

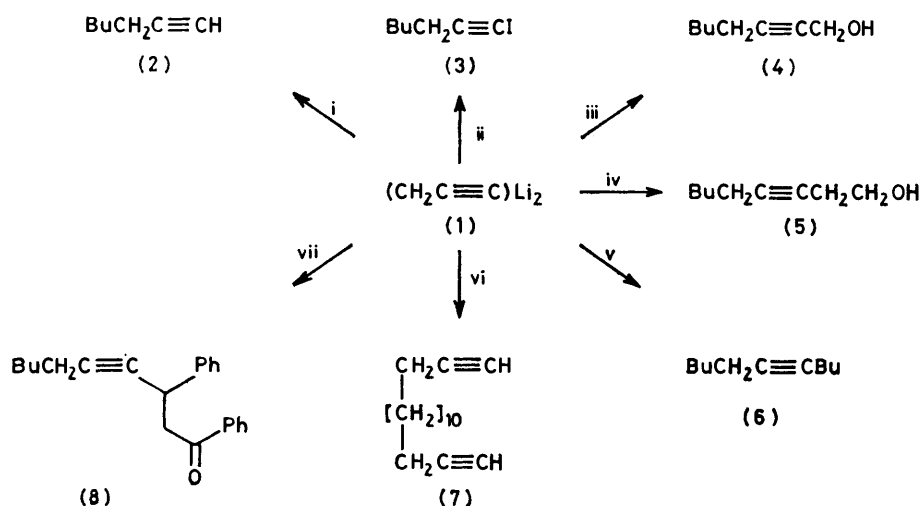
### Chain Extension Reactions of Acetylenes. Part 3.<sup>1</sup> 1,3-Disubstitution Reactions of Propyne, Conjugate Addition Reactions of Acetylides, and Further Reactions of 1,3-Dilithioacetylenes with two Different Electrophiles †

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\* 'One-pot' linear chain extensions at both termini of propyne are described. 1,3-Dilithiopropyne reacts regioselectively first at C-3 with 1-bromobutane then at C-1 with electrophiles such as iodine, benzylideneacetophenone, 1,10-dibromodecane, and 1-bromobutane. Preparations of prop-2-yn-1-ol derivatives are also described.

In previous papers<sup>1,2</sup> the preparation of branched acetylides by 1,3-disubstitution reactions and by alkylations of 1,3-dilithioacetylenes has been described. The studies of Eberly,<sup>3</sup> Jaffe,<sup>4</sup> Klein,<sup>5</sup> West,<sup>6</sup> and Brandsma<sup>7</sup> and their co-workers provide valuable contributions on the preparation, structure, and reactivity of various polythioacetylene intermediates. We now report an

Regiospecific reaction occurs first at the propargylic carbon as demonstrated by the formation of hept-1-yne (2) on addition to butyl bromide in hexane. 'One-pot' linear chain extensions at both termini of propyne can be achieved when alkylation at C-3 is followed by addition of various electrophiles. Thus butylation of 1,3-dilithiopropyne and addition of iodine, formaldehyde,



SCHEME Reagents: i, BuBr,  $\text{H}^+$ ; ii, BuBr,  $\text{I}_2$ ; iii, BuBr,  $(\text{HCHO})_n$ ; iv, BuBr,  $\text{CH}_2=\text{CH}_2$ ; v, BuBr then BuBr in HMPT; vi,  $\text{Br}[\text{CH}_2]_{10}\text{Br}$ ; vii, BuBr, PhCH=CHCOPh

extension of our work to the preparation of linear acetylenes from reactions at both termini of propyne.

Unlike the preparation of longer chain 1,3-dilithioacetylenes, satisfactory dilithiation of propyne required the presence of one equivalent of *NNNN*-tetramethylethylenediamine (TMEDA) to activate the butyllithium. In the presence of the catalyst, dilithiopropyne (1) was formed by passing a slow stream of propyne into a cooled ( $-60^\circ\text{C}$ ), stirred solution of two equivalents of butyl-lithium. Alternatively, 1,3-dilithiopropyne (1) can be generated by addition of butyllithium to a solution of propyne and TMEDA in hexane. The white insoluble monolithio-derivative initially formed immediately reacts further to give a yellow-brown solution or suspension of dilithiopropyne (1) which we have used for reactions with various electrophiles.

ethylene oxide, and butyl bromide give respectively 1-iodohept-1-yne (3), oct-2-yn-1-ol (4), non-3-yn-1-ol (5), and undec-5-yne (6) in good yields (Scheme).

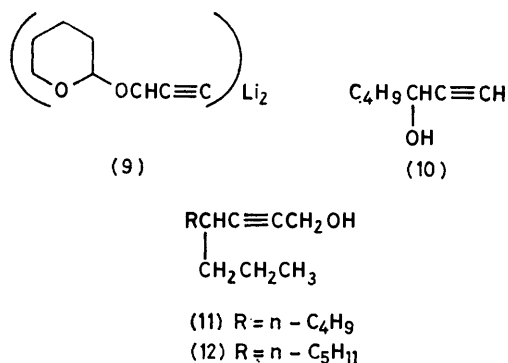
Other linear chain extension reactions to prepare terminal diacetylenes result from reactions of 1,3-dilithiopropyne (1) with  $\alpha,\omega$ -dihalogeno-compounds. Thus reaction of 1,10-dibromodecane gives hexadeca-1,15-diyne (7) (Scheme). This method is an alternative approach to the preparation of terminal diacetylenes to that recently described<sup>8</sup> and provides further synthetic possibilities for chain extension since the intermediate  $\alpha,\omega$ -dilithioacetylenes will also react with electrophiles.

Another approach to chain extension involves utilisation of conjugate addition of diethylalkynylalanes, which are readily obtained by reaction of diethylaluminium chloride with a lithium alk-1-ynide.<sup>9</sup> Thus, 1,4-addition to chalcone of the diethylalane derivatives of phenylacetylene<sup>9</sup> and hept-1-yne gave in each case

† Preliminary communication, S. Bhanu and F. Scheinmann, *J.C.S. Chem. Comm.*, 1975, 817.

good yields of the dihydrochalcones. The adduct (8) could be formed in a 'one-pot' reaction by regiospecific reaction of 1,3-dilithiopropyne with consecutive addition of butyl bromide, diethylaluminum chloride, and chalcone.

In order to prepare acetylenes with a hydroxy group at the propargylic carbon, some preliminary experiments were carried out on the preparation and properties of the dilithio-derivative of the tetrahydropyranyl ether of prop-2-yn-1-ol (9). The reactive intermediate (9) appears as a yellow suspension on addition of two equivalents of butyl-lithium in hexane to prop-2-ynyl tetrahydropyranyl ether and TMEDA. Reaction with butyl bromide followed by attempts to isolate hept-1-yn-3-ol (10) after hydrolysis gave a mixture from which



the product was isolated in low yield; it was characterised as the crystalline 3,5-dinitrobenzoate derivative. Further work is required to establish the course of the reaction and the nature of the by-products.

In contrast to the difficulties in preparing alk-1-yn-3-ols, branched alk-2-yn-1-ols were readily prepared by the regiospecific 'one-pot' reaction of 1,3-dilithioheptane and 1,3-dilithio-octyne with 1-bromopropane and formaldehyde to give 4-propyloct-2-yn-1-ol (11) and 4-propylnon-2-yn-1-ol (12), respectively.<sup>8</sup>

Jaffé<sup>10</sup> has previously reported the preparation of 1,3-lithiopropyne by the dimetallation of allene with two equivalents of butyl-lithium. From a preparative standpoint the use of allene instead of propyne may be superior since in the former case dimetallation is essentially complete and rapid at  $-50^\circ\text{C}$ . Alternatively reaction of geminal dihalogenocyclopropanes with alkyl-lithiums gives 1,3-dilithiopropyne derivatives from allene intermediates;<sup>7</sup> 1-bromopropyne can also be 1,3-dilithiated.<sup>2b</sup> Thus 1,3-dilithiopropyne is an accessible synthon capable of further exploitation in synthesis of acetylenes and their derivatives since it has been postulated that regioselective reactions occur at the softer propargylic position with soft electrophiles<sup>6a</sup> in accord with the concepts of HSAB theory.<sup>11</sup>

#### EXPERIMENTAL

I.r. spectra (for liquid films) were recorded with a Perkin-Elmer 257 grating spectrophotometer and  $^1\text{H}$  n.m.r. spectra with a Varian A-60 instrument. Mass spectra were

measured with an A.E.I. MS 12 spectrometer and accurate mass measurements determined with an MS 902 instrument. G.l.c. analysis was carried out with a Perkin-Elmer 880 gas chromatograph using a 6 ft  $\times$  0.125 in column packed with 11½% silicone oil MS 555 and 11½% Butone 34 on Chromosorb W; column temperature 102 and 180  $^\circ\text{C}$ ;  $\text{N}_2$  carrier gas pressure 16 lb in<sup>-2</sup>. Absolute yields were determined by internal standardisation with n-decane. Preparative g.l.c. was carried out with an Autoprep A-700 instrument, with helium as carrier gas (pressure 60 lb in<sup>-2</sup>).  $^{13}\text{C}$  N.m.r. spectra were measured with a Varian CFT 320 spectrometer; assignments of the chemical shifts follow from off-resonance decoupled spectra and from comparison with calculated data. Calculated values are based on  $\delta(\text{CH}_4) - 2.3$  p.p.m., with incremental values for  $\alpha$ -substituents + 8,  $\beta$ -substituents + 10, and  $\gamma$ -substituents - 2 p.p.m. for saturated carbon atoms. The propargylic carbon of an alk-1-yne is additionally influenced by the adjacent acetylene and ca. 12 p.p.m. is subtracted for good agreement with experimental data.<sup>12</sup> All the reactions were carried out under nitrogen.

*Preparation of 1,3-Dilithiopropyne.*—A known weight of liquid propyne was slowly bubbled through a cooled ( $-60^\circ\text{C}$ ) stirred solution containing butyl-lithium in hexane (2 mol equiv.) and TMEDA (1 mol equiv.). An initial thick precipitate of 1-lithiopropyne soon dissolved to give a pale yellow solution or precipitate of 1,3-dilithiopropyne. Stirring was continued for 1 h and the mixture subsequently treated with various electrophiles.

In an alternative route, 1,3-dilithiopropyne was prepared by adding slowly a solution of butyl-lithium (2 mol equiv.) in hexane to a precooled ( $-60^\circ\text{C}$ ) solution of propyne (1 mol equiv.) and TMEDA (1 mol equiv.). The resulting mixture was stirred for 1 h under nitrogen and then treated with various electrophiles.

*Reactions of 1,3-Dilithiopropyne.*—(a) *With 1-bromobutane.* 1-Bromobutane (3.28 g, 0.026 mol) was added dropwise, with stirring, to a cooled solution ( $-20^\circ\text{C}$ ) of 1,3-dilithiopropyne obtained from propyne (1.03 g, 0.026 mol) and two equivalents of n-butyl-lithium (20 ml; 2.7M) and TMEDA (5.25 g) in hexane-ether. Stirring was continued for 24 h. Addition of hydrochloric acid (5 ml; 6M) and distillation of the dried organic layer gave hept-1-yne (39%), b.p.  $97-98^\circ$  (lit.,<sup>13</sup>  $99.78^\circ$ ) and octane (47.6%), b.p.  $126-128^\circ$  (lit.,<sup>14</sup>  $125.59^\circ$ ) which were identified by g.l.c. peak enhancements with authentic samples.

(b) *With 1-bromobutane and iodine.* In a similar preparation of 1,3-dilithiopropyne followed by reaction with 1-bromobutane, a solution of iodine (6.6 g, 0.0026 mol) in ether (50 ml) was added prior to work-up with water. The product, 1-iodohept-1-yne (2.2 g, 52%), b.p.  $78-80^\circ$  at 12 mmHg (lit.,<sup>15</sup>  $78^\circ$  at 10 mmHg), was obtained by distillation and shown to be identical with an authentic sample. The other products were octane (1.6 g, 30%) and hept-1-yne (15%, identified by g.l.c.).

(c) *With 1-bromobutane and formaldehyde.* 1,3-Dilithiopropyne was prepared by the method described above, from propyne (2.0 g, 0.05 mol) and butyl-lithium in hexane (38 ml; 2.7M) in the presence of TMEDA (10.8 g). This was treated as in (a) with 1-bromobutane in ether (6.3 g, 0.05 mol). Dry ether (200 ml) was then added followed by paraformaldehyde (10.5 g) as a slurry in ether and the mixture was stirred for 24 h. Addition of hydrochloric acid (100 ml, 6M) was followed by further stirring for 24 h to ensure complete hydrolysis. The combined organic

layer was dried ( $\text{MgSO}_4$ ). The solvent was evaporated off and the residue distilled. Oct-2-yn-1-ol (2.5 g, 78%), b.p.  $70^\circ$  at 1 mmHg, was obtained as an oil (lit.,<sup>16</sup>  $98.9^\circ$  at 15 mmHg),  $R_t$  1 min 30 s at  $180^\circ\text{C}$ ;  $\nu_{\text{max}}$  (film)  $3\ 350\ \text{cm}^{-1}$  (—OH) and  $2\ 250\ \text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 4.25 (2 H, d,  $J$  2 Hz, 1- $\text{H}_2$ ), 3.75br (1 H, s, OH), 2.16 (2 H, 4- $\text{H}_2$ ), 1.40 (6 H, m,  $[\text{CH}_2]_3$ ), and 0.85 (3 H, t,  $J$  7 Hz,  $\text{CH}_3$ );  $m/e$  125 ( $M - 1$ )<sup>+</sup> and 95 ( $M - \text{CH}_2\text{OH}$ )<sup>+</sup>;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 85.25 (s, C-3), 79.25 (s, C-2), 50.65 (t, C-1), 31.63 (t, C-6), 28.95 (t, C-5), 22.78 (t, C-7), 19.14 (t, C-4), and 14.25 (q, C-8).

(d) *With 1-bromobutane and ethylene oxide.* 1-Lithiohept-1-yne was prepared *in situ* from propyne (1.03 g, 0.026 mol), butyl-lithium in hexane (20 ml; 2.7M) containing TMEDA (5.25 ml), and 1-bromobutane (3.35 ml, 0.026 mol) as described in (a). To the above solution at  $-70^\circ\text{C}$  was added a precooled ( $-30^\circ\text{C}$ ) solution of commercial ethylene oxide (1.3 g, 0.027 mol) in ether (20 ml) in three portions at intervals of 1 h; stirring was continued for a further 24 h. Work-up with hydrochloric acid (15 ml; 6M) gave a pale yellow organic layer which on drying ( $\text{K}_2\text{CO}_3$ ) and distillation gave non-3-yn-1-ol as a viscous liquid (2.4 g, 66%), b.p.  $120^\circ$  at 15 mmHg (lit.,<sup>17</sup>  $113\text{--}115^\circ$  at 15–20 mmHg). The spectral data were in complete agreement with those reported previously.<sup>17</sup>

(e) *Conjugate addition of the diethylalkynylalane derived from hept-1-yne with benzylideneacetophenone.* The acetylide ion from hept-1-yne was prepared as in (a) from prop-1-yne (1.03 g, 0.026 mol), butyl-lithium in hexane (20 ml; 2.7M), TMEDA (5.25 g), and 1-bromobutane (3.35 g, 0.027 mol). A solution of diethylaluminium chloride (12 ml of 8.1M solution in hexane) was added through a syringe to the mixture at  $0^\circ\text{C}$  and the resultant mixture stirred for 0.5 h. Benzylideneacetophenone (1.2 g) in dry ether (20 ml) was then added and the mixture stirred for 24 h. The aluminium complex was decomposed by pouring onto an excess of ice-concentrated hydrochloric acid. The organic layer was separated, washed, and dried. Evaporation of the solvent left a orange residue which upon bulb-to-bulb distillation gave a yellow liquid, 1,3-diphenyldec-4-yn-1-one (1.08 g, 60%), b.p.  $167\text{--}172^\circ$  at 0.1 mmHg,  $\nu_{\text{max}}$  (film)  $2\ 901$ ,  $2\ 940$ ,  $2\ 970$ ,  $2\ 230$ ,  $1\ 700$ ,  $1\ 610$ ,  $1\ 590$ ,  $750$ , and  $695\ \text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.88 (2 H, s,  $J$  8 Hz, ArH), 7.3 (8 H, m, ArH), 4.4br (1 H, t, H-3), 3.64–3.00 (2 H, m, H-2), 2.08br (2 H, t, H-6), 1.04 (6 H, m, H-7, -8, and -9), and 0.80br (3 H, t, H-10);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 196.16 (s, C-1), 142.23, 137.10, 132.81, 128.44, 127.68, and 126.82 ( $2 \times \text{Ph}$ ), 83.26 and 81.67 (s, C-4 and -5), 47.51 (t, C-2), 33.44 (d, C-3), 31.02 (t, C-8), 28.69 (t, C-7), 22.24 (t, C-9), 18.80 (t, C-6), and 14.03 (q, C-10).

Accurate mass		Found	Requires
$\text{C}_{22}\text{H}_{24}\text{O}^+$	$M^{++}$	304.1831	304.1827
$\text{C}_{17}\text{H}_{13}\text{O}^+$	$(M - \text{C}_5\text{H}_{11})^+$	233.0957	233.0966
$\text{C}_{14}\text{H}_{16}^+$	$(M - \text{PhCOCH}_3)^+$	184.1246	184.1252

(f) *With 1,10-dibromodecane.* To a stirred solution of 1,3-dilithio-propyne [from propyne (1.03 g, 0.026 mol), butyl-lithium in hexane (20 ml; 2.7M), TMEDA (5.25 g)] at  $-30^\circ\text{C}$ , a solution of 1,10-dibromodecane (7.8 g, 0.026 mol) in ether (25 ml) was added over 1 h. The mixture was stirred for a further 24 h, then worked up by adding hydrochloric acid (10–15 ml; 6M). The dried organic layer was concentrated and the resulting thick oil soon solidified to a solid. Crystallisation from aqueous methanol yielded needles of hexadeca-1,15-diyne (3.8 g, 66%), m.p.  $44\text{--}45^\circ$

(lit.,<sup>8</sup>  $44^\circ$ ) (Found: C, 87.6; H, 12.3. Calc. for  $\text{C}_{16}\text{H}_{26}$ : C, 88.05; H, 11.9%);  $\nu_{\text{max}}$  (Nujol)  $3\ 300\ \text{cm}^{-1}$  ( $\text{C}\equiv\text{H}$ ) and  $2\ 150\ \text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.15 (m,  $2 \times \text{CH}_2\text{C}\equiv\text{C}$ ), 1.90 (t,  $J$  2 Hz,  $\equiv\text{CH}$ ), and 1.25 (m,  $5 \times \text{CH}_2$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 84.57 (s, C-2 and -15), 68.15 (d, C-1, and -16), 29.58–28.81 (m, C-4 to C-13), and 18.46 (t, C-3 and -14);  $M^+$  not observed but significant peaks due to propargylic cleavage at  $m/e$  39 and higher homologues,  $m/e$  53, 67, 81, and 59.

(g) *With 1-bromobutane in ether and in hexamethylphosphoric triamide.* To a stirred solution of 1,3-dilithio-propyne [from propyne (1.03 g, 0.026 mol), butyl-lithium in hexane (20 ml; 2.7M), and TMEDA (5.25 g)] at  $-20^\circ\text{C}$ , a solution of freshly distilled 1-bromobutane (3.25 g, 0.026 mol) in ether (10 ml) was added. Stirring was continued for 6 h. Dry hexamethylphosphoric triamide (20 ml) was added to the mixture and a further quantity of 1-bromobutane (3.25 g, 0.026 mol) added at  $-20^\circ\text{C}$ . The mixture was allowed to warm to room temperature and stirred overnight. After addition of water crude undec-5-yne was obtained as a yellow oil from the organic layer. Distillation gave undec-5-yne (0.99 g, 30%) as a liquid, b.p.  $78\text{--}80^\circ$  at 13 mmHg. The spectral data were in complete agreement with the data reported previously.<sup>1</sup>

*3-Propyloct-1-yne.*—The dilithio derivative of oct-1-yne was prepared as follows. A solution of *n*-butyl-lithium (2.2M; 30 ml) was syringed into a rapidly stirred suspension of oct-1-yne (3.30 g, 0.03 mol) in hexane at  $-60^\circ\text{C}$ . An initial white suspension due to the formation of lithio-octyne soon dissolved to give a clear yellow solution containing the dilithio-octyne. Freshly distilled 1-bromopropane (3.69 g, 0.03 mol) was then added with cooling ( $-30^\circ\text{C}$ ) and the stirring continued for 24 h at room temperature. Work-up with hydrochloric acid (6M; 30 ml) in the usual manner gave a light yellow liquid which upon distillation using a 40 cm Vigreux column gave 3-propyloct-1-yne as a viscous liquid (6.8 g, 71%), b.p.  $60\text{--}62^\circ$  at 12 mmHg;  $R_t$  3 min 42 s at  $100^\circ\text{C}$ ;  $n_D^{20,50}$  1.439 5;  $\nu_{\text{max}}$  (film)  $3\ 350$  ( $\text{C}\equiv\text{H}$ ) and  $2\ 150\ \text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ),  $\delta_{\text{H}}$  ( $\text{CCl}_4$ ) 2.24 (m, CH), 1.85 (d,  $\equiv\text{CH}$ ), 1.41 (m,  $6 \times \text{CH}_2$ ), and 0.82 (t,  $2 \times \text{CH}_3$ );  $m/e$  109 [ $(M - \text{C}_3\text{H}_7)^+$ , 20%], 81 [ $(M - \text{C}_5\text{H}_{11})^+$ , 75], 68 [ $(\text{C}_5\text{H}_8)^+$ , 40], and 43 [ $(\text{C}_3\text{H}_7)^+$ , 100];  $\delta_{\text{C}}$  (neat) 87.32 (s, C-2), 69.52 (s, C-1), 37.82 (t, C-1' and -4), 35.62 (d, C-3), 31.76 (t, C-6), 27.44 (t, C-5), 22.96 (t, C-7), 20.76 (t, C-2'), and 14.18 (q, C-3' and -8).

*4-Propylnon-2-yn-1-ol.*—The acetylide ion from 3-propyloct-1-yne was prepared *in situ* by the reaction of oct-1-yne (3.0 g, 0.027 3 mol) with a 2 mol equiv. of butyl-lithium (2.2M; 28 ml) by the usual procedure, followed by the addition of freshly distilled 1-bromopentane (3.36 g, 0.027 3 mol). To the mixture was added dry tetrahydrofuran (25 ml) followed by paraformaldehyde (4.5 g) as a slurry in tetrahydrofuran. Work-up was performed as for 4-propyloct-2-yn-1-ol. 4-Propylnon-2-yn-1-ol (2.65 g, 58%) was obtained as a liquid, b.p.  $58\text{--}59^\circ$  at 0.5 mmHg;  $n_D^{20}$

Accurate mass		Found	Calc.
$(M - 1)^+$	$\text{C}_{12}\text{H}_{21}\text{O}^+$	181.1589	181.191
$(M - \text{CH}_2\text{OH})^+$	$\text{C}_{11}\text{H}_{19}^+$	151.1487	151.1487
$(M - \text{C}_3\text{H}_7)^+$	$\text{C}_8\text{H}_{15}\text{O}^+$	139.1121	139.1123
$(M - \text{C}_5\text{H}_{11})^+$	$\text{C}_7\text{H}_{13}\text{O}^+$	111.0809	111.0810
	$\text{C}_6\text{H}_{13}^+$	109.1010	109.1017
	$\text{C}_7\text{H}_{11}^+$	95.086 63	95.086 07

1.485 4;  $R_t$  3 min 55 s at  $180^\circ\text{C}$ ;  $\nu_{\text{max}}$  (film)  $3\ 340$  (O—H) and  $2\ 255\ \text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 4.26 (d,  $J$  2.5 Hz,  $\text{CH}_2\text{OH}$ ), 3.65br (s, OH), 2.34br (m, —CH), 1.43 (m,  $6 \times \text{CH}_2$ ), and

0.88 (t,  $2 \times \text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  89.36 (s, C-3), 79.78 (s, C-2), 50.98 (t, C-1), 37.51 (t, C-1'), 36.89 (t, C-5), 35.05 (t, C-7), 31.72 (d, C-4), 29.77 (t, C-6), 22.76 (t, C-8), 20.69 (t, C-2'), and 14.05 (q, C-3' and -9).

**4-Propyloct-2-yn-1-ol.**—To a rapidly stirred suspension of 1,3-dilithioheptyne in hexane prepared from hept-1-yne (2.88 g, 0.03 mol) and n-butyl-lithium in hexane (2.5M; 30 ml) in the usual manner was added freshly distilled 1-bromopentane (3.72 g, 0.03 mol), and the resulting light yellow slurry was stirred at room temperature for 12 h. Diethyl ether (50 ml) was added followed by paraformaldehyde (4.5 g) as a slurry in ether and the stirring was continued for a further 24 h. The formaldehyde trimer was hydrolysed by rapid stirring with 6M-hydrochloric acid for 6 h. The organic layer was washed with water and dried ( $\text{MgSO}_4$ ). Evaporation of the solvent and distillation of the residue with a 30 cm Vigreux column gave 4-propyloct-2-yn-1-ol (3.0 g, 60%), b.p. 51–52° at 0.5 mmHg, as a colourless liquid,  $n_{\text{D}}^{20}$  1.478 6;  $R_i$  3 min 30 s at 180 °C;  $\nu_{\text{max}}$  (film) 3 350 (O–H) and 2 250  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  4.25 (d,  $J$  2.3 Hz,  $\text{CH}_2\text{OH}$ ), 3.63br (s, OH), 2.32br (m, CH), 1.42 (m,  $5 \times \text{CH}_2$ ), and 0.86 (t,  $2 \times \text{CH}_3$ );  $\delta_{\text{H}}(\text{CDCl}_3)$  88.45 (s, C-3), 80.56 (s, C-2), 50.60 (t, C-1), 37.89 (t, C-1'),

Accurate mass		Found	Calc.
$M^+$	$\text{C}_{11}\text{H}_{20}\text{O}^+$	168.1499	168.1514
$(M - 1)^+$	$\text{C}_{11}\text{H}_{19}\text{O}^+$	167.1436	167.1436
$(M - \text{CH}_2\text{OH})^+$	$\text{C}_{10}\text{H}_{17}^+$	137.1320	137.1330
$(M - \text{C}_3\text{H}_7)^+$	$\text{C}_8\text{H}_{13}\text{O}^+$	125.0959	125.0966
$(M - \text{C}_4\text{H}_9)^+$	$\text{C}_7\text{H}_{11}\text{O}^+$	111.0809	111.0810
	$\text{C}_8\text{H}_{13}^+$	109.1019	109.1017
	$\text{C}_7\text{H}_{11}^+$	95.085 93	95.086 07

35.36 (t, C-5), 31.94 (g, C-4), 29.98 (t, C-6), 22.96 (t, C-7), 20.88 (t, C-2'), and 14.15 (q, C-3' and -8).

We thank the Commonwealth Scholarship Commission for an award (to S. B.) and the J. A. Pye No. 1 Charitable Trust for a grant to purchase equipment.

[8/340 Received, 27th February, 1978]

## REFERENCES

- Part 2, S. Bhanu, E. A. Khan, and F. Scheinmann, *J.C.S. Perkin I*, 1976, 1609.
- (a) A. J. G. Sagar and F. Scheinmann, *Synthesis*, 1976, 321; (b) A. J. Quillinan, E. A. Khan, and F. Scheinmann, *J.C.S. Chem. Comm.*, 1974, 1030.
- K. C. Eberly and H. E. Adams, *J. Organometallic Chem.*, 1965, **3**, 165.
- F. Jaffe, *J. Organometallic Chem.*, 1970, **23**, 53.
- E. g. J. Klein and J. Y. Becker, *Tetrahedron*, 1972, **28**, 5385; J. Y. Becker, S. Brenner, and J. Klein, *Israel J. Chem.*, 1972, **10**, 827; J. Klein and S. Brenner, *Tetrahedron*, 1970, **26**, 2345; *J. Amer. Chem. Soc.*, 1969, **91**, 3094, and other papers in the series.
- (a) W. Priester and R. West, *J. Amer. Chem. Soc.*, 1976, **98**, 8421, 8426; (b) W. Priester, R. West, and T. L. Chwang, *ibid.*, p. 8413 and previous papers in the series.
- L. Brandsma and E. Mugge, *Rec. Trav. chim.*, 1973, **92**, 628.
- W. Beckmann, G. Doerjer, E. Logemann, C. Merkel, G. Schill, and C. Zurcher, *Synthesis*, 1975, 423.
- J. Hooz and R. B. Layton, *J. Amer. Chem. Soc.*, 1971, **93**, 7320.
- A. J. G. Sagar, M.Sc. Thesis, University of Salford, 1975.
- R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.
- G. C. Levy and G. L. Nelson, 'C-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972, p. 71.
- A. L. Henne and K. W. Greenleel, *J. Amer. Chem. Soc.*, 1945, **67**, 484.
- A. F. Shepard, A. L. Henne, and T. Midgely, jun., *J. Amer. Chem. Soc.*, 1931, **53**, 1949.
- L. Brandsma, 'Preparative Acetylenic Chemistry,' Elsevier, Amsterdam, London and New York, 1971, p. 99.
- M. de Gaudermaris and P. Arnaud, *Bull. Soc. chim. France*, 1962, 315.
- R. W. Bradshaw, A. C. Day, E. R. H. Jones, C. B. Page, V. Thaller, and R. A. Vere Hodge, *J. Chem. Soc. (C)*, 1971, 1156.