonic acid (1·8 g., 17%), m. p. 70—71°, $\lambda_{max.}$ 2210 Å, ε 9700 in EtOH (Found: C, 63·4; H, 9·0. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·8%) (Gakhokidze, *Zhur. obshchei Khim.*, 1947, **17**, 1327, and Hauser *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1068, give m. p. 70—71°]. The *benzylamine salt* crystallised from ethyl acetate in needles, m. p. 106—107° (Found: C, 70·9; H, 8·6; N, 6·35. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6; N, 6·3%).

2 : 3-*Dimethylhexa*-2 : 5-*dien*-4-*ol*.—Acraldehyde (4 g.) in anhydrous ether (25 ml.) was added to 1 : 2-dimethylpropenyl-lithium (from lithium, 1 g., and the bromide, 10 g.) in ether (170 ml.) at 10°. The mixture was stirred for 1 hr. at room temperature and ice-cold saturated aqueous ammonium chloride (150 ml.) was then added. The ether layer was separated, dried ($Na_2SO_4$–$K_2CO_3$), and fractionated from a trace of potassium carbonate, giving 2 : 3-*dimethylhexa*-2 : 5-*dien*-4-*ol* (2·3 g., 27%), b. p. 75—76°/10 mm., $n_D^{22}$ 1·4702, ε <500 between 2100 and 4000 Å (Found: C, 75·9; H, 11·4. $C_8H_{14}O$ requires C, 76·1; H, 11·2%. Hydrogenation no. 53. Calc. for 2 double bonds, 63).

The dienol (0·6 g.) in dry pyridine (6 ml.) was added to chromium trioxide (0·6 g.) in pyridine (6 ml.). The mixture was kept for 3 days at room temperature and then added to water (100 ml.). The solution was extracted with ether, and the ether extract was dried ($Na_2SO_4$) and evaporated under reduced pressure. Treatment of the residue with 2 : 4-dinitrophenylhydrazine in methanol–sulphuric acid gave 2 : 3-*dimethylhexa*-2 : 5-*dien*-4-*one* 2 : 4-*dinitrophenylhydrazone* (0·2 g.) which .crystallised from ethyl acetate–methanol in dark red needles, m. p. 225—226°, $\lambda_{max.}$ 3970 Å (ε 30,000 in $CHCl_3$) (Found: C, 54·5; H, 5·6; N, 18·5. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3; N, 18·4%).

2 : 3-*Dimethylhepta*-2 : 5-*dien*-4-*ol*.—Crotonaldehyde (5 g.) in anhydrous ether (25 ml.) was added to a solution of 1 : 2-dimethylpropenyl-lithium (from lithium, 1 g., and bromide, 10 g.), in ether (170 ml.) at 0°. The solution was stirred for 2 hr. at room temperature. Isolation of the products as above gave 2 : 3-*dimethylhepta*-2 : 5-*dien*-4-*ol* (2·7 g., 29%), b. p. 60—61°/1 mm., $n_D^{24}$ 1·4758, ε <500 between 2100 and 4000 Å (Found: C, 76·7; H, 11·5. $C_9H_{16}O$ requires C, 77·1; H, 11·5%. Hydrogenation no., 69. Calc. for 2 double bonds, 70). The dienol was very unstable and decomposed even at 0°.

The dienol (0·6 g.), oxidised as above, gave, after treatment with Brady's reagent, 2 : 3-*dimethylhepta*-2 : 5-*dien*-4-*one* 2 : 4-*dinitrophenylhydrazone* (0·2 g.) which crystallised from ethyl acetate–methanol in red plates, m. p. 215—216°, $\lambda_{max.}$ 3980 Å (ε 32,000 in $CHCl_3$) (Found: C, 56·2; H, 6·2; N, 17·7. $C_{15}H_{18}O_4N_4$ requires C, 56·6; H, 5·7; N, 17·6%).

2 : 3 : 4 : 6-*Tetramethylhepta*-2 : 5-*dien*-4-*ol*.—Mesityl oxide (14 g.) in anhydrous ether (25 ml.) with 1 : 2-dimethylpropenyl-lithium (from lithium, 3·3 g., and bromide, 25 g.) in ether (350 ml.) gave, as above, 2 : 3 : 4 : 6-*tetramethylhepta*-2 : 5-*dien*-4-*ol* (16 g., 67%), b. p. 45°/0·1 mm., $n_D^{23}$ 1·4720, ε <1000 between 2100 and 4000 Å (Found: C, 78·4; H, 12·1. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%).

2 : 3-*Dimethyl*-1-*phenylbut*-2-*en*-1-*ol*.—Benzaldehyde (7 g.) in anhydrous ether (25 ml.)

with 1 : 2-dimethylpropenyl-lithium (from metal, 1 g., and bromide, 12 g.) gave, as above, the *alcohol* (5·8 g., 41%), b. p. 125° (bath-temp.)/$10^{-5}$ mm., $n_D^{20}$ 1·5370 (Found : C, 81·5; H, 9·25. $C_{12}H_{16}O$ requires C, 81·8; H, 9·15%. Hydrogenation no., 42. Calc. for 4 double bonds, 44).

3 : 4-*Dimethyl*-2-*phenylpent*-3-*en*-2-*ol*.—Acetophenone (14 g.) in anhydrous ether (50 ml.) was added dropwise to a solution of 1 : 2-dimethylpropenyl-lithium (from metal, 2 g., and bromide, 20 g.), in ether (300 ml.). The solution was stirred for 1 hour at room temperature. Isolation as above gave the *alcohol* (8 g., 36%), b. p. 53° (bath-temp.)/$10^{-5}$ mm., $n_D^{23}$ 1·5300 (Found : C, 82·0; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

2 : 3-*Dimethyl*-1 : 1-*diphenylbut*-2-*en*-1-*ol*.—Benzophenone (8·6 g.) in anhydrous ether (25 ml.) was added to 1 : 2-dimethylpropenyl-lithium (from metal, 0·8 g., and bromide, 8 g.) in ether (170 ml.), and the solution was stirred for 30 min. at room temperature. Working up as above gave the *alcohol* (7·5 g., 56%), b. p. 68° (bath-temp.)/5 × $10^{-5}$ mm., $n_D^{26}$ 1·5949 (Found : C, 85·6; H, 7·7. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

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