

## 200. *The Application of Lithium Alkynyls in the Synthesis of Long-chain Dialkylacetylenes.*

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The *n*-octadecynes have been synthesised in good yields and high purity, by metathetical reactions in liquid ammonia or dioxan, involving the appropriate lithium alkynyls and *n*-alkyl bromides. Further syntheses, of *n*-tricos-4-yne, *n*-octacos-9-yne, *n*-dotriacont-16-yne, and *n*-hexatriacont-17-yne, demonstrate that this method has wide application for the synthesis of dialkylacetylenes. An improved method for the preparation of lithium alkynyls is described, together with two modifications of the general method of synthesis of monoalkylacetylenes.

SEVERAL symmetrical dialkylacetylenes of low molecular weight have been prepared in good yield by Bried and Hennion (*J. Amer. Chem. Soc.*, 1937, **59**, 1310), who employed the simultaneous reaction in liquid ammonia between two mols. each of the appropriate *n*-alkyl bromides and one mol. each of sodium acetylide and sodamide. Later, however, they reported that the method was limited definitely to alkyl halides of small molecular weight and appreciable solubility in liquid ammonia. In the case of *n*-octyl bromide, for example, the yield of dialkylacetylene obtained under the best conditions was only 27%. These results have been confirmed during the present investigation.

We believed, however, that the diminished yields obtained from *n*-alkyl bromides of higher molecular weight were not entirely caused by their lower solubility but were more probably dependent largely on the lower solubility in liquid ammonia of the intermediate sodium alkynyls. Accordingly, the possibilities of using either a more suitable solvent, or a more soluble metal derivative, were investigated. The former approach failed since the sodium alkynyls were found to be only slightly soluble in the solvents investigated. With respect to the alternative, a literature survey revealed that the lithium alkynyls had not been extensively studied and we noted that, in general, the organometallic compounds of the first members of the metals in the same period exhibit certain abnormalities, particularly as regards solubility. Lithium alkynyls were found not only to be much more soluble in liquid ammonia than the sodium compounds, but also to be considerably more reactive. Following the procedure of Bried and Hennion (*loc. cit.*), *n*-octadec-9-yne was obtained in 60% yield from *n*-octyl bromide, lithium acetylide, and lithium amide in liquid ammonia.

This result led us to apply the reaction to syntheses of the unsymmetrical *n*-octadecynes (the 3-, 4-, 5-, 6-, 7-, and 8-isomers), which were obtained in yields of 78, 62, 52, 76, 76, and 67%, respectively. These syntheses were conducted conveniently on a 0.2 g.-mol. scale employing the normal two-stage method. The shorter alkyl group was substituted first by the method originally due to Lebeau and Picon (*Compt. rend.*, 1913, **156**, 1077), which has been used extensively by Vaughn, Vogt, Hennion, and Nieuwland (*J. Org. Chem.*, 1937, **2**, 1), and the lithium derivatives of these monoalkylacetylenes (but-1-yne, *n*-pent-1-yne, *n*-hex-1-yne, *n*-hept-1-yne, *n*-oct-1-yne, and *n*-non-1-yne) were then condensed with the appropriate *n*-alkyl bromides in liquid ammonia at room temperature.

The use of liquid ammonia as solvent for such metathetical reactions has many inherent disadvantages, the most obvious being manipulation. Attention was again directed, therefore, to the possible substitution of an alternative solvent. The lithium alkynyls, in marked contrast to the sodium alkynyls, were found to be freely soluble in anhydrous dioxan. Unfortunately, however, although it was possible to conduct these reactions in this solvent, the use of liquid ammonia solutions of lithium amide for the preparation of these lithium alkynyls was still necessary, and a means of obviating this also was sought.

The possibility of employing the diacetylenylmercury compounds  $(R \cdot C \equiv C)_2Hg$  in the synthesis of acetylenic compounds had always been considered attractive and appeared even more promising when it was found that such derivatives were very soluble in dioxan. These compounds are easily prepared from monoalkylacetylenes by Johnson and McEwan's method (*J. Amer. Chem. Soc.*, 1926, **48**, 469). When their solutions in dioxan were heated with lithium metal under nitrogen or in an autoclave, almost quantitative formation of the corresponding lithium alkynyls resulted, and mercury was liberated (cf. the early preparations of sodium and lithium alkyls by Schlenk and Holtz, *Ber.*, 1917, **50**, 262). In this way lithium alkynyls could be prepared without the use of either elaborate apparatus or liquid ammonia solutions of lithium amide. The method has the following advantages: (1) undesirable side-reactions, such as the formation of alkylamines, are eliminated; (2) unchanged monoalkylacetylenes can be recovered from the crude reaction products as their mercury derivatives (normal purification process), and subsequently used again; and (3) the monoalkylacetylenes can be brought into reaction in a very high degree of purity as their mercury derivatives, since these, unlike the free acetylenes, are not subject to autoxidation.

This modified method gave a 62% yield of *n*-octadec-2-yne, the intermediate *n*-heptadec-1-ynyl-lithium being prepared from di-*n*-heptadec-1-ynylmercury and treated (at 110° in an autoclave) with methyl sulphate. *n*-Octadec-4-yne (50%) and *n*-octadec-6-yne (54%) were similarly obtained from the appropriate mercury compounds and alkyl bromides under nitrogen in boiling dioxan.

Previously, the limit of application of sodium alkynyls with respect to the molecular weight of the intermediates involved had not been clearly defined. Therefore, several dialkylacetylenes of much higher molecular weight were synthesised. The yields decreased considerably with increasing molecular weight but, in view of the size of the alkyl groups involved, may still be considered practicable in comparison with those obtained by other methods. The following were synthesised: *n*-tricos-4-yne (54%, in liquid ammonia); *n*-octacos-9-yne (32%, in anhydrous dioxan); *n*-dotriacont-16-yne (34%, in dioxan by the mercury-lithium exchange reaction); and *n*-hexatriacont-17-yne (15% and 16%, in liquid ammonia and dioxan, respectively). Various modes of formation of the lithium alkynyls were employed in these syntheses.

The twelve monoalkylacetylenes required in this work, including *n*-octadec-1-yne, were prepared from sodium acetylide and the appropriate *n*-alkyl bromides in liquid ammonia. The procedures, but for two modifications, were those given by Nieuwland *et al.* (*loc. cit.*). These modifications were (1) the speedy formation of sodium acetylide in simple apparatus at -55° to -60°, at which temperature acetylene is considerably more soluble in solutions of sodium in liquid ammonia, and (2) the use of a 50% excess of sodium acetylide which minimised the formation of basic by-products. All of the  $C_{2-8}$  homologues were prepared in an autoclave at room temperature.

Although *n*-hexadec-1-yne had been obtained in good yield by the above method, it was also prepared from cetyl alcohol. Dehydration of the alcohol over alumina at 350° (Roberti, Minervini, and Berti, *Energia Termica*, 1941, 582; *Chem. Abs.*, 1942, **36**, 5767) yielded an impure mixture of *n*-hexadecenes which, on treatment with bromine and then with potassium hydroxide in boiling *n*-butanol, gave mixed *n*-hexadecynes containing none of the 1-isomer. Freshly prepared sodamide at 160—190° effected a 65% isomerisation of this mixture to the 1-isomer. The overall yield was of the order of 15% only.

Final purification of the liquid *n*-octadecynes was attempted by fractional distillation at low pressure in a still modelled on that described by Dixon (*J. Soc. Chem. Ind.*, 1949, **68**, 299). However, extensive decomposition occurred, mainly owing to polymerisation and oxidation caused by the long heating and presence of air in the distillation apparatus, although much polymerisation still occurred during distillation under nitrogen. Traces of *n*-octadecan-9-one were isolated from the residue after attempted fractionation of *n*-octadec-9-yne at 25 mm. in air, probably owing to vapour-phase hydration of the acetylene by atmospheric moisture, catalysed by the Nichrome-gauze packing of the still. No ketone could be detected when the distillation was attempted under dry nitrogen.

Purification by fractional crystallisation from acetone at low temperatures was satisfactory. The apparatus employed was a modification of that described by J. C. Smith (*J.*, 1939, 944). The purified hydrocarbons, pending the determination of their physical constants, were stored in evacuated ampoules.

We are indebted to Dr. H. W. Thompson, F.R.S., and Mr. D. C. McKean (Department of Physical Chemistry, Oxford University) for the determination of the infra-red absorption spectra of the *n*-octadecyne series. They report that the triple-bond stretching frequency (at 2128  $cm^{-1}$ )

was appreciably intense only in *n*-octadec-1-yne. Octadec-1-yne is readily recognised by the H-C≡ and -C≡C- stretching vibrations at 3315 and 2128 cm.<sup>-1</sup>, characteristic of monoalkylacetylenes. The spectra of the remaining members of the series show small but definite variations in frequency and intensity in the region 1500—700 cm.<sup>-1</sup> which enable them to be distinguished from each other. Other bands at 2223, 1720, and 1680 cm.<sup>-1</sup> in certain of the samples which were left exposed to air, indicated the presence of small quantities of oxidation products, one of which was probably an  $\alpha$ -acetylenic ketone.

These *n*-octadecynes were required as intermediates in an investigation of the *n*-octadecenes, the preparation of which will be reported later.

## EXPERIMENTAL.

(Analyses are by Mr. F. C. Hall, and Drs. Weiler and Strauss, Oxford. M. p.s and f. p.s below -10° were determined with pentane-in-glass thermometers; those between -10° and +30° were determined with Anschütz thermometers. All m. p.s above 30°, and all b. p.s were determined with mercury-in-glass thermometers, and are uncorrected.)

*Monoalkylacetylenes.—General.* Monoalkylacetylenes used as intermediates were synthesised from the appropriate *n*-alkyl bromides (except in the case of *n*-hept-1-yne, where *n*-amyl chloride was employed) and sodium acetylide (50% excess) in liquid ammonia. The C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> homologues were prepared under atmospheric pressure at -34°, all others in an autoclave at normal temperature. The transference of the liquid ammonia reaction mixtures to the autoclave was best carried out after precooling of the autoclave with liquid air. The yields and physical constants are recorded in the Table.

	Yields, %.	Present work.			Literature.		
		M. p.	B. p., mm.	$n_D^{20}$	M. p.	B. p., mm.	$n_D^{20}$
Pent-1-yne .....	65.0	—	40.2°/763	1.3865	—	39.7°/760	1.3860
Hex-1-yne .....	67.2	—	70.5°/758	1.3993	—	71.0°/760	1.3990
Hept-1-yne .....	35.0	—	98.6°/758	1.4086	—	99.6°/760	1.4083
Oct-1-yne .....	65.5	—	124.5°/757	1.4168	—	126.0°/760	1.4169
Non-1-yne .....	79.0	—	48.5°/17	1.4224	—	151.0°/760	1.4230
Dec-1-yne .....	82.0	—	170.5°/761	1.4269	?	?	?
Tridec-1-yne ...	86.6	2.5°	130.0°/30	1.4374	—	—	—
Pentadec-1-yne	79.0	15.0	158.0°/30	1.4422	*	*	*
Hexadec-1-yne	86.0	14.8	144.0°/10	1.4444	15.0°	155.0°/15	—
Heptadec-1-yne	82.6	26.0	171.0°/17	1.4421 †	—	—	—
Octadec-1-yne	74.0	28.0	175—177°/13	1.4440 †	28.0	180.0°/15	—

? = No reliable data recorded. \* = Ryden, Glavis, and Marvell (*J. Amer. Chem. Soc.*, 1937, 59, 1014) give b. p. 112—113°/5 mm.,  $n_D^{20}$  1.4410, for an apparently impure specimen. † At 30°. Literature values are taken from Egloff, "Physical Constants of Hydrocarbons," Vol. I.

*n*-Tridec-1-yne. A rapid stream of pure dry acetylene was passed into solution of sodium (8.6 g., 0.325 g.-atom) in liquid ammonia (500 c.c.), the solution being kept at -55° to -60° by means of ethanol-soluble carbon dioxide. A stainless-steel autoclave (750 c.c.) was meanwhile chilled by the addition of liquid air. *n*-Undecyl bromide (59 g., 0.25 mole; b. p. 132°/10 mm.;  $n_D^{20}$  1.4570) and the sodium acetylide solution were added to the autoclave, which was immediately sealed. The reaction was allowed to proceed at room-temperature for 24 hours, the autoclave being agitated by means of an eccentric. After venting of the ammonia *via* the needle-valve, crushed ice (300 g.) was added to the product to decompose any unchanged sodium acetylide. The crude hydrocarbon, in ether, was repeatedly washed with dilute hydrochloric acid (6%) to remove basic contaminants, before being dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the ether, followed by a preliminary distillation, yielded *n*-tridec-1-yne (42 g.) as a colourless liquid, fractionation (Dufton spiral column) of which gave the pure hydrocarbon (39 g., 86.6%) (Found: C, 86.5; H, 13.4. C<sub>13</sub>H<sub>24</sub> requires C, 86.7; H, 13.6%). The derived mercury compound crystallised from benzene as colourless needles of m. p. 87—88°.

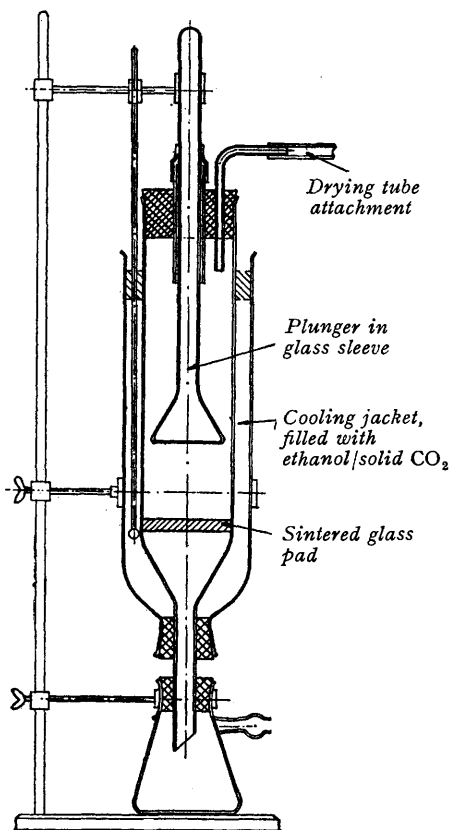
*n*-Heptadec-1-yne. *n*-Pentadecyl bromide (b. p. 184°/15 mm., f. p. 17.9°,  $n_D^{20}$  1.4612) was prepared from the alcohol in 81.5% yield by the method of Reid, Ruhoff, and Burnett (*Org. Synth.*, Coll. Vol. II, 1944, p. 246). The bromide (146 g., 0.502 mole), on treatment with sodium acetylide (from sodium, 17.5 g., 0.762 g.-atom) as above, yielded crude *n*-heptadec-1-yne as a golden-yellow oil which solidified when kept. Crystallisation from ethanol, following decolorisation with charcoal, gave the pure hydrocarbon (97.5 g., 82.6%) as large lustrous plates (Found: C, 86.6; H, 13.4. C<sub>17</sub>H<sub>32</sub> requires C, 86.4; H, 13.6%).

*n*-Octadecynes.—*n*-Octadec-9-yne. Interaction of *n*-octyl bromide (77 g., 0.4 mole), lithium acetylide, and lithium amide (both from lithium, 1.4 g., 0.2 g.-atom, in 250 c.c. of liquid ammonia), in an autoclave, followed by fractional distillation of the crude product obtained after 24 hours, yielded *n*-octadec-9-yne (30 g., 60%) and *n*-dec-1-yne (11.4 g., 41%). The hydrocarbon, after purification by fractional crystallisation from acetone at low temperature, had b. p. 179°/17 mm., m. p. -0.4°, f. p. -0.3°,  $n_D^{20}$  1.4503,  $n_D^{25}$  1.4458,  $d_4^{20}$  0.8040, and  $d_4^{25}$  0.7950 (the technique of low-temperature crystallisation from acetone is described later) (Found: C, 86.4; H, 13.5. Calc. for C<sub>18</sub>H<sub>34</sub>: C, 86.4; H, 13.6%). Bried and Hennion (*loc. cit.*) record b. p. 163—164°/7 mm. and  $n_D^{25}$  1.4488.

*n*-Octadec-8-yne. *n*-Nonyl bromide (27 g., 0.13 mole) and *n*-non-1-yne (17 g., 0.137 mole) in liquid ammonia (500 c.c.) containing lithium amide (from lithium 1 g., 0.144 g.-atom) similarly gave, after fractionation at 18 mm., *n*-non-1-yne (2 g.; b. p. 48°) and *n*-octadec-8-yne (23 g., 67%), which, after

low-temperature crystallisation, had b. p. 167—168°/11 mm., m. p. -2.5°, f. p. -2.4°,  $n_D^{20}$  1.4505,  $n_D^{25}$  1.4451,  $d_4^{20}$  0.8054, and  $d_4^{25}$  0.7957 (Found: C, 86.7; H, 13.3.  $C_{18}H_{34}$  requires C, 86.4; H, 13.6%).

Similarly were prepared: *n*-octadec-7-yne, (19 g., 76%), b. p. 169°/11 mm., m. p. -9.2°, f. p. -9.0°,  $n_D^{20}$  1.4504,  $n_D^{25}$  1.4447,  $d_4^{20}$  0.8043, and  $d_4^{25}$  0.7938 (Found: C, 86.5; H, 13.5.  $C_{18}H_{34}$  requires C, 86.4; H, 13.6%), from *n*-oct-1-yne (11 g., 0.1 mole), *n*-decyl bromide (23 g., 0.104 mole) and lithium amide (from lithium 0.8 g., 0.115 g.-atom), in liquid ammonia (500 c.c.); *n*-octadec-6-yne (38 g., 76%), b. p. 164°/9 mm., m. p. -1.4°, f. p. -1.4°,  $n_D^{20}$  1.4508,  $n_D^{25}$  1.4451,  $d_4^{20}$  0.8089, and  $d_4^{25}$  0.7984 (Found: C, 86.6; H, 13.6%), from *n*-undecyl bromide (47 g., 0.2 mole), *n*-hept-1-yne (19.5 g., 0.203 mole) and lithium amide (from lithium 1.6 g., 0.23 g.-atom) in liquid ammonia (500 c.c.); *n*-octadec-5-yne (26 g., 52%), b. p. 168—169°/11 mm., m. p. -7.8°, f. p. -7.8°,  $n_D^{20}$  1.4499,  $n_D^{25}$  1.4442,  $d_4^{20}$  0.8036, and  $d_4^{25}$  0.7939 (Found: C, 88.6; H, 13.8%), from *n*-dodecyl bromide (50 g., 0.2 mole) and *n*-hex-1-yne (17 g., 0.207 mole) in liquid ammonia (500 c.c.) containing the requisite amount of lithium amide (from lithium 1.6 g., 0.23 g.-atom); *n*-octadec-4-yne (31 g., 62%), b. p. 169—170°/12 mm., m. p. 3.7°, f. p. 3.8°,  $n_D^{20}$  1.4510,  $n_D^{25}$  1.4453,  $d_4^{20}$  0.8078,  $d_4^{25}$  0.7973 (Found: C, 86.4; H, 13.5%), by reaction, in liquid ammonia (500 c.c.) containing lithium amide (from lithium 1.6 g., 0.23 g.-atom), between *n*-tridecyl bromide (53 g., 0.2 mole) and *n*-pent-1-yne (14 g., 0.206 mole); and *n*-octadec-3-yne, b. p. 193.5°/25 mm., m. p. 2.4°, f. p. 2.2°,  $n_D^{20}$  1.4492,  $n_D^{25}$  1.4436,  $d_4^{20}$  0.8049, and  $d_4^{25}$  0.7944 (78%, 39 g.) (Found: C, 86.3; H, 13.5%), from but-1-yne (16 g., 0.296 mole; weighed in a small Dewar flask) and *n*-tetradecyl bromide (55.4 g., 0.2 mole) in a liquid ammonia solution of lithium amide (from lithium 1.6 g., 0.23 g.-atom).



Low-temperature crystallisation apparatus.

*n*-Octadec-2-yne. Di-*n*-heptadec-1-ynylmercury was obtained by adding *n*-heptadec-1-yne (50 g., 0.212 mole) in ethanol (1 l.) to a mechanically stirred solution of alkaline mercuric iodide (cf. Johnson and McEwan, *J. Amer. Chem. Soc.*, 1926, 48, 469). The reagent was prepared by adding 10% aqueous sodium hydroxide (125 c.c.) to mercuric chloride (66 g.) and potassium iodide (163 g.) in water (163 c.c.). The white precipitate of the mercury compound was well washed with 50% ethanol. After being dried on the water-bath, this material crystallised from benzene (400 c.c.) as sparkling white rectangular plates, m. p. 99° (66.1 g., 93.2%).

To the mercury compound (66.1 g., 0.099 mole) in dry dioxan (450 c.c.) in a dry stainless-steel autoclave (750-c.c. capacity), lithium (1.5 g., 0.216 g.-atom) which had been beaten to a fine foil under liquid paraffin was then added, and the autoclave immediately sealed. Heating at 110°, and agitation, were carried out for 12 hours. Methyl sulphate (31.5 g., 0.25 mole) was then added to the resultant milky suspension, and the autoclave was again heated to 110° and shaken for 30 hours. The resulting mixture, which contained a large amount of a light-yellow solid, was poured on crushed ice (500 g.). No evolution of hydrogen was observed (absence of unchanged lithium acetylide). Approx. 18 g. (ca. 90%) of mercury were recovered, which indicated that the metal exchange reaction had proceeded almost quantitatively. The product was extracted from the aqueous dioxan with ether. After washing and drying of this extract, the ether was removed. The crude product—a brown solid at room temperature—was distilled. The distillate (b. p. 182—186°/26 mm.; 38 g., 76%) contained traces of

mercury and volatile mercury salts. It gave a slight precipitate with ethanolic silver nitrate. The *n*-heptadec-1-yne was removed almost completely by treating the crude product with alkaline mercuric iodide as described above. Precipitated di-*n*-heptadec-1-ynylmercury was washed free from adsorbed *n*-octadec-2-yne with light petroleum (b. p. 60—80°), in which the diacetylenyl compound is but sparingly soluble. The diluted mother-liquors and washes were extracted thrice with more light petroleum, and the combined extracts were washed until neutral before drying ( $Na_2SO_4$ ). After removal of the light petroleum, the now almost pure *n*-octadec-2-yne (34 g.) was distilled (b. p. 178—180°/20 mm.). The product then still contained traces of *n*-heptadec-1-yne and was finally purified by crystallisation from methanol.

*n*-Octadec-2-yne, free from *n*-heptadec-1-yne, was obtained as lustrous white plates (30.5 g., 61.8%), b. p. 186°/22 mm., m. p. 30—30.5°,  $n_D^{20}$  1.4488,  $n_D^{25}$  1.4467, and  $d_4^{25}$  0.7980 (Krafft, *Ber.*, 1884, 17, 1372, gives b. p. 184°/15 mm., m. p. 30°, and  $d_4^{20}$  0.8016) (Found: C, 86.05; H, 13.6%).

*Fractional Distillation of n*-Octadec-9-yne.—The still employed was that described by Dixon (*J. Soc. Chem. Ind.*, 1949, 68, 299). The hydrocarbon distilled constantly at 191.8°/25 mm. During the distillation the liquid progressively darkened from colourless to a dark red, and distillation suddenly ceased when about half of the material had been collected. The dark residue could not be distilled under 0.01 mm., and its solution in light petroleum exhibited an intense green fluorescence. Chromatography on alumina and silica columns failed to separate any recognisable fraction.

A white crystalline compound (trace) was found adhering to the column packing and the lower part of the still-head, and was extracted with boiling acetone. Crystallisation from methanol yielded clusters of small plates (*ca.* 20 mg.), *m. p.* 47.5–48° (Found: C, 80.5; H, 13.5. Calc. for  $C_{18}H_{34}O$ : C, 80.6; H, 13.4%). No depression of *m. p.* occurred on admixture with an authentic specimen of *n*-octadecan-9-one, and the infra-red spectra of the specimens were identical. No ketonic material was detected when the distillation was done in an atmosphere of dry nitrogen. The ketone for comparison was obtained in 83% yield by heating *n*-octadec-9-yne (3 g.; Thomas, Campbell, and Hennion, *J. Amer. Chem. Soc.*, 1938, **60**, 718) in acetone (125 c.c.)—water (10 c.c.) in the presence of 1 g. each of concentrated sulphuric acid and mercuric sulphate for 12 hours under reflux, and formed small white plates (from methanol), *m. p.* 48° (Found: C, 80.4; H, 13.25%).

*Low-temperature Crystallisation of the Liquid n-Octadecynes.*—Ethereal solutions of the hydrocarbons were washed with dilute aqueous solutions of the usual reagents, to remove possible oxidation products. The recovered hydrocarbons were distilled through a small Vigreux column, and the constant-boiling fractions collected. These samples were then dissolved in acetone (*ca.* 20 g. in 100 c.c. of solvent). The hydrocarbons were crystallised at low temperature, by means of the apparatus illustrated.

The solution of the hydrocarbon, contained in a glass-stoppered conical flask, was slowly chilled in a bath of ethanol by the addition of small portions of solid carbon dioxide. Crystallisation, in the case of *n*-octadec-9-yne, began at  $-30^{\circ}$ , and the temperature was further lowered to  $-50^{\circ}$ . Meanwhile the cooling jacket of the filtration apparatus was cooled to  $-45^{\circ}$ , also by the addition of solid carbon dioxide. The mixture of solid and mother-liquor was then speedily transferred to the funnel, and the temperature kept at  $-45^{\circ}$  for 15 minutes. The solvent was withdrawn by means of the water-pump, and the solid washed with acetone chilled to  $-50^{\circ}$ . After three washes, each with 75 c.c. of acetone, the apparatus was left to regain room temperature. The liquid hydrocarbon was then collected in a clean flask and immediately distilled.

*n-Tricos-4-yne.*—The reaction between *n*-octadecyl bromide (33.5 g., 0.1 mole) and *n*-pent-1-yne (7 g., 0.103 mole) in liquid ammonia (500 c.c.) containing lithium amide (from lithium 0.7 g., 0.1 g.-atom), in an autoclave at room temperature for 48 hours, yielded the crude hydrocarbon, contaminated mainly with unchanged bromide. The product, dissolved in ether (250 c.c.), was purified by shaking it with liquid ammonia for 24 hours at room temperature in an autoclave. The recovered material was free from alkyl bromide. Pure *n-tricos-4-yne* (17.6 g., 54%) crystallised from methanol-ethanol as clusters of small plates, *m. p.* 24°, *b. p.* 232–233°/15 mm., and  $n_D^{25}$  1.4535 (Found: C, 86.3; H, 13.6.  $C_{23}H_{44}$  requires C, 86.2; H, 13.7%).

*n-Octacos-9-yne.*—A suspension of lithium amide (from lithium 0.4 g., 0.058 g.-atom) in dioxan (150 c.c.) was prepared by adding anhydrous dioxan to a liquid-ammonia solution of lithium amide, and heating the whole under reflux under anhydrous conditions until all the ammonia was dispelled. This suspension, together with *n*-octadecyl bromide (16.7 g., 0.05 mole) and *n*-dec-1-yne (6.9 g., 0.05 mole), was added immediately to a tilting autoclave of 250-c.c. capacity, and shaken at  $110^{\circ}$  for 15 hours. The product was isolated in the usual manner, and the part boiling below  $200^{\circ}/15$  mm. was discarded, being mainly unchanged bromide. The residue, a brown solid, was crystallised twice from glacial acetic acid (charcoal), yielding *n-octacos-9-yne* (6.25 g., 32%) as large glistening white plates, *m. p.*  $36^{\circ}$  (Found: C, 86.2; H, 13.7.  $C_{28}H_{54}$  requires C, 86.15; H, 13.85%).

*n-Dotriacont-16-yne.*—A solution of di-*n*-heptadec-1-ynylmercury (13.4 g., 0.02 mole) in boiling anhydrous dioxan (150 c.c.) was treated with excess of lithium (0.05 g., 0.072 g.-atom) under nitrogen. When the exchange reaction was complete (*ca.* 30 minutes), the solution of the lithium derivative was transferred, *via* a "bridge" of glass tubing incorporating a glass-wool filter, into a second all-glass apparatus by means of a pressure of nitrogen. To this solution was added *n*-pentadecyl bromide (11.64 g., 0.04 mole) in dioxan (100 c.c.), and the whole heated under reflux in a nitrogen atmosphere for 16 hours. The product was then isolated in the usual manner, and that part of *b. p.* higher than  $170^{\circ}/14$  mm., a brown solid, was crystallised twice (charcoal) from ethanol. *n-Dotriacont-16-yne* (6 g., 34%) was obtained as small nacreous plates, *m. p.*  $58^{\circ}$  (Found: C, 85.9; H, 13.8.  $C_{32}H_{62}$  requires C, 86.1; H, 13.9%). Catalytic hydrogenation (Raney nickel) of the acetylene in ethyl acetate gave the known *n*-dotriacontane (*m. p.*  $70^{\circ}$ ; *lit.*, *m. p.*  $70^{\circ}$ ) (Found: C, 85.0; H, 15.0. Calc. for  $C_{32}H_{66}$ : C, 85.3; H, 14.7%).

*n-Hexatriacont-17-yne.*—(a) *In liquid ammonia.* A solution of lithium amide (from lithium 0.35 g., 0.05 g.-atom) in liquid ammonia (200 c.c.) was heated in an autoclave for 20 hours with a light petroleum (*b. p.*  $40$ – $60^{\circ}$ ; 200 c.c.) solution of *n*-octadec-1-yne (12.5 g., 0.05 mole) and *n*-octadecyl bromide (16.7 g., 0.05 mole). The product of *b. p.*  $>208^{\circ}/11$  mm. crystallised from ethanol (charcoal) as a white solid (4 g.) of no definite crystalline form, but tending to needles, having *m. p.*  $51$ – $54^{\circ}$ . Recrystallisation from ethanol and glacial acetic acid in turn gave *n-hexatriacont-17-yne* as small nacreous plates, *m. p.*  $53$ – $53.5^{\circ}$  (15%, 3.75 g.) (Found: C, 86.2; H, 13.8.  $C_{36}H_{70}$  requires C, 86.1; H, 13.9%).

(b) *In anhydrous dioxan.* In an attempt to increase the yield, the synthesis was repeated, employing the mercury-lithium exchange reaction in dioxan for formation of the lithium derivative. *n*-Hexatriacont-17-yne was obtained in only 16% yield (1.75 g.) from *n*-octadec-1-ynyl-lithium (from di-*n*-octadec-1-ynylmercury, 9.3 g.) and *n*-octadecyl bromide (8.9 g.) under nitrogen in dioxan (150 c.c.) for 11 hours. The procedure was that described for *n*-dotriacont-16-yne.

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