**1047.** *Allenes. Part IX.* Carbenes from* 1-*Halogenoallenes* [1]

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Under basic conditions 1-halogenoallenes give carbene intermediates which add styrene or cyclohexene to give allenic cyclopropanes, ammonia to give acetylenic amines, t-butoxide to give t-butoxyallenes, ethylmalonate anion to give mixtures of acetylenic and allenic ethylmalonic esters, and phenyl-lithium to give phenyl-substituted acetylenes and allenes.

A MECHANISM involving the formation of carbenes from prop-2-ynylic halides was first put forward by Hennion and Maloney [2] to explain second-order kinetics for the solvolysis of 3-chloro-3-methylbut-1-yne in 80% ethanolic alkali. Hartzler [3] later demonstrated by trapping with styrene or cyclohexene that tertiary prop-2-ynylic chlorides gave carbenes under strongly basic conditions. The alkylation of amines with tertiary prop-2-ynylic chlorides was also explained by a carbene mechanism.[4] Similarly an elimination-addition mechanism was suggested for the slow solvolysis of 1-chloro-3-methylbutadiene.

The formation of carbene intermediates from a number of 1-bromoallenes is here demonstrated by addition of these intermediates to styrene and cyclohexene. Excellent yields of the corresponding allenic cyclopropane derivatives are obtained from styrene, but only moderate yields from cyclohexene. 1-Vinylidene-2-phenylcyclopropanes (II) all show
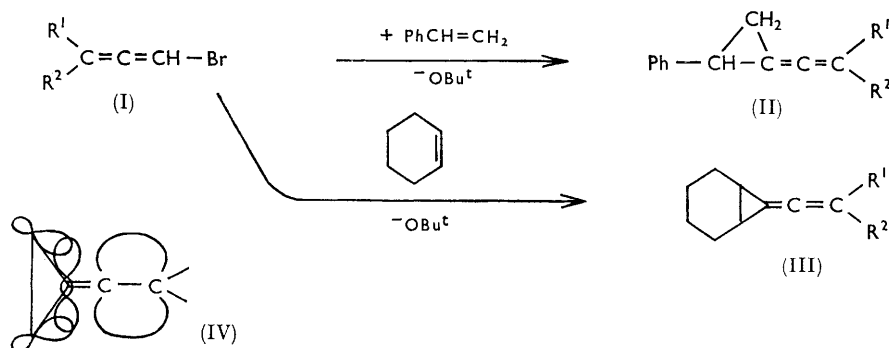
a strong band at 2020 cm.$^{-1}$, a hypsochromic shift from the normal 1950-cm.$^{-1}$ band of allenes. This is consistent with the more rigid structure of the allenic system when constrained by the cyclopropane ring. This, together with the short bond length also, gives rise to increased overlap of π- and bent-bond-electrons [see (IV)], resulting in a sharp band in the ultraviolet region at 203—204 mμ (ε 2400) for all allenic cyclopropanes. (Hartzler [3] reported that allenic cyclopropanes showed only end-absorption in the ultra-

violet region.) All the allenic cyclopropanes gave one band on gas–liquid chromatography (g.l.c.) with the exception of compound (III; R^1 = Me, R^2 = Et) which showed a slight shoulder on a silicone-oil column which was partly resolved on Apiezon. Preparative g.l.c. gave enriched samples of the two components with identical analyses and infrared

* Part VIII, C. S. L. Baker, P. D. Landor, and S. R. Landor, *J.*, 1965, 4659.

[1] A preliminary account was presented at the I.U.P.A.C. conference, July 1963.

[2] G. F. Hennion and D. E. Maloney, *J. Amer. Chem. Soc.*, 1951, **73**, 4735.

[3] H. D. Hartzler, *J. Amer. Chem. Soc.*, 1959, **81**, 2026; 1961, **83**, 4990, 4997.

[4] G. F. Hennion and K. W. Nelson, *J. Amer. Chem. Soc.*, 1957, **79**, 2142.

and ultraviolet spectra, and these must clearly be *exo-* and *endo-*forms.* Adducts derived from cyclohexene and allenic carbenes showed a doublet in the infrared spectrum at 2020 and 1990 cm.$^{-1}$ (cf. ref. 3). Earlier reports of doublets for allenes have not always been substantiated.[6]

The formation of allenic carbenes has thus been clearly demonstrated. Moreover, evidence has accumulated in our laboratories that substitution reactions of allenic halides proceed by an elimination-addition mechanism involving allenic carbenes. Thus, 1-chloro-vinylidene-2,2,6-trimethylcyclohexane[7] gave 1-amino-1-ethynyl-2,2,6-trimethylcyclo-hexane with sodamide in liquid ammonia which can reasonably be regarded as a solvation of the allenic carbene,† and the same chlorallene gave impure 1-(2-t-butoxyvinylidene)-2,2,6-trimethylcyclohexane with excess of potassium t-butoxide under conditions which, as we have already shown, give the carbene.† The t-butoxyallene hydrolysed to the same aldehyde previously isolated and identified by Landor and Landor.[8]

Reaction of 1-halogenoallenes with n-butyl-lithium gave complex mixture of products which contained substantial quantities of terminal acetylenes. Phenyl-lithium with iodo-butadiene gave mainly 3-phenylbut-1-yne but with 1-bromo-3-methylpenta-1,2-diene it gave 3-methyl-5-phenylpenta-3,4-diene in 21% yield. In all experiments using lithium compounds it was found essential to use at least two equivalents of the lithium compound for isolable quantities of product to be obtained. This is consistent only with a carbene mechanism, which utilises the first equivalent of lithium compound as a base for the α-elimination of hydrogen bromide with the formation of hydrocarbon, *e.g.*,
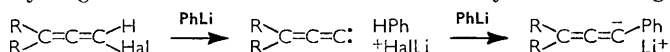

and only the second equivalent gives a slow addition to the carbene.

Condensation of malonates with 1-halogenoallenes[9] is also best explained by an elimination-addition mechanism. 1-Halogenoallenes and 3-halogenoacetylenes should give the same allenic carbene. We therefore reasoned that, if the tertiary acetylenic chloride and the corresponding 1-bromoallene give products with the same proportion of allene (V) and acetylene (VI), they must pass through a common intermediate, *i.e.*, the allenic
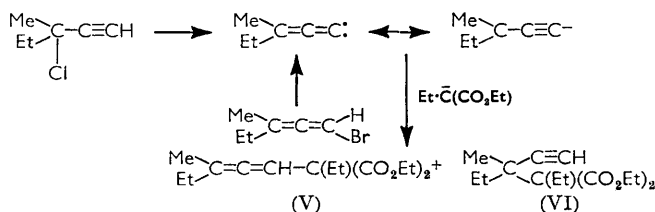
carbene. The chances of obtaining the same proportion of products by S_N2/S_N2' mechanisms from two such different halides as a tertiary acetylenic chloride and a 1-bromo-allene seemed remote.

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* Schoellkropf and Kueppers[5] obtained a mixture of *exo-* and *endo-*norcarane derivatives by adding phenylselenocarbene to cyclohexene.
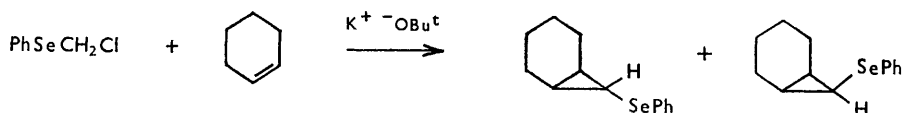
† The alternative S_N2, S_N2' mechanisms are very unlikely as the sterically hindered t-butoxide ion does not substitute but extracts protons, and the very sterically hindered 1-position on the ring is the least favoured for S_N2' attack by amide anion.

⁵ W. Schoellkropf and H. Kueppers, *Tetrahedron Letters*, 1963, 105.
⁶ Cf. J. H. Wotiz, *J. Amer. Chem. Soc.*, 1951, **73**, 693; but not found for a number of allenic acids (R. Evans, P. Greaves, and S. R. Landor, unpublished work).
⁷ Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J.*, 1959, 24.
⁸ P. D. Landor and S. R. Landor, *J.*, 1956, 1015.
⁹ S. R. Landor and P. F. Whiter, unpublished work.

We have shown that 1-bromo-3-methylpenta-1,2-diene and 3-chloro-3-methylpentyne gave the same proportion of allenic and acetylenic malonic ester, thus pointing clearly to a carbene intermediate. Details of the condensations of malonic esters with allenic halides will be reported elsewhere.[9]

The condensation of either chloroform or sodium trichloroacetate and sodium diethyl methylmalonate has been similarly explained by a carbene mechanism.[10]

Since completion of this work Hartzler[11] reported the formation of a carbene from 1-chloro-3-methylbuta-1,2-diene.

EXPERIMENTAL

Infrared spectra were determined with a Perkin-Elmer Infracord and ultraviolet spectra in absolute ethanol with a Bausch and Lomb Spectronic 505 spectrometer; all distillations were carried out under nitrogen. G.l.c. was carried out on a Griffin and George instrument with 6-ft. glass columns, N_2 carrier gas, flow rate 2 l./hr., unless otherwise stated.

1-(2-Methylbut-1-enylidene)-2-phenylcyclopropane.—Dry potassium (3·91 g., 0·1 g.-atom), cut and weighed under benzene, was added to anhydrous t-butyl alcohol (65 ml.); after the initial reaction the mixture was stirred vigorously and gently refluxed until all the metal had reacted. The excess of alcohol was distilled off *in vacuo*, dry benzene (10 ml.) was added to the flask, and the mixture heated *in vacuo* on a water-bath for 30 min. Further addition and removal of benzene (10 ml.) gave $KOBu^t,HOBu^t$ (17·83 g., 96%) to which distilled styrene (b. p. 38°/15 mm.; 50 ml.) was added. The mixture was stirred vigorously, cooled to −10°, and 1-bromo-3-methylpenta-1,2-diene (16·1 g., 0·1 mole) added dropwise over 80 min. The reaction mixture was then stirred for 3 hr. at 0° and filtered. The excess of styrene and t-butyl alcohol were removed by distillation *in vacuo* through a short fractionating column. The residue was shaken with light petroleum (b. p. 40—60°; 60 ml.), filtered, the solid residue washed with light petroleum (b. p. 40—60°; 3 × 20 ml.), and the petrol extracts dried ($MgSO_4$). After solvent and residual styrene had been removed by distillation, fractionation of the residue gave 1-(2-methylbut-1-enylidene)-2-phenylcyclopropane, b. p. 78—81°/0·15 mm. (13·5 g., 73% (Found: C, 89·7; H, 8·7. $C_{14}H_{16}$ requires C, 91·2; H, 8·8%), $ν_{max.}$ 2020s ($\triangleright$=C=C$\triangleleft$), 3050, 1610, 1490s, 1450s, 755s, and 700s cm.$^{-1}$ (all monosubstituted benzene); $λ_{max.}$ 204 mμ, (ε 23,850), $λ_{infl.}$ 216 (ε 1400) and 275 mμ (ε 760). G.l.c. on silicone oil at 174° gave one peak (t 17·5 min.).

1-(Pent-1-enylidene)-2-phenylcyclopropane.—Redistilled styrene (34 ml.) and potassium t-butoxide [from potassium (2·5 g.) and t-butyl alcohol (42 ml.)] cooled and reacted with 1-bromohexa-1,2-diene[12] (10·3 g., 0·064 mole), gave 1-(pent-1-enylidene)-2-phenylcyclopropane (i), b. p. 82—83°/0·25 mm. (6·2 g., 67%) (Found: C, 89·9; H, 8·8. $C_{14}H_{16}$ requires C, 91·2; H, 8·8%), $ν_{max.}$ 2020s ($\triangleright$=C=C$\triangleleft$), 3050s, 1610s, 1490s, 1450s, 757s, and 700s cm.$^{-1}$ (all monosubstituted benzene).

1-(2-Methylprop-1-enylidene)-2-phenylcyclopropane.—Redistilled styrene (50 ml.) was added to dry potassium t-butoxide [from potassium (3·91 g.) and t-butyl alcohol (65 ml.)], cooled to −10°, 1-bromo-3-methylbuta-1,2-diene[12] (14·7 g., 0·1 mole) added dropwise over 20 min. and the mixture stirred at 0° for 3 hr. Working up as described earlier gave 1-(2-methylprop-1-enylidene)2-phenylcyclopropane (13·7 g., 81%), b. p. 70°/0·2 mm., n_D^{21} 1·5731, $ν_{max.}$ 2020s ($\triangleright$=C=C$\triangleleft$), 3060s, 1490s, 1440s, 760s, and 700s cm.$^{-1}$ (all monosubstituted Benzene); (Hartzler[3] obtained the same compound from 3-chloro-3-methylbutyne in 48% yield and gave b. p. 78—80°/0·5 mm., n_D^{25} 1·5717—1·5722; $ν_{max.}$ 2020 cm.$^{-1}$).

7-(2-Methylbut-1-enylidene)bicyclo[4,1,0]heptane.—1-Bromo-3-methylpenta-1,2-diene[12] (16·1 g., 0·1 mole) was reacted with potassium t-butoxide [from potassium (3·90 g.) and anhydrous t-butyl alcohol (65 ml.)] in cyclohexene (50 ml.) as described for the reaction of 1-bromo-3-methylbuta-1,2-diene with potassium t-butoxide in styrene.

The mixture became very dark during the course of the reaction. Fractionation of the residue after the removal of the solvent, cyclohexene and t-butyl alcohol gave fractions (i), b. p. 42—54°/0·4 mm. (0·7 g., 4%), and (ii), b. p. 54—59°/0·6 mm. (5·0 g., 31%). $ν_{max.}$ doublet 2020ms and 1990mw ($\triangleright$=C=C$\triangleleft$); fraction (i) had additional bands at $ν_{max.}$ 3400 (OH), 3300mw (C≡CH), and 2120w cm.$^{-1}$ (C≡CH). G.l.c. on silicone oil at 179° gave one main peak for both fractions (t 10 min.), but (i) had three other peaks accounting for *ca.* 20% of the total. The

[10] A. P. Krapcho, *J. Org. Chem.*, 1962, **27**, 2375.
[11] H. D. Hartzler, *J. Org. Chem.*, 1964, **29**, 1311.
[12] D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 1963, 483.

main peak showed a suggestion of a shoulder in each case. On Apiezon L at 147° two peaks (*t* 17 and 19 min.), appeared still not completely resolved. The ratios for the peak heights were for (ii) 56 : 44.

Successive samples (4 × 0·25 ml.) of fraction (ii) were passed through a preparative Apiezon L column and fractions, (1), (2), and (3), were collected. Analytical chromatograms of (1) and (3) showed that, owing to the closeness of the peaks, only enrichment had occurred. The ratios of the peak heights of these preparative fractions were (1) 73% (*t* 19 min.): 27% (*t* 22 min.) (3) 43% (*t* 19 min.): 57% (*t* 22 min.). Fractions (1) and (3) were analysed in duplicate [Found: (1) C, 88·4, 88·8; H, 11·0, 11·2%; (3) C, 88·9, 88·7; H, 11·25, 11·1%. Calc. for $C_{12}H_{18}$: C, 88·1; H, 11·2%). Fraction (1) showed $\lambda_{max.}$ 203 mμ (ε 12,000) and fraction (3) $\lambda_{max.}$ 203 mμ (ε 13,000). The infrared spectra of (1) and (3) were identical and the same as that of the unchromatographed material above.

These data are consistent with the product being a mixture of *exo*- and *endo*-7-(2-methyl-but-1-enylidene)bicyclo[4,1,0]heptane.

7-(2-Methylprop-1-enylidene)bicyclo[4,1,0]heptane.—To dry potassium t-butoxide [from potassium (3·91 g.) and anhydrous t-butyl alcohol (65 ml.)] cyclohexene (90 ml.) was added, the mixture stirred at −10°, and a solution of 1-bromo-3-methylbuta-1,2-diene [12] (14·7 g., 0·1 mole) in cyclohexene (10 ml.) was added dropwise over 20 min. and stirred for 3 hr. at 0°, and the mixture worked up. Fractionation gave (i), b. p. 37—42°/0·5 mm. (1·6 g.) and (ii) 7-(2-methyl-prop-1-enylidene)bicyclo[4,1,0]heptane, b. p. 42—44°/0·5 mm. (3·65 g., 25%), n_D^{20} 1·5225, $\nu_{max.}$ 3400w (OH), doublet 2020ms and 2000mw ($\triangleright$=C=C$\triangleleft$), $\lambda_{max.}$ 202—203 mμ (ε 12,700) Hartzler [3] obtained 26% of this compound from 3-chloro-3-methylbutyne and gave b. p. 84—87°/12 mm., n_D^{25} 1·5215—1·5218; $\nu_{max.}$ doublet 2030 and 2000 cm.$^{-1}$). G.l.c. on Apiezon L at 147° showed that fraction (ii) consisted of one main peak (*t* 12 min.) and two impurities (*ca.* 4%, *t* 1·5 and 3 min.). Fraction (i) showed the same peaks except that it was approximately a 1 : 1 mixture of the materials *t* 3 and 12 min. Neither of the more volatile impurities was t-butyl alcohol (*t* 1 min.).

Reaction of n-Butyl-lithium with 1-Iodobuta-1,2-diene.—n-Butyl-lithium [from n-butyl bromide (15·1 g., 0·11 mole) in dry ether (40 ml.) and lithium wire (1·83 g.)] was filtered through glass wool and a solution of 1-iodobuta-1,2-diene [13] (9 g., 0·05 mole) in dry ether (10 ml.) was added slowly to the stirred, cooled mixture. After the addition was complete the mixture was stirred for a further 30 min., the lithium complexes were decomposed by the slow addition of water with cooling, the mixture was extracted with ether, and the extracts were dried (MgSO$_4$). The solvent was removed by distillation and fractionation of the residue gave a product, b. p. 47—48°/66 mm. (2·9 g., 53%), $\nu_{max.}$ 3300vs and 2100 cm.$^{-1}$ (C≡CH). G.l.c. on GEO 100 at 100° showed six peaks. (*t* 1,2,5,7,8, and 17 min.).

Reaction of n-Butyl-lithium with 1-Bromo-3-methylpenta-1,2-diene.—1-Bromo-3-methyl-penta-1,2-diene [12] (8·05 g., 0·05 mole) and n-butyl-lithium [from n-butyl bromide (15·1 g., 0·11 mole) and lithium wire (1·6 g.) in dry ether (50 ml.)] gave five products, b. p. 23—66°/12 mm. (2·25 g., 34%). G.l.c. on dinonyl phthalate at 160° (*t* 5·5 min., 20%; *t* 13 min., 5%; *t* 19·5 min., 25%; *t* 36 min., 15%; *t* 48 min., 35%). The presence of 3-methylnona-3,4-diene and 3-ethynyl-3-methylheptane, together with insertion compounds of diethyl ether, was indicated by $\nu_{max.}$ 3300, 2100, 1950, and 1100 cm.$^{-1}$, but separation was not achieved.

Reaction of Phenyl-lithium with 1-Bromo-3-methylpenta-1,2-diene.—A solution of 1-bromo-3-methylpenta-1,2-diene [12] (16·1 g., 0·1 mole) in dry ether (20 ml.) was added dropwise to a stirred, cooled solution of phenyl-lithium [from lithium wire (2·8 g., 0·4 g.-atom) in dry ether (100 ml.) and a solution of bromobenzene (31·4 g., 0·2 mole) in dry ether (20 ml.)]. After the addition was complete the mixture was refluxed for 30 min. cooled, and damp ether added, followed by water (considerable heat evolved). The aqueous layer was separated, extracted with ether, and the combined ether layer and extracts were dried (MgSO$_4$). Removal of the solvent followed by fractionation gave (i) b. p. 25—80°/3 mm. (3·9 g.), (ii) *3-methyl-5-phenyl-penta-3,4-diene*, b. p. 80—90°/3 mm. (3·4 g., 21%), and a residue (5 g.). Fraction (i) had $\nu_{max.}$ 3300m (C≡CH), 3050m (aromatic CH) 1380s, 1965s, 1020s, 735s, 685s, and 670s cm.$^{-1}$. G.l.c. on silicone oil at 128° showed four peaks (*t* 2 min., trace; *t* 6 min.; *t* 11·5 min.; *t* 35·5 min. trace). Fraction (ii) had $\nu_{max.}$ 3300mw (C≡CH), 3050m (aromatic CH), 1960m (C=C=C), 1610ms, 825 and 745s, 695s cm.$^{-1}$ (monosubstituted benzene). G.l.c. in silicone oil at 128° showed one peak (*t* 39 min.) (Found: C, 90·5; H, 9·25. $C_{12}H_{24}$ requires C, 91·1; H, 8·9%).

3-Phenylbut-1-yne.—A solution of 1-iodobuta-1,2-diene (8·95 g. 0·05 mole) in dry ether (15 c.c.)

[13] C. S. L. Baker, P. D. Landor, S. R. Landor, and A. N. Patel, *J.*, 1965, 4348.

was added dropwise to phenyl-lithium [from lithium (1·6 g.), bromobenzene (15·7 g., 0·1 mole), and dry ether (100 ml.)]; the reaction mixture became warm. After working up in the usual way, distillation gave 3-*phenylbut*-1-*yne* (3 g., 45%) (Found: C, 92·4; H, 7·9. $C_{10}H_{10}$ requires C, 92·34; H, 7·66%), b. p. 30—35°/1 mm., $\nu_{max.}$ 3300s (C≡CH), and 2100w cm.$^{-1}$ (C≡CH); there were no bands at 1950 (C=C=C) and 875 cm.$^{-1}$ (HC=C=CH). G.l.c. on dinonylphthalate at 128° gave one band (*t* 19 min.).

2,2,6-*Trimethylcyclohexylidenevinyl Chloride and Potassium t-Butoxide in t-Butyl Alcohol* (with L. A. GOODSON).—2,2,6-Trimethylcyclohexylidenevinyl chloride (18·5 g., 0·10 mole) and potassium t-butoxide [from potassium, (6 g.) and dry t-butyl alcohol (150 ml.)] under reflux for 4 hr. and at room temperature overnight gave, after extracting with ether, washing with water (4 × 50 ml.), drying (MgSO$_4$), and distilling, (i) 1-ethynyl-2,2,6-trimethylcyclohex-6-ene, b. p. 79—80°/2 mm. (0·9 g., 6%), $\nu_{max.}$ 3375ms (C≡CH), 2100mw (C≡CH), 1670ms (C=C); $\lambda_{max.}$ 228 mμ (ε 10,500) [lit.,[8] $\lambda_{max.}$ 227 mμ (ε 11,000)], (ii) 1-(2-butoxyvinylidene)-2,2,6-trimethylcyclohexane, b. p. 96—98°/2 mm. (7·7 g., 35%) [Found: *M* (cryoscopic in benzene), 221. $C_{15}H_{26}O$ requires *M*, 222], $\nu_{max.}$ 1945s (C=C=C), and 1110, 1060vs cm.$^{-1}$ (C–O); [weak bands at 1690, 1650 cm.$^{-1}$ and $\lambda_{max.}$ 242 mμ (ε 640), as well as poor analyses, indicated the presence of 10% of aldehyde], (iii) 2,2,6-trimethylcyclohexylideneacetaldehyde b. p. 98°/2 mm. (0·4 g., 2%), $\nu_{max.}$ 1670vs (C–O) and 1600w cm.$^{-1}$ (C=C); $\lambda_{max.}$ 243 mμ (ε 5630) [lit.,[8] $\lambda_{max.}$ 244 mμ, ε (4931) for an impure sample].

Fraction (ii) (1·00 g.) with 2,4-dinitrophenylhydrazine (1·11 g.) in methanol (240 ml.) and sulphuric acid (8·3 ml.), gave a precipitate after 1 hr. and, after keeping for 24 hr., 2,2,6-trimethylcyclohexylideneacetaldehyde 2,4-dinitrophenylhydrazone (1·24 g., 66·5%), m. p. and mixed m. p. 183° (from methanol–chloroform) with an authentic sample,[8] $\lambda_{max.}$ 263, 295, and 388 mμ (ε 16,000, 10,300, and 32,500) [lit.,[8] $\lambda_{max.}$ 262, 295, and 388 mμ (ε 16,400, 10,250, 32,600]. Fraction (iii) gave an immediate precipitate of the same dinitrophenylhydrazone.

1-*Ethynyl*-2,2,6-*trimethylcyclohexylamine* (with L. A. GOODSON).—2,2,6-Trimethylcyclohexylidenevinyl chloride [7] (9·2 g., 0·05 mole) was added slowly to sodamide [from sodium (2·5 g.)] in liquid ammonia (250 ml.) and the liquid ammonia became red. After 24 hr., addition of ammonium chloride (10 g.) extraction with ether, washing with water, and distillation gave 1-ethynyl-2,2,6-trimethylcyclohexylamine, b. p. 62°/2 mm. (4·4 g., 53·4%) containing approximately 3% of 1-ethynyl-2,6,6-trimethylcyclohexene, $\lambda_{max.}$ 226 mμ (ε 800). The amine was purified further by addition of ether and extraction with dilute hydrochloric acid; the aqueous solution was made alkaline and the amine extracted with ether, dried (MgSO$_4$), solvent removed and the residue distilled yielding 1-ethynyl-2,2,6-trimethylcyclohexylamine (Found: C, 80·25; H, 11·55, N, 8·1%. $C_{11}H_{19}N$ requires C, 80·0; H, 11·5; N, 8·5%) $\nu_{max.}$ 3370m (NH$_2$); 3280s (C≡CH), 2100w (C≡CH), 1570s (NH$_2$) and 850vs cm.$^{-1}$ (NH$_2$), end-absorption only in the ultra-violet spectrum. The amine (0·3211 g.) absorbed 85 ml. of hydrogen (98% of theory for 2 moles), and gave a white precipitate of the amine hydrochloride with hydrochloric acid.

Reaction of 1-*Bromo*-3-*methylpenta*-1,2-*diene and* 3-*Chloro*-3-*methylpent*-1-*yne with Diethyl Ethylmalonate*.—Reactions (*a*) and (*b*) were performed simultaneously, under identical conditions.

(*a*) Sodium (2·41 g., 0·105 g.-atom) was added to absolute ethanol (60 ml.); when the reaction was complete diethyl ethylmalonate (30 g., 0·16 mole) was added quickly with stirring and the mixture heated gently under reflux for 15 min. 1-Bromo-3-methylpenta-1,2-diene [12] (16·1 g., 0·1 mole) was added dropwise over 30 min. to the warm, stirred mixture, which was heated under reflux for 1 hr., allowed to cool in air for 1 hr. and then in an ice-bath. Ether (80 ml.) and water (40 ml.) were added, the aqueous layer was separated and extracted with ether (3 × 20 ml.), the combined ether layers were dried (MgSO$_4$), and ether was distilled off. G.l.c. on silicone oil at 166° gave a peak (*t* 40 min.) of diethyl 4-ethyl-4-methylhex-5-yne-3,3-dicarboxylate (VI) (43·6%) and a peak (*t* 50 min.) of diethyl 6-methylocta-4,5-diene 3,3-dicarboxylate (V), (56·4%).

(*b*) 3-Chloro-3-methylpent-1-yne (11·05 g., 0·1 mole) was added in place of 1-bromo-3-methylpenta-1,2-diene and the reaction performed and worked up as in (*a*). G.l.c. on silicone oil at 166° gave a peak (*t* 40 min.) of the diester (VI), (43·5%) and a peak (*t* 50 min.) of the diester (V) (56·5%).

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