

Alkenylation with Lithium Alkenyls. Part XI. A New
Synthesis of Ethylenic Aldehydes.*

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Lithium alkenyls with dimethylformamide give ethylenic aldehydes in moderate yields. In this way, 3-methyl- and 2 : 3-dimethyl-crotonaldehyde, 1-formylcyclohexene, and 1-formylcycloheptene have been prepared. The reaction with *cis*-propenyl-lithium gave a mixture from which neither *cis*- nor *trans*-crotonaldehyde could be isolated.

In previous parts of this series, the reactions of lithium alkenyls with aldehydes and ketones to give ethylenic alcohols, and with carboxylic acid derivatives to give ethylenic ketones, have been explored. In this paper the use of lithium alkenyls for the synthesis of ethylenic aldehydes is described.

A variety of reagents have been employed for the conversion of Grignard reagents and organic lithium compounds into aldehydes. The most common of these is ethyl orthoformate, but it was previously reported (Braude and Coles, Part III, *J.*, 1950, 2012) that no reaction can be effected with *isobutenyl*-lithium under the usual conditions and a negative result has now been obtained with trimethylvinyl-lithium. *N*-substituted formamides have been less widely used as formylating agents, but Sicé (*J. Amer. Chem. Soc.*, 1953, **75**, 3697; *J. Org. Chem.*, 1954, **19**, 70) has recently described the conversion of thienyl-lithium into 1-thenaldehyde by *N*-dimethylformamide. This amide, which is available commercially, was also found to react with lithium alkenyls to give the expected aldehydes. Although the yields are only moderate, the method is of practical value.



In the case of *isobutenyl*-lithium which yields 3-methylcrotonaldehyde (I) (see Table), a compound accessible by a variety of other routes (*inter al.*, Fischer and Löwenberg, *Annalen*, 1932, **494**, 263; Young and Linden, *J. Amer. Chem. Soc.*, 1947, **69**, 2912; Wendler and Slates, *ibid.*, 1950, **72**, 5341), the product is contaminated with 4-formyl-3-hydroxy-1 : 5 : 5-trimethylcyclohexene (a dimer known to be formed from the aldehyde under basic conditions) and its dehydration product, 4-formyl-1 : 5 : 5-trimethylcyclohexa-1 : 3-diene (Fischer and Löwenberg, *loc. cit.*). Trimethylvinyl-lithium afforded 2 : 3-dimethylcrotonaldehyde (II), which was characterised as the semicarbazone and 2 : 4-dinitrophenylhydrazone, both exhibiting the expected light absorption properties. The preparation of this aldehyde was claimed by Prévost (*Bull. Soc. chim. France*, 1944, **11**, 218), but the

* Part X, preceding paper.




melting point of the semicarbazone recorded by him is different from that obtained here. No aldehyde dimer was encountered in this case.

The reaction of dimethylformamide with cyclohexenyl-lithium gave 1-formylcyclohexene (III) the properties of which were in excellent agreement with those previously recorded (Plattner and Jampolsky, *Helv. Chim. Acta*, 1943, **26**, 687; Heilbron *et al.*, *J.*, 1949, 737; Seifert and Schinz, *Helv. Chim. Acta*, 1951, **34**, 728). cycloheptenyl-lithium similarly furnished 1-formylcycloheptene (IV) which exhibited light-absorption properties almost identical with those of the lower homologue and gave a semicarbazone (m. p. 211°) and a 2:4-dinitrophenylhydrazone. This aldehyde was first prepared by Wallach and Köhler (*Annalen*, 1906, **345**, 152) from methylenecycloheptane, though only isolated as the semicarbazone (m. p. 203°).

Unlike the other lithium alkenyls, *cis*-propenyl-lithium failed to give the corresponding aldehyde. This case was of particular interest, since *cis*-crotonaldehyde, which appears to be isomerised to the *trans*-isomer with great ease and has never been isolated, might possibly have survived under the present (basic) reaction conditions (cf. Raphael and Sondheimer, *J.*, 1951, 2693, Schinz and his co-workers, *Helv. Chim. Acta*, 1955, **38**, 239, 255). However, only higher-boiling products could be isolated; some of these gave crystalline carbonyl derivatives but were not further investigated.

The ultraviolet-light absorption properties of the above ethylenic aldehydes and their derivatives (see Table) mostly conform to well-known generalisations (cf. Evans and Gillam, *J.*, 1943, 565; Braude and Jones, *J.*, 1945, 498), but certain minor anomalies are apparent, particularly in the short-wavelength bands of the aldehydes. The low ultraviolet absorption intensity exhibited by 3-methylcrotonaldehyde suggested that it might be a mixture of the conjugated and the unconjugated isomer (3-methylbut-3-en-1-al), as observed for mesityl oxide (Gray, Rasmussen, and Tunnicliff, *J. Amer. Chem. Soc.*, 1947, **69**, 1630) and a number of related ethylenic ketones (Braude, Jones, Koch, Sondheimer, and Toogood, *J.*, 1949, 1890), but the infrared spectrum showed no bands expected for an isolated >C=O or >C=CH₂ group.

Ultraviolet-light absorption of some ethylenic aldehydes and their derivatives.

	Aldehyde ¹		Semicarbazone ²		2:4-Dinitrophenylhydrazone ³	
	λ_{\max} . (Å)	ϵ	λ_{\max} . (Å)	ϵ	λ_{\max} . (Å)	ϵ
CH ₂ :CH·CHO	2080	>10,000 ^a	2640	19,000	3660	25,500 ^c
	3280	13				
CHMe:CH·CHO ...	2170	16,000	2645	24,000	3720	29,000 ^c
	3210	20				
(I) CMe ₂ :CH·CHO	2300	6500	2700	28,000	3810	30,000
(II) CMe ₂ :CMe·CHO ...	2390	13,500	2710	27,000	3860	27,000
	2370	12,000 ^b	2670	30,500 ^b	3770	29,500 ^b
(III) 	2270	11,000	2660	26,000	3810	27,600
	3200	22				
(IV) 	2280	12,000	2680	27,000	3810	29,000
	3200	24				

¹ In hexane.

² In ethanol.

³ In chloroform.

^a Evans and Gillam, *J.*, 1943, 565. ^b Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827. ^c Braude and Jones, *J.*, 1945, 498.

EXPERIMENTAL

For general methods, see Part IX, *J.*, 1955, 3324. Spectral data are given only when not included in the Table.

3-Methylcrotonaldehyde.—Dimethylformamide (7.3 g.) in anhydrous ether (25 ml.) was added to *isobutenyl*-lithium (from metal, 1.5 g., and *isobutenyl* bromide, 13.5 g., see Part IX, *loc. cit.*) in ether (250 ml.) at room temperature. The solution was then refluxed for 30 min. and, after being stirred at room temperature overnight, was treated with excess of saturated aqueous ammonium chloride at 0°. The ethereal layer was separated, dried (Na₂SO₄), and fractionated through an 8" Dufton column, giving (i) 3-methylcrotonaldehyde (2.3 g., 27%), b. p. 30–32°/

12 mm., ν_{\max} (liquid film) 1682 (s, C=O stretching) and 835 (s, C-H bending in $R_2C:CHR$), no bands near 1710 and 890 cm^{-1} , identified as the semicarbazone, m. p. and mixed m. p. 213° (from methanol), and as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 183° (from ethyl acetate) (Found : N, 21.1. Calc. for $C_{11}H_{12}O_4N_4$: N, 21.2%), (ii) the dimer (2 g., 12%), b. p. 113°/20 mm., which was dehydrated by distillation from a trace of naphthalene-2-sulphonic acid to give slightly impure 4-formyl-1 : 1 : 5-trimethylcyclohexa-1 : 3-diene, b. p. 102°/18 mm., n_D^{25} 1.5175, λ_{\max} 3080 Å (ϵ 9000 in hexane) (Found : C, 79.4; H, 10.0. Calc. for $C_{10}H_{14}O$: C, 79.95; H, 9.4%) (Fischer and Löwenberg, *Annalen*, 1932, 494, 263, give b. p. 85°/9 mm., n_D^{20} 1.5267), which formed a semicarbazone, m. p. 209° (from methanol), λ_{\max} 3220 Å (ϵ 20,000 in EtOH) (Fischer and Löwenberg, *loc. cit.*, give m. p. 213°). Both the dimer and its dehydration product furnished 4-formyl-1 : 5 : 5-trimethylcyclohexadiene-2 : 4-dinitrophenylhydrazone, m. p. 204° (from ethyl acetate-methanol), λ_{\max} 4080 Å (ϵ 30,500 in CHCl_3), identical with a specimen prepared by Dr. E. S. Waight.

2 : 3-Dimethylcrotonaldehyde.—Dimethylformamide (9 g.) in ether (50 ml.) was added to a solution of 1 : 2-dimethylpropenyl-lithium (from lithium, 2.0 g., and bromide, 20 g.; cf. Part X, *loc. cit.*) in ether (300 ml.) at room temperature. The mixture was stirred for 2 hr. at room temperature and saturated ammonium chloride (300 ml.) was then added. The ethereal layer was separated, dried (Na_2SO_4), and distilled, giving the aldehyde (5.5 g., 40%), b. p. 42—43°/9 mm., n_D^{19} 1.4702, λ_{\max} 2830 Å (ϵ 11,800 in hexane) (Found : C, 73.4; H, 10.5. Calc. for $C_6H_{10}O$: C, 73.4; H, 10.3%) (Prévost, *Bull. Soc. chim. France*, 1944, 11, 218, gives b. p. 81°/65 mm., n_D^{25} 1.4686). This was converted into the semicarbazone which crystallised from methanol in plates, m. p. 239—240° (Found : C, 54.4; H, 8.6; N, 27.2. $C_7H_{13}ON_3$ requires C, 54.2; H, 8.4; N, 27.1%) (Prévost, *loc. cit.*, gives m. p. 276°). Steam-distillation of a mixture of the semicarbazone (8 g.) and phthalic anhydride (12 g.) in water (140 ml.) gave 2 : 3-dimethylcrotonaldehyde (3.5 g., 69%) which on redistillation had b. p. 41°/8 mm., n_D^{18} 1.4704. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in red needles, m. p. 200—201° (Found : 52.1; H, 5.1; N, 20.6. $C_{12}H_{14}O_4N_4$ requires C, 51.8; H, 5.1; N, 20.1%).

1-Formylcyclohexene.—Dimethylformamide (10 g.) in ether (30 ml.) was added to cyclohexenyl-lithium (from metal, 2.3 g., and 1-chlorocyclohexene, 15 g.; cf. Braude and Coles, *J.*, 1950, 2014) in ether (200 ml.) at room temperature. The mixture was stirred for 30 min. and then treated with excess of saturated ammonium chloride solution. Isolation of the product as above and fractionation gave 1-formylcyclohexene (3.5 g., 26%), b. p. 72°/15 mm., n_D^{23} 1.4920 (Seifert and Schinz, *Helv. Chim. Acta*, 1951, 34, 728, give b. p. 60—61°/11 mm., n_D^{19} 1.4914). It was identified as the semicarbazone, m. p. 217—218° (from methanol) (Plattner and Jampolsky, *ibid.*, 1943, 26, 687, give m. p. 213—216°; Heilbron *et al.*, *J.*, 1949, 737, give m. p. 213—214°), and as the 2 : 4-dinitrophenylhydrazone, m. p. 223—224° (from ethyl acetate) (Found : C, 53.7; H, 4.9; N, 19.8. Calc. for $C_{13}H_{14}O_4N_4$: C, 53.8; H, 4.9; N, 19.3%) (Heilbron, *et al.*, *loc. cit.*, give m. p. 219—220°; Seifert and Schinz, *Helv. Chim. Acta*, 1951, 34, 728, give m. p. 212°).

1-Formylcycloheptene.—Dimethylformamide (35 g.) in ether (100 ml.) was added to cycloheptenyl-lithium (from metal, 9 g., and 1-chlorocycloheptene, 70 g.; cf. Braude, Forbes, and Evans, *J.*, 1953, 2202) in ether (1 l.). After being stirred for 2 hr., the mixture was treated with excess of saturated ammonium chloride, and the products were isolated as above. Fractionation gave 1-formylcycloheptene (37 g., 70%), b. p. 82—83°/9 mm., n_D^{20} 1.4983 (Found : C, 77.7; H, 9.95. $C_8H_{12}O$ requires C, 77.45; H, 9.7%). The semicarbazone crystallised from methanol in plates, m. p. 210—211° (Found : C, 59.7; H, 8.5; N, 23.6. Calc. for $C_9H_{15}ON_3$: C, 59.6; H, 8.3; N, 23.2%) (Wallach and Köhler, *Annalen*, 1906, 345, 152, give m. p. 203—204°). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in red needles, m. p. 210—211° (Found : C, 54.9; H, 5.4; N, 19.7. $C_{14}H_{16}O_4N_4$ requires C, 55.25; H, 5.3; N, 18.4%). Microhydrogenation of the aldehyde in glacial acetic acid-platinum oxide resulted in the uptake of 0.9 mol. of hydrogen.

α -(cyclohept-1-enyl)benzyl Alcohol.—The foregoing aldehyde (3.5 g.) in ether (25 ml.) was added to a stirred solution of phenylmagnesium bromide (from magnesium, 0.8 g., and bromobenzene, 5.3 g.) in ether (75 ml.). After 4 hr. excess of aqueous ammonium chloride was added and the ethereal layer was separated, dried (Na_2SO_4 - K_2CO_3), and fractionated from a trace of potassium carbonate, giving the alcohol (3.5 g., 61%), b. p. 73° (bath-temp.)/10⁻⁴ mm., n_D^{25} 1.5521, ϵ <1000 between 2000 and 4000 Å (Found : C, 82.9; H, 9.15. Calc. for $C_{14}H_{18}O$: C, 83.1; H, 9.0%) (Braude and Forbes give b. p. 94°/0.002 mm., n_D^{24} 1.5429, for a sample prepared from cycloheptenyl-lithium and benzaldehyde and probably contaminated with hydrobenzoin).

Reaction of cis-Propenyl-lithium with Dimethylformamide.—The amide (11 g.) in ether (25 ml.) was added to a stirred solution of cis-propenyl-lithium (from metal, 2.1 g., and 1-bromopropene,

18 g.; cf. Braude and Coles, *J.*, 1951, 2078) in ether (600 ml.) at 0°. The solution was allowed to attain room temperature (*ca.* 1 hr.), cooled again to 0°, and treated with saturated aqueous ammonium chloride (250 ml.). The ethereal layer was separated, dried (Na₂SO₄), and fractionated, giving a range of fractions (total 1.6 g.), b. p. 80°/90 mm. to 60°/17 mm., n_D^{20} 1.428—1.462. The middle fractions gave strong positive Schiff's tests and afforded a *semicarbazone* which crystallised from aqueous methanol in plates, m. p. 211—213°, λ_{\max} 2950 Å ($E_{1\text{cm}}^{1\%}$ 1750 in EtOH) (Found: C, 55.8; H, 7.7; N, 25.7. C₈H₁₃ON₃ requires C, 57.5; H, 7.8; N, 25.1%), and a 2:4-dinitrophenylhydrazone which crystallised from ethyl acetate-methanol in crimson needles, m. p. 204—205°, λ_{\max} 3920 Å ($E_{1\text{cm}}^{1\%}$ 1040 in CHCl₃) (Found: C, 54.0; H, 5.1; N, 19.9. C₁₃H₁₄O₄N₄ requires C, 53.8; H, 4.9; N, 19.3%). The analytical and spectral data suggest that these are the derivatives of a conjugated diene-aldehyde C₇H₁₀O, possibly hepta-2:4-dien-1-al.

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