

## Chain-extension Reactions of Acetylenes. Part 4.<sup>1</sup> Reaction of 1,3-Dilithioacetylides with Carbonyl Electrophiles, Hexamethylphosphoric Triamide, and Benzylideneaniline †

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The regioselectivity of the reactions of 1,3-dilithioalk-1-yne with various electrophiles has been examined. With formaldehyde and cyclic ketones, reactions occur both at C-1 and C-3 to give alk-2-yne-1,5-diols. In contrast reactions with carbon dioxide give allene-1,3-dicarboxylic acids.

1,3-Dilithioalk-1-yne decompose hexamethylphosphoric triamide and the resulting *N*-methylmethyleamine undergoes addition *only* at the propargylic site. Further reaction with either 1-bromobutane or water gives alkynylamines. Benzylideneaniline also reacts with 1,3-dilithiohex- and hept-1-yne only at the propargylic site to give *N*-phenylbut-3-ynylamines.

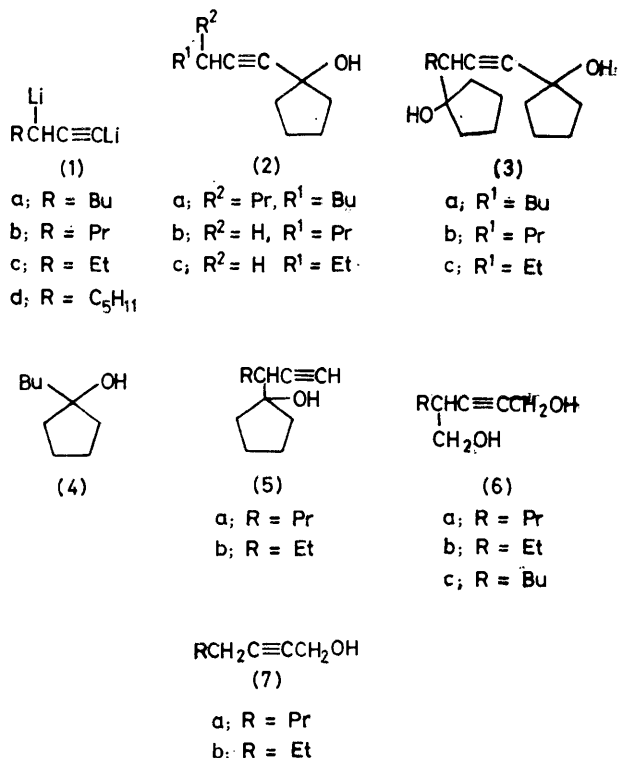
In previous papers the preparation of linear<sup>1</sup> and branched acetylides<sup>2</sup> has been described by reactions of 1,3-dilithioacetylides with alkyl halides and other electrophiles, and this has followed the work of others<sup>3-7</sup> on the structure and reactivity of polythioacetylides.

1,3-dilithioacetylides react with hexamethylphosphoric triamide and add onto benzylideneaniline.

In studying the reactions of 1,3-dilithioacetylides with two different electrophiles, 1,3-dilithiohept-1-yne (1a) was treated successively in 'one pot' with 1-bromopropane and cyclopentanone.<sup>2a</sup> In addition to the isolation of the 1-(1-hydroxycyclopentyl)-3-propylhept-1-yne (2a) some 1,3-bis(1-hydroxycyclopentyl)hept-1-yne (3a) was obtained.<sup>2a</sup> Clearly the latter product (3a) had been formed because the slow alkylation at the propargylic (prop-2-ynylic) carbon was incomplete and thus subsequent addition of the more reactive electrophile, cyclopentanone, enabled it to react both at C-3 and C-1.

In attempting exclusive reactions of cyclopentanone with 1,3-dilithioalk-1-yne (1b) and (1c) the ketone was added at 0 °C, 1 h after formation of a yellow solution from addition of 2.2 equiv. of butyl-lithium to the alk-1-yne at -20 °C. Under these conditions only the cyclopentan-1-ols (4),<sup>8</sup> (2b), and (2c) were isolated. Formation of these derivatives indicated that the 1,3-dilithioalk-1-yne (1b) and (1c) had not been formed in appreciable quantities and that butyl-lithium in hexane dissolves 1-lithioalkyne to give a yellow soluble complex (*e.g.* BuLi·*x*RCH<sub>2</sub>C≡CLi). Recently West and his co-workers<sup>9</sup> have pointed out that the extent of polythiation of acetylenes and allenes can be followed by i.r. spectroscopy and that the band at *ca.* 2 050 cm<sup>-1</sup> of 1-lithioalk-1-yne is replaced by one at *ca.* 1 870 cm<sup>-1</sup> on forming 1,3-dilithioalk-1-yne (1). We monitored the formation of the propargylide ions (1) using i.r. spectroscopy and confirmed that at room temperature it was necessary to wait 24 h prior to ketone addition. In the case of 1,3-dilithiohept-1-yne and lower homologues a yellow precipitate was formed but the higher homologues usually remained in solution.

For propargylic alkylation of 1,3-dilithioacetylides with 1-bromoalkanes in hexane, the addition of the



We have extended these studies by allowing 1,3-dilithioacetylides to react with cyclic ketones, formaldehyde, and carbon dioxide. In addition it has been shown that

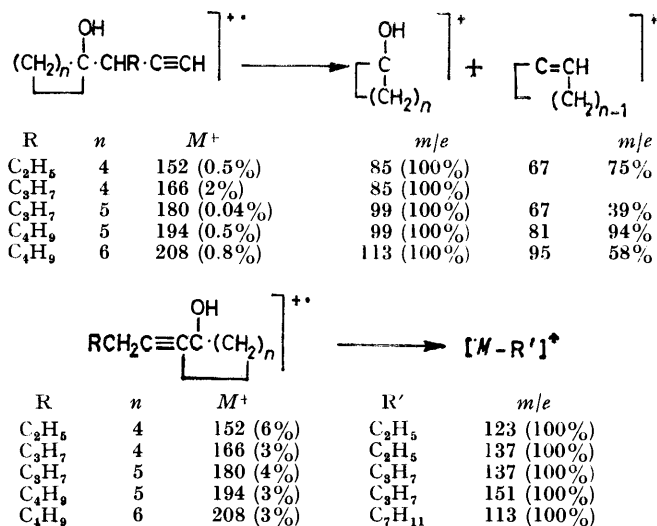
† Preliminary communication, G. R. Khan, K. A. Pover, and F. Scheinmann, *J.C.S. Chem. Comm.*, 1979, 215.

electrophile prior to formation of the 1,3-dilithioacetylide is of no consequence since reaction only occurs in the presence of the propargylic ion (1).<sup>10</sup>

Reaction of cyclopentanone at ambient temperatures with 1,3-dilithioalk-1-yne (1b) and (1c) gave the alk-2-yne-1,5-diols (3b) and (3c) together with an inseparable mixture of the monohydric alcohols (2b) and (5a); (2c)

gens at C-1 as two doublets between *ca.*  $\delta$  3.55 and 3.64. The methylene groups at C-5 resonate at *ca.* 4.3 and show long-range coupling (*J ca.* 2 Hz) with the methine hydrogen at C-2.

Reaction of 1,3-dilithiohex-1-yne (1b) with a slurry of carbon dioxide led to the formation of an allenedicarboxylic acid (8a) and the corresponding acetylenedi-



SCHEME 1 Mass spectral fragmentation patterns for the mixture of alkynols showing preferred cleavage

and (5b). Similar results were obtained with cyclohexanone and cycloheptanone but with formaldehyde only alk-2-yne-1,5-diols (6a), (6b), and (6c) and alk-2-yn-1-ols (7a), (7b), and (7c) were isolated. The mixture of monohydric alcohols (2b) and (5a); (2c) and (5b) was analysed by g.c.-m.s. which showed the presence of two isomeric compounds having characteristic fragmentation patterns (Scheme 1). The C-13 data is diagnostic for the structures of the alk-2-yne-1,5-diols since it is possible to assign the propargylic and acetylenic carbon atoms (Table 1).

In addition the <sup>1</sup>H n.m.r. spectrum for the formaldehyde adducts (6a) and (6b) shows the pro-chiral hydro-

carboxylic acid (9) was not isolated. The structure of the product (8a) follows largely from spectral data with the characteristic allene stretching frequency appearing at 1950 cm<sup>-1</sup>, the proton magnetic resonance spectrum showing the allenic hydrogen at C-4  $\delta$  at 6.03 having long-range coupling with the allylic methylene group (*J ca.* 2 Hz).<sup>11</sup> The <sup>13</sup>C n.m.r. data also supported the assignments showing the three allenic carbon atoms as two singlets ( $\delta$  103.69 and 217.71) and a doublet (at  $\delta$  91.86). Catalytic hydrogenation gave the known 2-propylglutaric acid.<sup>12</sup> Allene-1,3-dicarboxylic acids were also obtained on reaction of 1,3-dilithiopent-1-yne (1c), 1,3-dilithiohept-1-yne (1a), and 1,3-dilithio-oct-1-yne

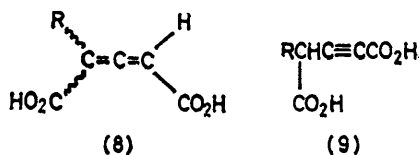
TABLE 1

<sup>13</sup>C N.m.r. chemical shifts (p.p.m. from SiMe<sub>4</sub>) for 4-alkylpent-2-yne-1,5-diols  $\text{(CH}_2\text{)}_n\text{-C}^5\text{(OH)-C}^4\text{(OH)-C}^3\text{(R)-C}^2\text{(C}\equiv\text{C)-C}^1\text{(CH}_2\text{)}_n$

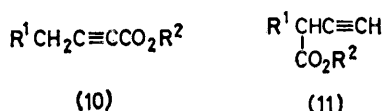
R/n	C-1	C-2	C-3	C-5	C-4	R	and	Ring system
C <sub>2</sub> H <sub>5</sub> /0	50.66	81.05	86.54	36.77	64.93	11.35, 24.04		
C <sub>3</sub> H <sub>7</sub> /0	50.68	80.88	86.77	34.89	65.21	13.50, 20.11, 33.05		
C <sub>3</sub> H <sub>7</sub> /0	50.65	80.85	86.75	34.90	65.20	13.53, 20.13, 33.07, 33.07		
C <sub>2</sub> H <sub>5</sub> /4	74.40	83.67 †	83.86 †	44.74 †	87.19 †	12.57	23.04, 23.22, 23.73, 24.08, 37.37, 38.94, 42.53	
C <sub>3</sub> H <sub>7</sub> /4	74.38	83.70 †	84.00 †	not assigned	86.94 †	13.78, 21.11	23.24, 23.76, 24.09, 31.97, 37.34, 38.97, 42.50	
C <sub>3</sub> H <sub>7</sub> /5	68.39	84.42 †	87.63 †	43.61	72.39 †	13.68, 21.21, 21.69, 23.30, 25.03, 25.63, 30.48		
C <sub>4</sub> H <sub>9</sub> /5	68.36	84.51 †	87.53 †	43.83	72.38 †	13.74, 21.70, 22.22, 22.88, 23.32, 24.00, 25.04, 40.04		
C <sub>5</sub> H <sub>11</sub> /6	75.31	84.23 †	88.49 †	45.04	76.16 †	13.78, 22.18, 27.57, 28.55, 29.28, 30.38, 37.71		
						39.22, 43.18		

\* Spectra measured as solutions in deuteriochloroform. † These values may be interchanged.

(1d) with carbon dioxide and the diagnostic spectral data for the products (8a—d) are summarised in Table 3. We noticed that substantially lower yields were obtained when carbon dioxide gas was passed into the reaction



- a; R = Pr  
b; R = Et  
c; R = Bu  
d; R = C<sub>3</sub>H<sub>11</sub>  
e; R = H

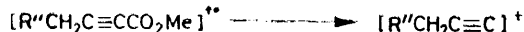
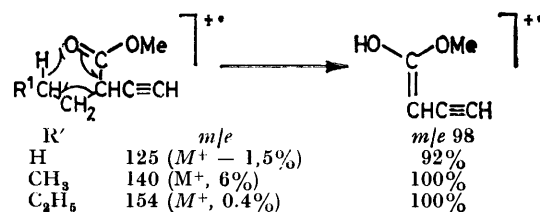


- a, R<sup>1</sup> = Pr, R<sup>2</sup> = H  
b, R<sup>1</sup> = Et, R<sup>2</sup> = H  
c, R<sup>1</sup> = Bu, R<sup>2</sup> = H

mixture at -40 °C, instead of adding the dilithioacetylide to solid carbon dioxide (Table 4).

Mixtures of acetylenic monocarboxylic acids were also isolated by chromatography from these reactions.

That carboxylation had occurred at either C-1 and C-3 of the 1,3-dilithioalk-1-yne was shown by Raman spectroscopy on the mixtures which showed two  $\nu(\text{C}\equiv\text{C})$  signals (2 110 and 2 220 cm<sup>-1</sup>). In addition <sup>13</sup>C n.m.r. spectroscopy indicated the presence of terminal and internal



R''	m/e	R''	m/e
C <sub>2</sub> H <sub>5</sub>	126 (M <sup>+</sup> , 8%)	C <sub>2</sub> H <sub>5</sub>	67 (20%), 95 (M <sup>+</sup> - 31, 100%)
C <sub>3</sub> H <sub>7</sub>	140 (M <sup>+</sup> , 3%)	C <sub>3</sub> H <sub>7</sub>	71 (100%)
C <sub>4</sub> H <sub>9</sub>	154 (M <sup>+</sup> , 2%)	C <sub>4</sub> H <sub>9</sub>	85 (100%)

SCHEME 2 Mass spectral fragmentation of the acetylene carboxylic ester RCH(CO<sub>2</sub>Me)C≡CH and RCH<sub>2</sub>C≡CCO<sub>2</sub>Me showing the preferred cleavage for each component in the mixture

acetylenes with signals at *ca.* 8 72.0 p.p.m., which appears as a doublet in the off-resonance spectrum, and singlets at *ca.* 72.7 and *ca.* 92 p.p.m. G.c.-m.s. on the methyl ester (10a) and (11a) → (10c) and (11c) (R<sup>2</sup> = Me instead of H) shows two isomeric methyl alkynoates in each case. Their structures are supported by characteristic

TABLE 2

Physical constants, and spectral and analytical data for the 4-alkylpent-2-yne-1,5-diols  $(\text{CH}_2)_n\text{C}\equiv\text{C}(\text{CH}(\text{R}))\text{C}\equiv\text{C}(\text{CH}_2)_n$

R/n	I.r. $\nu(\text{C}\equiv\text{C})/\text{cm}^{-1}$	M.p. or b.p. (°C/mmHg) [% yield]	<sup>1</sup> H N.m.r. (δ) CDCl <sub>3</sub>	M <sup>+</sup> /C, H, O
C <sub>2</sub> H <sub>5</sub> /0	2 240	B.p. 54—56/0.04 [35]	4.28 (d, 2 H, C≡CCH <sub>2</sub> OH), 3.75 (s, 2 H, 2 × O-H), 3.69—3.59 (d of d, 2 H, CH <sub>2</sub> OH, J ~ 1 Hz, J ~ 2 Hz), 2.5 (m, 1 H, CHC≡C), 1.5 (m, 2 H, 1 × CH <sub>3</sub> ), 1.0 (t, 3 H, CH <sub>3</sub> )	m/e = 110 [M <sup>+</sup> - 18, 110.0731, C <sub>7</sub> H <sub>10</sub> O requires 110.0731], 80 [M <sup>+</sup> - 48, 80.062 53, C <sub>6</sub> H <sub>8</sub> requires 80.062 56]
C <sub>3</sub> H <sub>7</sub> /0	2 240	B.p. 42—45/0.1 [46.5]	4.25 (d, 2 H, C≡CCH <sub>2</sub> OH), 3.62—3.57 (m, 4 H, CH <sub>2</sub> OH, 2 × O-H), 2.6 (m, 1 H, CHC≡C), 1.45 (m, 4 H, 2 × CH <sub>2</sub> ), 0.9 (t, 3 H, CH <sub>3</sub> )	m/e = 94 (M <sup>+</sup> - 48, 94.078 20, C <sub>7</sub> H <sub>10</sub> requires 94.078 20)
C <sub>4</sub> H <sub>9</sub> /0	2 240	B.p. 59/0.02 [28]	4.3 (d, 2 H, C≡CCH <sub>2</sub> OH), 3.81 (s, 2 H, 2 × O-H), 3.63—3.57 (d of d, 2 H, CH <sub>2</sub> OH, J ~ 2 Hz, J ~ 3 Hz), 2.6 (m, 1 H, CHC≡C), 1.4 (m, 6 H, 3 × CH <sub>2</sub> ), 0.9 (t, 3 H, CH <sub>3</sub> )	m/e = 108 (M <sup>+</sup> - 48, 108.0938, C <sub>8</sub> H <sub>12</sub> requires 108.0938)
C <sub>2</sub> H <sub>5</sub> /4	2 210	M.p. 120—121 [6]	3.0 (s, 1 H, O-H), 2.73 (s, 1 H, O-H), 2.35 (m, 1 H, CHC≡C), 1.7 (m, 18 H, 9 × CH <sub>2</sub> ), 1.0 (t, 3 H, CH <sub>3</sub> )	m/e = 219 (M <sup>+</sup> - 17), 201 (M <sup>+</sup> - 35), 134 (M <sup>+</sup> - 102, 100%), 85 (C <sub>5</sub> H <sub>9</sub> O) (Found: C, 76.55; H, 10.2. C <sub>15</sub> H <sub>24</sub> O <sub>2</sub> requires C, 76.27; H, 10.16%)
C <sub>3</sub> H <sub>7</sub> /4	2 225	M.p. 115—116 [32]	2.43 (m, 1 H, CHC≡C), 1.8—1.4 (m, 22 H, 10 × CH <sub>2</sub> , 2 × O-H), 0.9 (t, 3 H, CH <sub>3</sub> )	m/e = 148 (M <sup>+</sup> - 102, 100%), 119 (M <sup>+</sup> - 131), 91 (C <sub>7</sub> H <sub>7</sub> ), 85 (C <sub>5</sub> H <sub>9</sub> O) (Found: C, 76.7; H, 10.4. C <sub>16</sub> H <sub>26</sub> O <sub>2</sub> requires C, 76.80; H, 10.40%)
C <sub>3</sub> H <sub>7</sub> /5	2 210	M.p. 90 [23]	2.48 (s, 2 H, 2 × O-H), 2.36 (m, 1 H, CHC≡C), 1.6 (m, 24 H, 12 × CH <sub>2</sub> ), 0.92 (t, 3 H, CH <sub>3</sub> )	m/e = 162 (M <sup>+</sup> - 116, 100%), 133 (M <sup>+</sup> - 145), 119 (C <sub>8</sub> H <sub>11</sub> O), 99 (C <sub>6</sub> H <sub>11</sub> O) (Found: C, 77.8; H, 10.75. C <sub>18</sub> H <sub>30</sub> O <sub>2</sub> requires 77.96; H, 10.79%)
C <sub>4</sub> H <sub>9</sub> /5	2 220	M.p. 96 [16]	2.4 (m, 3 H, CHC≡C, 2 × O-H), 1.6 (m, 26 H, 13 × CH <sub>2</sub> ), 0.9 (t, 3 H, 1 × CH <sub>3</sub> )	m/e = 176 (M <sup>+</sup> - 116, 100%), 161 (M <sup>+</sup> - 131), 147 (M <sup>+</sup> - 145), 99 (C <sub>8</sub> H <sub>11</sub> O) (Found: C, 78.15; H, 10.9. C <sub>19</sub> H <sub>32</sub> O <sub>2</sub> requires C, 78.08; H, 10.95%)
C <sub>5</sub> H <sub>11</sub> /6	2 240	M.p. 95 [21]	2.4 (m, 1 H, CHC≡C), 1.95 (s, 2 H, O-H), 1.6 (m, 32 H, 16 × CH <sub>2</sub> ), 0.9 (t, 3 H, CH <sub>3</sub> )	m/e = 302 (M <sup>+</sup> - 18), 284 (M <sup>+</sup> - 36), 190 (C <sub>14</sub> H <sub>22</sub> O), 113 (C <sub>7</sub> H <sub>13</sub> O) (Found: C, 78.9; H, 11.5. C <sub>21</sub> H <sub>36</sub> O <sub>2</sub> requires C, 78.75; H, 11.25%)

fragmentation patterns (Scheme 2) with 3-methoxycarbonylalk-1-yne undergoing a preferential fragmentation by the McLafferty rearrangement.

Eberly and Adams<sup>3</sup> have previously studied the carbonylation of the dilithio-derivative of but-1-yne and

disubstituted acetylenes, and no allenic by-products could be detected. In contrast for the dicarboxylation of 1,3-dilithioalk-1-yne only the allene-1,3-dicarboxylic acids were isolated. These results are in accord with previous attempts to prepare pent-2-yne-1,5-dicarboxylic acid

TABLE 3  
Spectral data and physical constants for the mixture of acetylenic monohydric alcohols

R/n	$\nu(\text{cm}^{-1})$		$^1\text{H}$ N.m.r.	$^{13}\text{C}$ N.m.r.	B.p. ( $^{\circ}\text{C}/\text{mmHg.}$ ) [% yield]
	I.r.	Raman	( $\delta$ p.p.m. from $\text{SiMe}_4$ )	( $\delta$ p.p.m. from $\text{SiMe}_4$ )	
$\text{C}_2\text{H}_5/0^a$	2 230		4.25 (t, 2 H, $\text{C}\equiv\text{CCH}_2\text{OH}$ ), 2.5 (s, 1 H, O-H), 2.2 (m, 2 H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.5 (sext, 2 H, $1 \times \text{CH}_2$ ), 0.99 (t, 3 H, $1 \times \text{CH}_3$ )	51.15 (C-1), 78.62 (C-2), 86.19 (C-3), 20.52 (C-4), 21.86 (C-5), 13.14 (C-6)	46/0.6 (lit., <sup>c</sup> 75/18) [9]
$\text{C}_3\text{H}_7/0^a$	2 210		4.1 (t, 2 H, $\text{C}\equiv\text{CH}_2\text{OH}$ ), 3.6 (s, 1 H, O-H), 2.1 (m, 2 H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.4 (m, 4 H, $2 \times \text{CH}_2$ ), 0.9 (t, 3 H, $1 \times \text{CH}_3$ )	50.68 (C-1), 79.31 (C-2), 85.44 (C-3), 18.76 (C-4), 31.36 (C-5), 22.44 (C-6), 13.78 (C-7)	77-79/9 (lit., <sup>d</sup> 84/16) [22]
$\text{C}_4\text{H}_9/0^a$	2 225		4.24 (t, 2 H, $\text{C}\equiv\text{CCH}_2\text{OH}$ ), 3.1 (s, 1 H, O-H), 2.2 (m, 2 H, $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.4 (m, 6 H, $3 \times \text{CH}_2$ ), 0.9 (t, 3 H, $1 \times \text{CH}_3$ )	50.89 (C-1), 78.38 (C-2), 86.04 (C-3), 18.44 (C-4), 28.15 (C-5), 30.87 (C-6), 21.90 (C-7), 13.54 (C-8)	42-44/0.02 (lit., <sup>e</sup> 98-9, 1) [35]
$\text{C}_2\text{H}_5/4^b$	2 222		2.5-2.2 (m, $\text{CHC}\equiv\text{C}$ , $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.05 (d, $\text{C}\equiv\text{CH}$ , $J \sim 2$ Hz)	85.06, 83.10, 82.02, 70.61 (d, $\text{C}\equiv\text{CH}$ ) 44.42 (d, $\text{CHC}\equiv\text{C}$ )	38-45/0.01 56-58/0.05
$\text{C}_3\text{H}_7/4^b$	2 233		2.6-2.25 (m, $\text{CHC}\equiv\text{C}$ , $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.113 (d, $\text{C}\equiv\text{CH}$ , $J \sim 2$ Hz)	83.34, 83.26, 82.31, 74.58, 70.56 (d, $\text{C}\equiv\text{CH}$ ) 42.39 (d, $\text{CHC}\equiv\text{C}$ )	
$\text{C}_3\text{H}_7/5^b$	2 236		2.6-2.2 (m, $\text{CHC}\equiv\text{C}$ , $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.109 (d, $\text{C}\equiv\text{CH}$ , $J \sim 2$ Hz)	84.82, 72.01, 71.52, 70.80 (d, $\text{C}\equiv\text{CH}$ ), 68.22, 43.82 (d, $\text{CHC}\equiv\text{C}$ )	62-66/0.05
$\text{C}_4\text{H}_9/5^b$	2 215		2.6-2.2 (m, $\text{CHC}\equiv\text{C}$ , $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.110 (d, $\text{C}\equiv\text{CH}$ , $J \sim 2$ Hz)	84.70, 83.73, 71.77, 71.28, 67.95 (d, $\text{C}\equiv\text{CH}$ ), 43.74 (d, $\text{CHC}\equiv\text{C}$ )	68-71/0.02
$\text{C}_5\text{H}_{11}/6^b$	2 215		2.6-2.2 (m, $\text{CHC}\equiv\text{C}$ , $\text{CH}_2\text{C}\equiv\text{C}$ ), 2.110 (d, $\text{C}\equiv\text{CH}$ , $J \sim 2$ Hz)	85.07, 84.83, 75.54, 71.34 (d, $\text{C}\equiv\text{CH}$ ), 45.03 (d, $\text{CHC}\equiv\text{C}$ )	80-83/0.05

<sup>a</sup> These entries have data for pure compounds. <sup>b</sup> These entries represent mixtures and only the diagnostic n.m.r. has been included. N.m.r. spectra were measured as solutions in deuteriochloroform. <sup>c</sup> J. Colonge and G. Descotes, *Bull. Soc. chim. France*, 1959, 815. <sup>d</sup> A. Schaap, L. Brandsma, and J. F. Arens, *Rec. Trav. chim.*, 1965, **84**, 1200. <sup>e</sup> M. de Gaudemaris and P. Arnaud, *Bull. Soc. chim. France*, 1962, 315.

methylallene but the crude dicarboxylic acid was not characterised. Hydrogenation gave 2-methylglutaric acid indicating that carboxylation of the reactive intermediate had occurred at C-1 and C-3.

Our previous synthetic studies on reactions of 1,3-dilithioalk-1-yne with electrophiles produced 1,3-

(glutinic acid) (8e) or its dimethyl ester<sup>13</sup> which led only to the isolation of penta-2,3-dienedioic acid (8e)<sup>14</sup> or its dimethyl ester.<sup>13</sup> Even careful oxidation of 5-hydroxypent-2-ynoic acid led only to the isolation of the allene-1,3-dicarboxylic acid (8e). In this case, as in our examples, the acetylenic dicarboxylic acid, which is

TABLE 4  
Physical constants, yields, and spectral and analytical data for allene-1,3-dicarboxylic acids  $\text{RC}=\text{C}=\text{CHCO}_2\text{H}$

R	M.p. ( $^{\circ}\text{C}$ ) [% yield]	I.r. $\text{cm}^{-1}$ $\nu(\text{C}=\text{C})$	$^1\text{H}$ N.m.r.	$^{13}\text{C}$ N.m.r.	Analysis C, H, O
			( $\delta$ p.p.m. from $\text{SiMe}_4^a$ )	( $\delta$ p.p.m. from $\text{SiMe}_4^b$ )	
$\text{C}_2\text{H}_5$	170-172 [33]	1 950 1 695	10.25 (s, 2 H, $\text{COOH}$ ), 6.07 (t, 1 H, $\text{C}=\text{C}-\text{CH}$ , $J \sim 2.5$ Hz), 2.3 (m, 2 H, $\text{CH}_2\text{C}=\text{C}$ ), 1.1 (t, 3 H, $1 \times \text{CH}_3$ )	C-1, C-5 (164.98, 165.84), C-2 (105.54), C-3 (217.50), C-4 (d, 92.11), C-3' (21.09), C-4' (11.92)	(Found: C, 53.8; H, 5.2. $\text{C}_7\text{H}_8\text{O}_4$ requires C, 53.84; H, 5.12%)
$\text{C}_3\text{H}_7$	144-145 [37]	1 950 1 690	9.05 (s, 2 H, $\text{COOH}$ ), 6.04 (t, 1 H, $\text{C}=\text{C}-\text{CH}$ , $J \sim 2.5$ Hz), 2.3 (m, 2 H, $\text{CH}_2\text{C}=\text{C}$ ), 1.55 (sext. 2 H, $\text{CH}_2$ ), 0.97 (t, 3 H, $\text{CH}_3$ )	C-1, C-5 (165.34, 166.20), C-2 (103.69), C-3 (217.71), C-4 (d, 91.86), C-3' (29.95), C-4' (20.59), C-5' (13.29)	(Found: C, 56.15; H, 6.15. $\text{C}_8\text{H}_{10}\text{O}_4$ requires C, 56.47; H, 5.98%)
$\text{C}_4\text{H}_9$	136-138 [31.5]	1 960 1 695	10.20 (s, 2 H, $\text{COOH}$ ), 6.05 (t, 1 H, $\text{C}=\text{C}-\text{CH}$ , $J \sim 2.5$ Hz), 2.24 (m, 2 H, $\text{CH}_2\text{C}=\text{C}$ ), 1.38 (m, 4 H, $2 \times \text{CH}_2$ ), 0.85 (t, 3 H, $\text{CH}_3$ )	C-1, C-5 (165.81, 166.67), C-2 (104.40), C-3 (218.40), C-4 (d, 92.22), C-3' (27.99), C-4' (29.94), C-5' (22.01), C-6' (14.08)	(Found: C, 58.3; H, 6.3. $\text{C}_9\text{H}_{12}\text{O}_4$ requires C, 58.69; H, 6.52%)
$\text{C}_5\text{H}_{11}$	146-147 [13.5]	1 950 1 695	10.90 (s, 2 H, $\text{COOH}$ ), 6.05 (t, 1 H, $\text{C}=\text{C}-\text{CH}$ , $J \sim 2.5$ Hz), 2.4 (m, 2 H, $\text{CH}_2\text{C}=\text{C}$ ), 1.4 (m, 6 H, $3 \times \text{CH}_2$ ), 0.9 (t, 3 H, $\text{CH}_3$ )	C-1, C-5 (165.41, 166.29), C-2 (103.90), C-3 (217.93), C-4 (d, 91.94), C-3' (27.13), C-4' (27.88), C-5' (30.68), C-6' (22.12), C-7' (13.99)	(Found: C, 60.3; H, 7.2. $\text{C}_{10}\text{H}_{14}\text{O}_4$ requires C, 60.60; H, 7.07%)

<sup>a</sup> These spectra were measured as hexadeuterioacetone solutions. <sup>b</sup> These spectra were measured as  $(\text{CD}_3)_2\text{SO}$  solutions.

probably the intermediate, rapidly undergoes a 1,3-hydrogen transfer to give the more stable allene-1,3-dicarboxylic acid.

Recently West and his co-workers<sup>9</sup> used hexamethyl-

give *N*-methylmethyleamine (13) and subsequent reaction of this intermediate.<sup>17</sup> Regioselective nucleophilic addition of 1,3-dilithiohex-1-yne to the imine<sup>18</sup> occurs only with the propargylic carbon followed by

TABLE 5

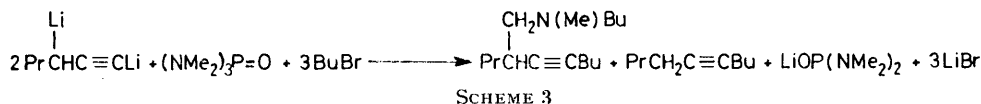
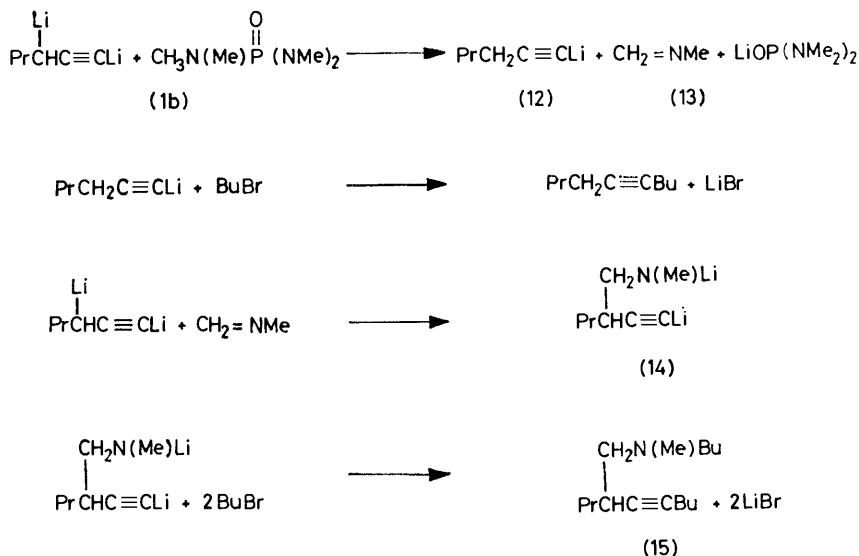
Spectral data for the mixtures of acetylene monocarboxylic acids RCH(CO<sub>2</sub>H)C≡CH and RCH<sub>2</sub>C≡CCO<sub>2</sub>H<sup>a</sup>

R	Raman (ν/cm <sup>-1</sup> )	<sup>1</sup> H N.m.r. (δ p.p.m. from SiMe <sub>4</sub> <sup>b</sup> )	<sup>13</sup> C N.m.r. (δ p.p.m. from SiMe <sub>4</sub> <sup>b</sup> )
C <sub>2</sub> H <sub>5</sub>	2 244 2 129	3.25 (m, CHC≡C), 2.25 (t, CH <sub>2</sub> C≡C), 2.18 (d, C≡CH)	180.41 (>CHCO <sub>2</sub> H), 158.05 (C≡CCO <sub>2</sub> H), 92.14 (C≡CCO <sub>2</sub> H), 72.74, 71.12 (d, C≡CH), 38.23 (d, CHC≡C)
C <sub>3</sub> H <sub>7</sub>	2 243 2 124	3.4 (m, CHC≡C), 2.35 (m, CH <sub>2</sub> C≡C, CC≡H)	179.99 (>CHCO <sub>2</sub> H), 157.96 (C≡CCO <sub>2</sub> H), 91.79 (C≡CCO <sub>2</sub> H), 72.75, 71.80 (d, C≡CH), 37.47 (d, CHC≡C)
C <sub>4</sub> H <sub>9</sub>	2 230 2 115	3.4 (m, CHC≡C), 2.38 (t, CH <sub>2</sub> C≡C), 2.3 (d, CC≡H)	176.65 (>CHCO <sub>2</sub> H), 158.00 (C≡CCO <sub>2</sub> H), 92.42 (C≡CCO <sub>2</sub> H), 72.55, 72.04 (d, C≡CH), 37.74 (d, CHC≡C)

<sup>a</sup> These entries represent mixtures and only the resonances of diagnostic importance have been included. <sup>b</sup> The spectra were measured as CDCl<sub>3</sub> solutions.

phosphoric triamide (HMPT) as a co-solvent in tetrahydrofuran to silylate and alkylate tetralithiopropyne sequentially.<sup>9</sup> Reactions of 1-lithioalk-1-ynes with alkyl halides also occur readily in HMPT.<sup>15</sup> HMPT has also been used in i.r. spectral studies on polyolithiated acetylenes<sup>9,16</sup> and the shift to higher frequencies in the

butylation of the dilithio-intermediate (14) both at the nitrogen and acetylide sites to give the ynamine product (15) (34%) [Scheme 3; (1b)→(12) + (15)]. Dec-5-yne was also isolated from butylation of 1-lithiohex-1-yne (12) formed in the first stage of the reaction. The internal acetylene (15) can be shunted to the end of the



presence of the co-ordinating solvent has been attributed to the solvent co-ordinating to lithium. In view of these results we attempted to accelerate the alkylation of 1,3-dilithiohex-1-yne (1b) with 1-bromobutane by using HMPT as a co-solvent in hexane.

Butylation at the propargylic site did not occur but instead an amine was isolated which results from the decomposition of hexamethylphosphoric triamide to

chain to give (16) (60%) by the isomerisation reaction of Brown.<sup>19</sup> Although hexamethylphosphoric triamide has been successfully used in organolithium reactions to solvate the lithium cation,<sup>20</sup> and less-reactive reagents are stable in this medium, decomposition of the solvent has been previously reported to occur in the presence of *n*-butyl-lithium, *s*-butyl-lithium, and phenyl-lithium.<sup>17</sup>

The implications of the above reaction are that it

should be possible to synthesise branched *N*-substituted alkynamines having a terminal acetylenic group and a secondary amine function using either hexamethylphosphoric triamide or a Schiff's base. Thus reaction of

propargylic site to give *N*-phenyl-2-alkyl-1-phenylbut-3-ynylamine (18; R = Bu<sup>n</sup> and Pr) (*ca.* 50%).

The structures of the ynamines were confirmed by spectral methods (Table 6) with the <sup>13</sup>C n.m.r. spectrum

TABLE 6

B.p.s, yields, and spectral data for alkynamines of the type R <sup>1</sup> R <sup>2</sup> NCH(R <sup>3</sup> )CH(R <sup>4</sup> )C≡CR <sup>5</sup>					
	B.p. (°C/mmHg) [% yield]	I.r. (ν/cm <sup>-1</sup> )	<sup>1</sup> H N.m.r. (p.p.m. from SiMe <sub>4</sub> )	<sup>13</sup> C N.m.r. (p.p.m. from SiMe <sub>4</sub> )	<i>m/e</i>
$\begin{array}{c} \text{CH}_2\text{N}(\text{Me})\text{C}_4\text{H}_9 \\   \\ \text{C}_3\text{H}_7\text{CHC}\equiv\text{C}_4\text{H}_9 \end{array}$	102—104/1.5 [34]	2 780 2 238 (Raman)	2.5—2.05 (m, 10 H, CHC≡CCH <sub>2</sub> , 2 × CH <sub>2</sub> -N N-CH <sub>3</sub> ), 1.4 (m, 12 H, 6 × CH <sub>2</sub> ), 0.9 (m, 9 H) 3 × CH <sub>3</sub> )	82.27, 80.58 (C≡C), 62.52, 57.50 (CH <sub>2</sub> -N-CH <sub>3</sub> ), 42.22 (N-CH <sub>3</sub> ), 35.06, 30.89, 30.03, 29.28, 21.41, 20.09, 19.91, 18.05, 13.43, 13.06	237 [M <sup>+</sup> , 237.2455, C <sub>16</sub> H <sub>31</sub> N requires 237.2454], 194 [M <sup>+</sup> - 43, 194.1906, C <sub>13</sub> H <sub>24</sub> N requires 194.190], 137 (C <sub>10</sub> H <sub>17</sub> , 137.1329, C <sub>10</sub> H <sub>17</sub> requires 137.1329) 237 (M <sup>+</sup> , 237.2458, C <sub>16</sub> H <sub>31</sub> N requires 237.2454), 100 (M <sup>+</sup> - 137, 100.1123, C <sub>8</sub> H <sub>14</sub> N requires 100.1126)
$\begin{array}{c} \text{CH}_2\text{N}(\text{Me})\text{C}_4\text{H}_9 \\   \\ \text{C}_3\text{H}_7\text{CH}(\text{CH}_2)_4\text{C}\equiv\text{CH} \end{array}$	96—98/1.5 [60]	3 310 2 783 2 120	2.5—2.0 (m, 9 H, CH <sub>2</sub> C≡C, 2 × CH <sub>2</sub> -N N-CH <sub>3</sub> ), 1.9 (t, 1 H, C≡CH), 1.3 (m, 15 H 7 × CH <sub>2</sub> , 1 × CH), 0.9 (m, 6 H, 2 × CH <sub>3</sub> )	84.33 (C≡CH), 67.81 (d, C≡CH), 62.65, 58.06 (CH <sub>2</sub> -N-CH <sub>2</sub> ), 42.65 (N-CH <sub>3</sub> ), 35.40, 34.54, 31.61, 29.40, 28.75, 20.43, 19.58, 18.19, 14.21, 13.79	139 (M <sup>+</sup> , 139.1359, C <sub>9</sub> H <sub>17</sub> N requires 139.1360) 82 (M <sup>+</sup> - 57 82.065 88, C <sub>5</sub> H <sub>9</sub> N requires 82.065 67)
$\begin{array}{c} \text{CH}_2\text{NHMe} \\   \\ \text{C}_4\text{H}_9\text{CHC}\equiv\text{CH} \end{array}$	95/60 [40]	3 400 3 300 2 800 2 110	2.6 (m, 3 H, CHC≡C, N- CH <sub>3</sub> ), 2.45 (s, 3 H, N- CH <sub>3</sub> ), 2.08 (d, 1 H, C≡CH) 1.85br (s, 1 H, N-H), 1.4 (m, 6 H, 3 × CH <sub>2</sub> ), 0.9 (t, 3 H, CH <sub>3</sub> )	C-3 (85.65), C-4 (d, 69.52), C-1 (55.35), 35.50 (N-CH <sub>3</sub> ), 31.89, 31.45, C-4' (28.83), C-5' (21.91), C-6' (13.25)	139 (M <sup>+</sup> , 139.1359, C <sub>9</sub> H <sub>17</sub> N requires 139.1360) 82 (M <sup>+</sup> - 57 82.065 88, C <sub>5</sub> H <sub>9</sub> N requires 82.065 67)
$\begin{array}{c} \text{PhCHNHPH} \dagger \\   \\ \text{C}_3\text{H}_7\text{CHC}\equiv\text{CN} \end{array}$	63—65/0.006 [37]	3 400 3 300 2 110 1 600	7.5—6.9 (m, 7 H, aromatic C-H), 6.65—6.45 (m, 3 H, aromatic C-H), 4.5br (s, 1 H, N-H), 4.35 (t, 1 H, CH-N), 2.9—2.75 (m, 1 H, CHC≡C), 2.05 (d, 1 H, C≡CH), 1.5—1.3 (m, 4 H, 2 × CH <sub>2</sub> ), 0.85 (m, 3 H, CH <sub>3</sub> )	130.98—113.22 (aromatic carbons) C-3 (83.80, 83.31), C-4 (d, 72.57), C-1 (d, 59.64), C-2 (d, 40.07; d, 38.15) C-3' (34.78, 33.04), C-4' (20.36), C-5' (13.48)	263 (M <sup>+</sup> , 263.1472, C <sub>19</sub> H <sub>21</sub> N requires 263.1673), 182 (M <sup>+</sup> - C <sub>2</sub> H <sub>7</sub> CHC≡CH, 182.0965, C <sub>13</sub> H <sub>12</sub> N requires 182.0970), 104 (PhN=CH, 104.0503, C <sub>7</sub> H <sub>8</sub> N requires 104.0500)
$\begin{array}{c} \text{PhCHNHPH} \dagger \\   \\ \text{C}_4\text{H}_9\text{CHC}\equiv\text{CH} \end{array}$	77—80/0.006 [54]	3 400 3 300 2 110 1 600	7.4—6.95 (m, 7 H, aromatic C-H), 6.7— 6.45 (m, 3 H, aromatic C-H), 4.38br (t, 2 H, CH- N, N-H), 2.9—2.7 (m, 1 H, CHC≡C), 2.1 (d, 1 H, C≡CH), 1.4 (m, 6 H, 3 × CH <sub>2</sub> ), 0.85 (m, 3 H, CH <sub>3</sub> )	128.85—113.28 (aromatic carbons) C-3 (83.86, 83.37), C-4 (d, 72.56; d, 72.43), C-1 (d, 59.71), C-2 (d, 40.39 d, 38.42), C-3' (32.46, 30, 64), C-4' (29.41), C-5' (22.09), C-6' (13.67)	277 (M <sup>+</sup> , 277.1821, C <sub>21</sub> H <sub>23</sub> N requires 277.1829) 182 (M <sup>+</sup> - C <sub>4</sub> H <sub>9</sub> CHC≡CH, 182.096, C <sub>13</sub> H <sub>12</sub> N requires 182.0970), 104 (PhN=CH, 104.0498, C <sub>7</sub> H <sub>8</sub> N requires 104.0500)

† Additional signals in the <sup>13</sup>C n.m.r. spectra may be attributed to the presence of diastereoisomers.

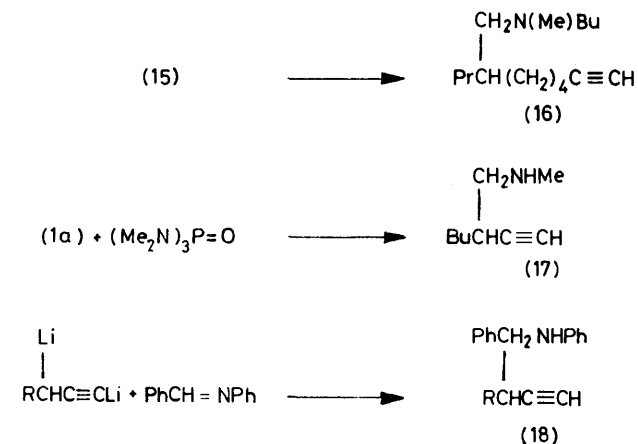
1,3-dilithiohept-1-yne with hexamethylphosphoric triamide followed by protonation gives *N*-methyl-2-butylbut-3-ynylamine (17) (40%). Addition reaction of 1,3-

being diagnostic for the acetylenic, *N*-methyl, and *N*-methylene carbon atoms. These results with imines are in marked contrast to the reactions of 1,3-dilithioacetylides with carbonyl electrophiles where reaction occurs readily at both the acetylide and propargylic positions.

## EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 297 grating spectrophotometer and <sup>1</sup>H n.m.r. spectra with a Perkin-Elmer R32 (90 MHz) instrument. <sup>13</sup>C n.m.r. spectra were recorded on a Varian CFT-20 spectrometer. Low-resolution mass spectra were determined on a A.E.I. MS 12 single focusing spectrometer and accurate mass measurements on a A.E.I. MS 902S instrument. Elemental analysis was performed by Butterworth Laboratories. Dry-column chromatography used Merck Kieselgel G, equilibrated with 10% of the eluting solvent for several hours. M.p.s and b.p.s are uncorrected. All solvents were distilled prior to use and all reactions were performed under argon.

*General Procedure for Dilithiation of Alk-1-ynes.*—To a solution of the alk-1-yne in hexane, *n*-butyl-lithium (2 equiv.) in hexane was added at -20 °C under argon. The



dilithiohex- and -hept-1-ynes with benzylideneaniline confirm that the ambident nucleophile utilizes only the

initial white precipitate of lithium alk-1-ynide slowly dissolved on addition of the second equivalent of *n*-butyllithium to give a light yellow solution. After being stirred for 16–24 h solutions containing hex-1-yne and higher homologues had changed to a red-brown colour. I.r. spectra of these solutions using a 0.5-mm NaCl solution cell showed a strong absorption at  $1\ 850\text{ cm}^{-1}$ . The formation of 1,3-dilithio-pent-1-yne could not be followed by i.r. spectroscopy due to 1,3-dilithio-pent-1-yne (bright yellow precipitate) being insoluble in hexane.

*Reaction of 1,3-Dilithioalk-1-yne with Paraformaldehyde: General Procedure.*—To a hexane solution of 1,3-dilithioalk-1-yne was added a mixture of ether and tetrahydrofuran (3:2). Paraformaldehyde (2.2 equiv.) was then added during 5 min. After being stirred at room temperature for 45 min the solution was then refluxed for 2.5 h. The solution was then cooled and acidified with hydrochloric acid (6M). The organic phase was then separated and the aqueous solution extracted with ether. The combined extracts were then dried ( $\text{MgSO}_4$ ). Removal of solvent followed by distillation gave the corresponding alk-2-yne-1,5-diol and the alk-2-yn-1-ol. Analytical and spectral data are given in Tables 2 and 3.

*Reaction of 1,3-Dilithioalk-1-yne with Cyclic Ketones: General Procedure.*—To a hexane solution of 1,3-dilithioalk-1-yne was added the cyclic ketone (2 equiv.) in ether at  $-20^\circ\text{C}$ . Stirring was continued for 5–18 h at room temperature after which saturated ammonium chloride was added with cooling. The organic phase was then separated and the aqueous solution extracted with ether. The combined extracts were then dried ( $\text{MgSO}_4$ ). Removal of solvent followed by distillation gave a mixture of acetylenic monocyclic alcohols which was analysed by g.c.-m.s. (see Scheme 1). Addition of light petroleum (b.p.  $40\text{--}60^\circ\text{C}$ ) to the residue resulted in the precipitation of a white solid. Recrystallisation [light petroleum (b.p.  $30\text{--}40$ )–ether] gave the alk-2-yne-1,5-diol. Analytical and spectral data are given in Tables 1 and 2 for the dihydric alcohols and Table 3 for the monohydric alcohols.

*Reactions of 1,3-Dilithioalk-1-yne with Carbon Dioxide.*—  
(a) *With a slurry of solid carbon dioxide.* A hexane solution of 1,3-dilithioalk-1-yne was added at  $-80^\circ\text{C}$  to a hexane slurry of solid carbon dioxide (previously washed with tetrahydrofuran). After 1.5–2 h the reaction mixture was acidified with hydrochloric acid (6M). The organic phase was then separated and the aqueous solution extracted with ether. The combined organic phases were combined, washed with brine, and dried ( $\text{MgSO}_4$ ). Removal of solvent followed by dry-column chromatography [toluene–ethyl acetate–acetic acid (80:17:3)] gave two fractions, a mixture of acetylenic mono-acids and the 2-alkyl-2,3-diene-1,5-dioic acid. The mixture of acetylenic mono-acids were esterified with ethereal diazomethane and analysed by g.c.-m.s. (see Scheme 2). Analytical and spectral data for the allene-1,3-dicarboxylic acids are given in Table 4, and for the acetylenic monocarboxylic acids in Table 5.

(b) *With carbon dioxide gas.* Carbon dioxide was bubbled through a hexane solution of 1,3-dilithio-oct-1-yne prepared from oct-1-yne (2.7 g, 0.024 mol) and butyl-lithium (28 ml, 1.9 mol) at  $-40^\circ\text{C}$  for 1 h. The solution was then allowed to rise to  $-20^\circ\text{C}$  and acidified with hydrochloric acid (ca. 6M). The organic phase was then separated and the aqueous phase extracted with ether (3  $\times$  25 ml). The combined extracts were then washed with brine and dried ( $\text{MgSO}_4$ ). Removal of solvent followed by distillation gave

non-2-ynoic acid (1 g, 26%), b.p.  $43\text{--}44^\circ\text{C}/0.005\text{ mmHg}$  (lit.,<sup>21</sup>  $122^\circ\text{C}/2.2\text{ mmHg}$ ).

Light petroleum (b.p.  $30\text{--}40^\circ\text{C}$ ) was added to the residue, resulting in the precipitation of a white solid. Recrystallisation from ether–light petroleum (b.p.  $30\text{--}40^\circ\text{C}$ ) gave 2-pentylpent-2,3-diene-1,5-dioic acid (0.63 g, 13.5%), m.p.  $146\text{--}147^\circ\text{C}$ . Spectral data has been included in Table 4.

*Reaction of 1,3-Dilithiohex-1-yne with Butyl Bromide in the Presence of Hexamethylphosphoric Triamide.*—To a solution of 1,3-dilithiohex-1-yne, prepared from hex-1-yne (5.0 g, 0.06 mol) and butyl-lithium (80 ml, 1.5 mol), was added, with cooling, hexamethylphosphoric triamide (40 ml). After the solution had been stirred for a further 30 min butyl bromide (16.5 g, 0.12 mol) was added and the solution stirred overnight. Water (50 ml) was then added and the mixture extracted with hexane (3  $\times$  50 ml). The combined organic extracts were then washed with water (5  $\times$  100 ml) and dried ( $\text{MgSO}_4$ ). Removal of solvent and distillation gave dec-5-yne (3.2 g, 77%), b.p.  $52^\circ\text{C}/5\text{ mmHg}$  (lit.,  $58^\circ\text{C}/10\text{ mmHg}$ ,<sup>22</sup> and *N*-butyl-*N*-methyl-2-butyl-2-butyl-3-ynylamine (2.4 g, 34%), b.p.  $102\text{--}106^\circ\text{C}/1.5\text{ mmHg}$ . The analytical data has been included in Table 6.

*Reaction of 1,3-Dilithiohept-1-yne with Hexamethylphosphoric Triamide.*—To a hexane solution of hexamethylphosphoric triamide (3.6 g, 0.02 mol) cooled to  $-60^\circ\text{C}$  was added a hexane solution of 1,3-dilithiohept-1-yne prepared from hept-1-yne (2.0 g, 0.02 mol) and butyl-lithium (22 ml, 1.8 mol), during 10 min. The solution was then allowed to warm to room temperature and stirred for a further 3 h after which it was worked up as before. Removal of solvent and distillation gave *N*-methyl-2-butylbut-3-ynylamine (0.55 g, 40%), b.p.  $95/60\text{ mmHg}$ . The analytical and spectral data have been included in Table 6.

*Reaction of 1,3-Dilithioalk-1-ynes with Benzylideneaniline: General Procedure.* To a hexane solution of 1,3-dilithioalk-1-yne, benzylideneaniline (1 equiv.) in hexane was added during 30 min. After being stirred for 24 h the reaction mixture was acidified with hydrochloric acid (6M). The resulting mixture was then vigorously stirred for 30 min and the solution basified with sodium hydroxide. The organic layer was then separated and the aqueous phase extracted with hexane. The combined organic phases were then washed with brine and dried ( $\text{MgSO}_4$ ). Removal of solvent followed by distillation gave the *N*-phenyl-2-alkyl-1-phenylbut-3-ynylamine. For analytical and spectral data see Table 6.

*Reduction of 2-Propylpent-2,3-dienedioic Acid.*—To a solution of 2-propylpent-2,3-dienedioic acid (0.2 g) in methanol, palladium (5% on charcoal) was added. Reduction was carried out in an atmosphere of hydrogen until 2 equiv. of hydrogen had been absorbed. The reaction mixture was then filtered and the solvent removed to leave a white solid. Recrystallisation from ether–light petroleum (b.p.  $30\text{--}40^\circ\text{C}$ ) gave 2-propylpentanedioic acid (0.19 g, 95%), m.p.  $70$  (lit.,<sup>12</sup>  $70^\circ\text{C}$ ),  $\nu_{\text{max}}$  (Nujol)  $3\ 700\text{--}2\ 500$  and  $1\ 710\text{ cm}^{-1}$ ;  $^1\text{H}$  n.m.r. [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  8.1br (s, 2 H,  $2 \times \text{CO}_2\text{H}$ ), 2.5–2.2 (m, 3 H,  $\text{CHCO}_2\text{H}$ ,  $\text{CH}_2\text{CO}_2\text{H}$ ), 1.9 (m, 2 H,  $\text{CH}_2$ ), 1.5 (m, 4 H,  $2 \times \text{CH}_2$ ), and 0.9 (t, 3 H,  $\text{CH}_3$ ).

*Preparation of N-Butyl-N-methyl-2-propylhept-7-ynylamine.*—To a solution of potassium-3-aminopropylamide in 3-aminopropylamine, prepared from potassium amide (potassium, 0.98 g, 0.025 mol) and 3-aminopropylamine (10 ml), was added *N*-butyl-*N*-methyl-2-propyl-2-butyl-3-ynylamine (1.0 g, 0.004 mol). The mixture was heated at  $70^\circ\text{C}$  for 1 h.

After the mixture had been cooled in ice-water, water (50 ml) was added. The aqueous solution was then extracted with hexane (3 × 50 ml) and the combined extracts were then washed with water and brine and dried (MgSO<sub>4</sub>). Removal of solvent followed by bulb distillation gave the title compound (0.6 g, 60%), b.p. 96—98 °C/1.5 mmHg.

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[0/042 Received, 9th January, 1980]

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