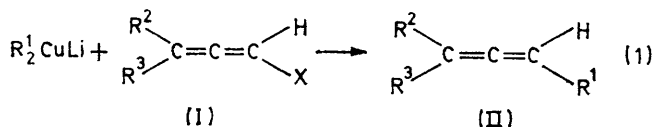


## Allenes. Part XXVII.<sup>1</sup> Reaction of Dialkyl(lithio)copper Reagents with 1-Bromoallenes, 1-Iodoallenes, and 3-Chloroalk-1-yne

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Allenic hydrocarbons are obtained in high yield by the reaction of 1-halogenoallenes or 3-chloroalk-1-yne with dialkyl(lithio)copper reagents at low temperature.

DIALKYL(LITHIO)COPPER reagents<sup>2</sup> have proved useful as alkylating agents for replacing halogen atoms attached to a variety of  $sp^2$  and  $sp^3$  carbon atoms.<sup>3</sup> We now report their use in replacing a halogen atom attached



to an allenic system,<sup>4</sup> which provides a useful general synthesis of 1,3-di- and 1,1,3-tri-alkyl allenes from readily available allenic halides [equation (1)].

the allenic hydrocarbon was isolated by preparative g.l.c.; for preparative scale experiments, a 1.25 : 1 molar ratio of reagent to allenic halide was used and the product was separated by fractional distillation. Reactions with  $Me_2CuLi$  were carried out at  $-5^\circ$ , with  $Et_2CuLi$  at  $-30^\circ$ , and with  $Bu_2CuLi$  at  $-60^\circ$  for 1–3 h. Products were characterised by elemental analysis and i.r. and n.m.r. spectra.

An alternative preparative method used 3-chloroalk-1-yne (III) and  $R_2CuLi$  reagents (Table 3) and gave high yields of allenic hydrocarbons [equation (2)]. The chloroacetylenes are readily prepared by literature methods.<sup>8</sup>

TABLE 1

Preparation and physical data for allenic hydrocarbons from bromo-allenes [equation (1); X = Br]

Product (II)			Yield (% from g.l.c.)	G.l.c. (silicone oil) [temp. and $t_R$ (min)]	Found (%)		Required (%)		$n_D^{20}$
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>			C	H	C	H	
Me	Me	Me	74	25°; 5·4	87·8	12·2	87·8	12·2	1·4395
Me	Me	Et	85	25°; 10·5	87·1	12·7	87·4	12·6	1·4410
Me	Pr <sup>n</sup>	H	85	25°; 13·8	87·2	12·6	87·4	12·6	1·4401
Me	Bu <sup>t</sup>	Me	87	25°; 16·2	86·9	12·7	87·0	13·0	1·4437
Et	Me	Me	51	40°; 4·8	86·9	12·6	87·4	12·6	1·4385
Et	Me	Et	59	40°; 9·6	87·1	12·7	87·2	12·8	1·4433
Et	Pr <sup>n</sup>	H	68	40°; 12·3	86·9	12·9	87·2	12·8	1·4391
Et	Bu <sup>t</sup>	Me	74	40°; 24·6	87·0	12·9	86·9	13·0	1·4465
Bu <sup>n</sup>	Me	Me	85	60°; 9·5	86·8	12·9	87·0	13·0	1·4550
Bu <sup>n</sup>	Me	Et	87	60°; 25·8	87·0	12·9	86·9	13·0	1·4485
Bu <sup>n</sup>	Pr <sup>n</sup>	H	81	60°; 34·2	86·9	13·0	86·9	13·0	1·4516
Bu <sup>n</sup>	Bu <sup>t</sup>	Me	80	60°; 19·5	86·9	13·0	86·7	13·3	1·4513

3-Alkyl- and 3,3-dialkyl-1-bromoallenes (I; X = Br) were prepared from prop-1-yn-3-ols and hydrobromic acid in the presence of copper(I) bromide,<sup>5</sup> 1-iodo-3-methylpenta-1,2-diene (I; R<sup>2</sup> = Me, R<sup>3</sup> = Et, X = I) was prepared from 3-methylpent-1-yn-3-ol and hydriodic acid in the presence of copper(I) iodide,<sup>6</sup> and 1-iodohexa-1,2-diene (I; R<sup>2</sup> = Pr, R<sup>3</sup> = H, X = I) was prepared from hex-1-yn-3-ol and triphenyl phosphite methiodide.<sup>7</sup> Dialkyl(lithio)copper reagents were prepared according to published procedures.<sup>2,3</sup> Small-scale experiments (Tables 1 and 2) were carried out with 2·5 mol of dialkyl(lithio)copper reagent per mol of halogen compound and

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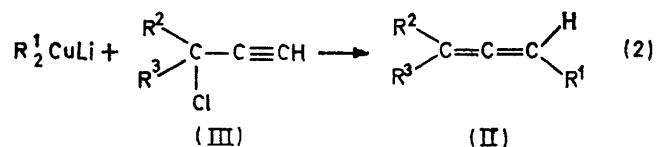
<sup>1</sup> Part XXVI, Z. T. Fomum, P. M. Greaves, P. D. Landor, and S. R. Landor, *J.C.S. Perkin I*, 1973, 1108.

<sup>2</sup> H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, 1952, **17**, 1630.

<sup>3</sup> E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, 1967, **89**, 3911; 1968, **90**, 5615; G. M. Whitesides, W. F. Fischer, J. S. Filippo, R. W. Bashe, and H. O. House, *ibid.*, 1969, **91**, 4871.

<sup>4</sup> Preliminary report, M. Kalli, P. D. Landor, and S. R. Landor, *J.C.S. Chem. Comm.*, 1972, 593.

1-Halogenoallenes are known<sup>9</sup> to react with alkyl-lithium reagents *via* a carbene mechanism to give a mix-



ture of products in which acetylenes predominate. Since dialkyl(lithio)copper reagents directly replace a halogen

<sup>5</sup> S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc.*, 1966, 1223; S. R. Landor, B. Demetriou, R. J. Evans, R. Grysekowiak, and D. Pavey, *J.C.S. Perkin II*, 1972, 1995.

<sup>6</sup> P. M. Greaves, M. Kalli, P. D. Landor, and S. R. Landor, *J. Chem. Soc. (C)*, 1971, 667.

<sup>7</sup> C. S. L. Baker, P. D. Landor, S. R. Landor, and A. N. Patel, *J. Chem. Soc. (C)*, 1965, 4348.

<sup>8</sup> G. F. Hennion and A. B. Boisselle, *J. Org. Chem.*, 1961, **26**, 725; G. F. Hennion, J. J. Sheehan, and D. E. Mahoney, *J. Amer. Chem. Soc.*, 1950, **72**, 3542.

<sup>9</sup> S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 1965, 5625.

on C-1 by an alkyl group to give only allenic, and no acetylenic products, we tentatively suggest that the

TABLE 2

Preparation of allenic hydrocarbons from iodoallenes  
[equation (1); X = I]

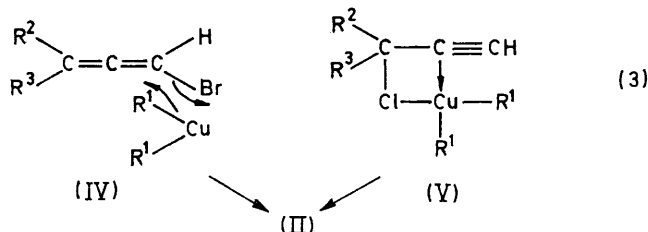
Product (II)			Yield (% from g.l.c.)
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	
Me	Me	Et	63
Et	Me	Et	66
Bu <sup>a</sup>	Me	Et	68
Me	Pr <sup>a</sup>	H	68
Et	Pr <sup>a</sup>	H	67
Bu <sup>a</sup>	Pr <sup>a</sup>	H	64

TABLE 3

Preparation of allenic hydrocarbons from chloro-acetylenes  
[equation (3)]

Product (II)			Yield (% from g.l.c.)
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	
Me	Me	Et	66
Et	Me	Et	63
Bu	Me	Et	64
Me	Pr <sup>a</sup>	H	62
Et	Pr <sup>a</sup>	H	66
Bu	Pr <sup>a</sup>	H	71

reaction goes through a four-centre transition state (IV) [equation (3)]. A similar mechanism was suggested for



the reaction of 1-bromoallenes and copper(I) cyanide,<sup>10</sup> supported by the fact that optically active 1-bromoallene<sup>5</sup> gave optically active 1-cyanoallene.<sup>10</sup>

Crabbé has suggested an addition-elimination mechanism for a similar replacement of acetate by an alkyl group,<sup>11</sup> through a radical-anion intermediate, which was shown to be non-stereospecific. The reaction of 3-chloroalk-1-yne and R<sub>2</sub>CuLi is believed to proceed *via* the  $\pi$ -complex (V), as suggested for the formation of 1-bromoallenes from prop-1-yn-3-ols.<sup>5</sup>

#### EXPERIMENTAL

I.r. spectra were determined for liquid films (0.025 mm cell) and for 5% solutions in chloroform with a Perkin-Elmer 337 spectrophotometer. N.m.r. spectra were determined on a Varian A60 instrument for solutions in deuteriochloroform with tetramethylsilane as internal standard. Analytical g.l.c. was carried out using a Pye 104 instrument on glass

<sup>10</sup> P. M. Greaves, S. R. Landor, and D. R. J. Laws, *J. Chem. Soc. (C)*, 1968, 291; P. M. Greaves and S. R. Landor, unpublished work.

columns (5 ft) with nitrogen as carrier gas at a flow rate of 40 ml min<sup>-1</sup> and preparative g.l.c. on glass columns (7 ft) with N<sub>2</sub> flow rate 60 ml min<sup>-1</sup>. Silicone oil refers to grade SE 30 on Chromosorb W. All reactions were carried out under an atmosphere of pure nitrogen.

*Dialkyl(lithio)copper Reagents.*—(a) Dimethyl(lithio)copper<sup>2</sup> was prepared from a standardised solution of methyl-lithium<sup>12</sup> (1.1 g, 0.05 mol) in anhydrous ether (50 ml) and a vigorously stirred suspension of copper(I) iodide (4.75 g, 0.025 mol) in ether (50 ml) at -5°.

(b) Diethyl(lithio)copper<sup>3</sup> was prepared from ethyl-lithium (1.8 g, 0.05 mol; Alpha Inorganics, Inc.) in benzene (50 ml) and a vigorously stirred suspension of copper(I) iodide (4.75 g, 0.025 mol) in dry ether (100 ml) at -30°.

(c) Di-n-butyl(lithio)copper<sup>3</sup> was prepared from butyl-lithium (3.2 g, 0.05 mol; Alpha Inorganics, Inc.) in hexane (25 ml) and a vigorously stirred suspension of copper(I) iodide (4.75 g, 0.025 mol) in dry ether (25 ml) at -60°.

*Allenic Hydrocarbons.*—The 1,3-di- and 1,1,3-tri-alkyl allenes prepared from 1-bromoallenes<sup>5</sup> and the appropriate dialkyl(lithio)copper reagent are listed in Table 1. Reactions with Me<sub>2</sub>CuLi were carried out at -5°, with Et<sub>2</sub>CuLi at -30°, and with Bu<sub>2</sub>CuLi at -60° for 1–3 h. Typical small-scale and preparative scale experiments are described below.

*4-Methylhexa-2,3-diene.* (a) 1-Bromo-3-methylpenta-1,2-diene (1.61 g, 0.01 mol) in dry ether (25 ml) was added to an ethereal solution of dimethyl(lithio)copper (0.025 mol) kept at -5°, prepared as above. After vigorous stirring for 2.5 h, the mixture was hydrolysed by careful addition of water, filtered, and dried (MgSO<sub>4</sub>). The residue from evaporation was analysed by g.l.c. (silicone oil; 25°) and gave one product ( $t_R$  10.5 min; estimated yield 85%). Purification by preparative g.l.c. (silicone oil; 65°;  $t_R$  15 min) gave 4-methylhexa-2,3-diene,  $\nu_{\max}$  1950 (C=C=C) cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 9.05 (3H, t, CH<sub>3</sub>·CH<sub>2</sub>), 8.38 (3H, d,  $J_{1,2}$  7 Hz, CH<sub>3</sub>·CH), 8.35 (3H, d,  $J_{4,2}$  2.5 Hz, CH<sub>3</sub>C=), 8.20 (2H, dq, CH<sub>2</sub>·CH<sub>3</sub>), and 5.10 (1H, m, =CH). (See Table 1.)

(b) 1-Bromo-3-methylpenta-1,2-diene (16.1 g, 0.1 mol) in dry ether (50 ml) was treated with dimethyl(lithio)copper (0.125 mol) at -5° and the product was worked up as before. Distillation through an 8 in column of Fenske rings gave 4-methylhexa-2,3-diene (6.5 g, 68%), b.p. 92° at 760 mmHg, identical with the sample obtained from the small-scale experiment.

*3-Methylhepta-3,4-diene.*—1-Bromo-3-methylpenta-1,2-diene (16.1 g, 0.1 mol) in dry ether (50 ml) was added to an ethereal solution of diethyl(lithio)copper (0.125 mol) at -30° and the product was worked up as before. Fractional distillation of the residue (11.2 g) as before gave 3-methylhepta-3,4-diene (6.25 g, 57%), b.p. 50° at 80 mmHg, identical (g.l.c., spectra, and refractive index) with an authentic sample.

*3-Methylnona-3,4-diene.*—A solution of 1-bromo-3-methylpenta-1,2-diene (16.1 g, 0.01 mol) in dry ether (50 ml) was added dropwise to a solution of di-n-butyl(lithio)copper (0.125 mol) at -60° and the product was worked up as before. The residue (14.7 g) was fractionated as before to give 3-methylnona-3,4-diene, identical (g.l.c., spectra, and refractive index) with an authentic sample.

In a similar manner 1,3-di- and 1,1,3-tri-alkyl allenes were prepared from 1-iodoallenes,<sup>5,7</sup> with dialkyl(lithio)copper

<sup>11</sup> P. Rona and P. Crabbé, *J. Amer. Chem. Soc.*, 1969, **91**, 3289.

<sup>12</sup> A. Gilman and F. Cartledge, *J. Organometallic Chem.*, 1964, **2**, 447.

reagents, and the physical constants of the products were identical with those given in Table 1; the yields are given in Table 2. Yields of products from 3-chloroacetylenes<sup>9</sup> and dialkyl(lithio)copper reagents are given in Table 3. All the

allenes prepared showed a typical i.r. band at 1950—1970  $\text{cm}^{-1}$  and in the n.m.r. the allenic protons gave a signal at  $\tau$  5.2—4.95.

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