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## Allenes. Part XV.\* The Addition of Dihalocarbenes to Allenes and Conversion of 1,1-Dihalo-2-methylenecyclopropanes to Cumulenes

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The addition of dichloro- and dibromo-carbenes to the more substituted double bond of five different allenes gave 1,1-dichloro- and 1,1-dibromo-2-methylenecyclopropanes. Some of these have been converted by means of n-butyl lithium to cumulenes.

DOERING and HOFFMANN<sup>1</sup> first showed that dihalocarbenes add to alkenes to yield dihalocyclopropanes. It has since been well established that dihalocarbenes are electrophiles which add preferentially to the more nucleophilic double bond *i.e.*, the one substituted with the most electron donating groups as shown from competitive reactions with mixtures of alkenes<sup>2,3</sup> and the reaction with isoprene.4,5

$$CH_9=CMe-CH=CH_2 \xrightarrow{:CX_2} CH_2-CMe+CH=CH_2$$

cv

However, Skattebol<sup>6</sup> has shown that predominant addition to the less-substituted double bond occurred with dienes having terminal methyl substituents,

bond which is preferentially attacked. 1,1-Dihalo-2methylene-3-alkyl- and -3,3-dialkyl-cyclopropanes gave one band only on g.l.c. whereas 1,1-dibromo-2-ethylidene-**3.3**-dimethylcyclopropanes showed a main peak (95%)and an isomer (5%) (see Table 1). The infrared spectra of dichloromethylenecyclopropanes showed strong bands at 865 and 910 cm.<sup>-1</sup> with overtones at 1730 and 1820 cm.<sup>-1</sup> whereas dibromomethylenecyclopropanes showed maxima at 800, 905 (>C=CH deformations), 1750, and 1810 cm.<sup>-1</sup> (overtones). All the cyclopropanes showed a band at 1000-1070 cm.-1 which may be ascribed to the cyclopropane skeletal vibrations. Shoulders in the ultraviolet absorption spectra at 255 mµ which show up as maxima with increasing methyl substitution would

TABLE 1



1.1	Dihalo-2-methy	vlenecvclopropanes	, RR'C-C=CHR''

R	R′	$\mathbf{R}^{\prime\prime}$	х	B. p./mm.	Yield (%)	ν <sub>max</sub> cm. <sup>-1</sup>	$\lambda_{\max} m \mu (\varepsilon)$
$\mathbf{Me}$	Me	н	Cl	$65-66/80^{\circ}$	49	1820w, 1730w, 1010m, 910s, 865s	205 (5200), 234sh (500)
Me	Me	н	$\mathbf{Br}$	66-68/20	68	1820w, 1750w, 1040m, 905s, 800s	206 (5250), 225sh (3000)
Me	Et	н	Cl	70/90	50	1820w, 1730w, 1002m, 910s, 865s	206 (5250), 234sh (500)
Me	Et	н	Br	49-50/2	58	1820w, 1750w, 1040m, 905s, 800s	207 (5300), 225sh (3000)
Me	n-Pentyl	н	Cl	64 - 65/70	36	1820w, 1730w, 1012m, 910s, 865s	
н	n-Pr	н	Br	$46 - 50/3 \cdot 5$	<b>43</b>	1750w, 1070s, 900, 795s	
Me	Me	Me	$\mathbf{Br}$	3940/4	50	1750m, 1000m, 840m, 730s	

penta-1,3-diene and 2,4-dimethylpenta-1,3-diene; this was rationalised in terms of an increase in the electron density of the terminal double bond due to the hyperconjugative effect of the methyl substituent.

We now describe in detail (for preliminary report see ref. 7) the addition of dichloro- and dibromo-carbene to 1,2- and 2,3-dienes and the conversion of four of the adducts to cumulenes. In all cases, addition takes place predominantly at the more substituted double bond.

$$\begin{array}{c} CX_2 \\ CX_2 \\ C=C=CHR'' \xrightarrow{:CX_2} RR'C=C=CHR'' \\ (I) & (II) \end{array}$$

Since hyperconjugative and inductive effects of alkyl substituents would only affect the near, *i.e.*, the more substituted double bond of the allene, it is this double

<sup>3</sup> W. v. E. Doering and W. A. Henderson, J. Amer. Chem. Soc., 1958, 80, 5274.

suggest non-bonded interaction of the bromine atoms with the  $\pi$ -orbital (cf. bromoallenes<sup>8</sup>). Nuclear mag-



netic resonance (n.m.r.) spectroscopy showed two nonequivalent protons for the exocyclic methylene group (R'' = H) ( $\tau$  4·1 and 4·5). Ozonolysis gave formaldehyde (acetaldehyde where R = Me) and during hydrogenation one equivalent of hydrogen was absorbed. As a further check, 1,1-dibromo-2,2,3-trimethylcyclopropane was synthesised from 2-methyl-but-2-ene and dibromocarbene<sup>2</sup> and the infrared spectrum compared with that of the hydrogenation product of (II; R =R' = Me, R'' = H) and found to be superimposable.

It is interesting to note that 1-bromo-3,3-dialkyl-

- J. Chem. Soc. (C), 1966, 1223.

<sup>\*</sup> Part XIV, S. R. Landor, E. S. Pepper, and J. P. Regan, J. Chem. Soc., preceding Paper.

<sup>&</sup>lt;sup>1</sup> W. v. E. Doering and A. K. Hoffman, J. Amer. Chem. Soc., 1954, 76, 6162.

<sup>&</sup>lt;sup>2</sup> P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc., 1956, 78, 5430.

<sup>4</sup> A. Ledwith and R. B. Bell, Chem. Ind., 1959, 459.

<sup>&</sup>lt;sup>5</sup> T. Shono and R. Oda, J. Chem. Ind., 1939, 439.
<sup>5</sup> T. Shono and R. Oda, J. Chem. Soc. Japan, 1959, 80, 1200.
<sup>6</sup> L. Skattebol, J. Org. Chem., 1964, 29, 2951.
<sup>7</sup> W. J. Ball and S. R. Landor, Proc. Chem. Soc., 1961, 246.
<sup>8</sup> S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, Chem. Soc. (1966, 1929).

allenes seem to be inert to attack by dihalocarbenes despite the fact that inductive electron withdrawal by the bromine from the alkyl-substituted double bond must be very weak. Non-bonded interaction between bromine and the 2,3-bond which has already tentatively been suggested <sup>9</sup> might explain this inertness.

Treatment of (II; R = Me, R' = Me or Et, R'' = H, X = Br or Cl) with n-butyl lithium below  $-30^{\circ}$  gave approximately 75% yields of the corresponding cumulene (III), 4-methylpenta-1,2,3-triene, and 4-methylhexa-1,2,3-triene, in admixture with ether.

$$RR'C-C=CHR'' \xrightarrow{BunLi} RR'C=C=C=CHR''$$
(II; R''=H) (III)

As these compounds are extremely sensitive to oxygen and rapidly turned yellow on exposure to air, preparative g.l.c. was found to be impracticable. The cumulenes had a strong infrared band at 2080 cm.<sup>-1</sup> (cf. ref. 10 >=C=C<  $\nu_{max.}$  2020 cm.^1; a conjugated cumulene aldehyde reported in the literature  $^{11}$  had  $\nu_{max.}$  2066 cm.^1) ascribed and Lomb Spectronic 505 spectrometer; n.m.r. with a Perkin-Elmer 60 Mc./sec. spectrometer for 20% solutions in carbon tetrachloride with tetramethylsilane as internal standard; t-butyl alcohol was freshly distilled from sodium wire.

1,1-Dichloro-2,2-dimethyl-3-methylenecyclopropane. Potassium metal (4 g., 0.1 g.-atom) was added to dry t-butyl alcohol in small pieces and the mixture heated under reflux until the potassium had completely dissolved. The excess of alcohol was distilled off, and the last traces removed under reduced pressure; the resulting white solid was powdered, washed with sodium-dried benzene  $(3 \times 50 \text{ ml.})$ , (the benzene siphoned off), and then sodium dried pentane. The solvents were removed in vacuo, and the solid dried in vacuo at 100° for 2 hr. 3-Methylbut-1,2-diene 9 (6.8, 0.1 mole) and dry pentane (10 ml.) were added to the solid and the mixture cooled in an ice-salt bath; chloroform (12 g., 0.1 mole) was added dropwise to the rapidly stirred mixture during 1 hr. The mixture was stirred for a further 1 hr. at 0°, and then 1 hr. at room temperature after which it was poured into ice-water and extracted with pentane  $(3 \times 50 \text{ ml.})$  and the extracts dried (MgSO<sub>4</sub>). After filtration, the solvents were removed, and the remaining material distilled to give crude product, b. p.  $65-68^{\circ}/80$  mm. (7.4 g.,

## TABLE 2

Infrared and ultraviolet spectra of cumulenes

Cumulene	$v_{max}$ , cm. <sup>-1</sup>		$\lambda_{\max}$ m ( $\epsilon$ ) in n-hexane	
CH <sub>2</sub> =C=C=CH <sub>2</sub> *	2030m, 1610s, 860		240 (20,300) in EtOH	310 (250)
$Me_2C=C=C=CH_2$	2080s, 820	220 (3500)	254 (13,000)	294sh (700)
$Me(Et)C=C=C=CH_{2}$	2080m, 1640w, 820	218 (7700)	256 (16,000)	294sh (900)
$Me_2C = C = C = CMe_2 \dagger$	1900w, 1645m	230 (7000)	<b>262·Š</b> (17,000)	
Me <sub>2</sub> C=C=C=CH-CHO ‡	2066s, 1600m, 780		292 (not given) (in MeOH)	
* See W. M. Schubert, T. H. Liddicœt, and	W. A. Lanka, J. Amer.	Chem. Soc.,	1952, 74, 569. † See ref. 12.	t See ref. 11.

to the rigid cumulene system and ultraviolet spectra as shown in Table 2. Increasing methyl substitution gives the expected bathochromic shift in the u.v. absorption maxima of cumulenes.

Hydrogenation of cumulene (III; R = R' = Me) gave 2-methylpentane and cumulene (III; R = Me, R' = Et) gave 3-methylhexane identified by g.l.c.

On keeping overnight at room temperature, solutions of cumulenes in ether or alcohol gave a heavy white precipitate, probably polymeric in nature. Skattebol<sup>12</sup> reacted 1,1,3,3-tetramethylallene with dihalocarbene and converted the resulting dihalocyclopropane into the cumulene, 2,5-dimethyl-2,3,4-hexatriene, with properties similar to those of the cumulenes described in this Paper. It is, however, interesting to note that the C=C stretching band near 2080 cm.<sup>-1</sup> was absent, possibly due to the symmetrical structure of the tetramethyl cumulene.

Two reports 13,14 on the addition of carbenes to allenes appeared after this work had been completed.

## EXPERIMENTAL

Infrared spectra were determined on liquid films on a Perkin-Elmer Infracord spectrometer; u.v. spectra on ethanolic solutions (unless otherwise stated), with a Bausch

<sup>9</sup> Y. I. Ginzburg, J. Gen. Chem. (U.S.S.R.), 1940, **10**, 513; G. F. Hennion and J. J. Sheehan, J. Amer. Chem. Soc., 1949, **71**, 1964.

<sup>10</sup> S. R. Landor and P. F. Whiter, J. Chem. Soc., 1965, 5625.

49%). Redistillation gave pure 1,1-dichloro-2,2-dimethyl-2-methylenecyclopropane, b. p. 65-66°/88 mm. (6.3 g., 41%). G.l.c. on 10% Apiezon-Celite at 70°, with nitrogen (flow rate of 1.8 l./hr.) gave a single component (t 8 min.) (Found: C, 47.4; H, 5.1; Cl, 46.9. C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub> requires C, 47.7; H, 5.3; Cl, 46.9%);  $\nu_{max}$  1820w, 1750w (overtone), 1010s (cyclopropane), 910s ( $\supset$ C=CH<sub>2</sub>) and 865s cm.<sup>-1</sup>;  $\lambda_{max}$  205sh ( $\varepsilon$  5200) and 234 mµ ( $\varepsilon$  500). N.m.r. showed two nonequivalent protons for the exocyclic methylene group

Ozonolysis of the product (0.8 g.) in dry ethyl acetate (50 ml.) followed by hydrogenolysis (PtO2, 0.032 g.) and distillation gave formaldehyde as its dimedone derivative (0.25 g.), m. p. and mixed m. p. 189.5°.

1,1-Dibromo-2,2-dimethyl-3-methylenecyclopropane. - Dry potassium t-butoxide (from potassium 6 g., 0.15 g.-atom and t-butyl alcohol) was covered with 3-methylbuta-1,2diene<sup>9</sup> (10 g., 0.15 mole) and the reaction mixture cooled in an ice-bath; bromoform (38 g., 0.15 mole) was added dropwise during 1 hr. Stirring was continued for 2 hr. at room temperature, after which the mixture was poured on to ice.

<sup>11</sup> E. M. Kosower and T. S. Sorensen, J. Org. Chem., 1963, 28, 687; 1961, 83, 3153. <sup>12</sup> L. Skattebol, Tetrahedron Letters, 1965, 2175.

- M. A. Bezaguet, Compt. rend., 1962, 254, 3371.
   W. Rahman and H. Kuivila, J. Org. Chem., 1966, 31, 772.

The product was extracted with ether, the solution dried  $(MgSO_4)$ , and distilled to give 1,1-dibromo-2,2-dimethyl-3-methylenecyclopropane (24 g., 68%), b. p. 66-68°/20 mm. (Found: C, 29.7; H, 3.9; Br, 66.5.  $C_{6}H_{8}Br_{2}$  requires C, 30.0; H, 3.3; Br, 66.55%);  $v_{max}$ , 1820w, 1750w, 1040m (cyclopropane ring), 905s ( $\sum C=CH_{2}$ ), and 800s cm.<sup>-1</sup>;  $\lambda_{max}$  206sh mµ ( $\epsilon$  5250), 225mµ ( $\epsilon$  3000); g.l.c. at 140° on dinonyl phthalate on Celite showed one peak. N.m.r. showed two nonequivalent protons for the exocyclic

methylene group  $\left(\begin{array}{c} & H \\ Br & Br \end{array}\right)$  at T 4.14 and T 4.51, and a singlet for the two equivalent methyl protons

 $\begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$  at T 8.52. The product (1 g.) in an-

hydrous ether (30 ml.) with Adams platinum catalyst (0.024 g.) absorbed 97 ml. of hydrogen at 20°/758 mm. (1 mole requires 99.9 ml.) in 10 min. and showed little further absorption after 5 hr. shaking. The catalyst was filtered off, the ether evaporated, to give a residue with a superimposable infrared spectrum to that of an authentic sample of 1,1-dibromo-2,2,3-trimethylcyclopropane; <sup>9</sup> v<sub>max</sub>, 905m, 800, and 760s cm.<sup>-1</sup>.

Ozonolysis of the product (1 g.) in dry ethyl acetate (30 ml.) followed by hydrogenolysis (PtO2, 0.046 g.) and distillation gave formaldehyde as its dimedone derivative (0.23 g.), m. p. and mixed m. p. 289°.

1.1-Dichloro-2-ethyl-2-methyl-3-methylenecyclopropane.-To potassium t-butoxide [from dry t-butyl alcohol (150 ml.) and potassium (4 g., 0.1 g.-atom)] and 3-methylpenta-1,2-diene 9 (8.2 g., 0.1 mole) in dry pentane (10 ml.) in an ice-salt bath, chloroform (12 g., 0.1 mole) was added dropwise during 1 hr. The mixture was stirred for 1 hr. at  $0^{\circ}$ , and a further 1 hr. at room temperature, it was then poured into ice-water and extracted with pentane (3 imes50 ml.), dried (MgSO<sub>4</sub>), filtered, and distilled to give 1.1-dichloro-2-ethyl-2-methyl-3-methylenecyclopropane, b. p. 70°/90 mm. (8.3 g., 50%) (Found: C, 50.8; H, 6.1; Cl, 42.9.  $C_7H_{10}Cl_2$  requires C, 50.9; H, 6.2; Cl, 42.9%);  $\nu_{max}$  1820w, 1720w, 1625m (overtone), 1002s (cyclopropane), 910s ( $>C=CH_2$ ) and 865s cm.<sup>-1</sup>;  $\lambda_{max}$  206 ( $\epsilon$  5250), 234sh m $\mu$  ( $\epsilon$  500). G.l.c. on 10% Apiezon–Celite at 70°, nitrogen flow 1.8 l./hr. gave a single component (t 17 min.). N.m.r. showed two nonequivalent protons for the exocyclic

methylene group  $\left( \sum_{C \in C} C \lesssim_{H}^{H} \right)$  at  $\tau$  4.17 and 4.51, a

singlet for the methyl protons (  $\overset{H_3C}{\sim}$  ) at  $\tau$  8.61,

a triplet for the methyl protons  $(H_3C \cdot H_2C)$  at au 8.94 (J = 6.5 c./sec.) and a quartet for the methylene protons  $\left(\begin{array}{c} H_3C \cdot H_2C \end{array}\right)$  at  $\tau 8.27 \ (J = 6.5 \ c./sec.).$ 

Ozonolysis of dichloro-2-ethyl-2-methyl-3-methylenecyclopropane (0.8 g.) in dry ethyl acetate and hydrogenolysis (PtO2, 0.032 g.) and distillation at 40°, gave formaldehyde as the dimedone derivative (0.26 g.), m. p. 189.5. A mixed m. p. with an authentic sample prepared from formaldehyde showed no depression.

1,1-Dibromo-2-ethyl-2-methyl-3-methylenecyclopropane.-To potassium t-butoxide (from potassium 7.6 g., 0.19 g.-

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atom and t-butyl alcohol) at 0° 3-methylpenta-1,2-diene 9 (15 g., 0.19 mole) and then bromoform (48 g., 0.19 mole) were added dropwise during 30 min. At the end of the addition the flask was warmed to room temperature and stirred for 2 hr. The reaction mixture was poured on to ice and extracted with ether (3 imes 100 ml.), dried (MgSO<sub>4</sub>), and distilled to give 1,1-dibromo-2-ethyl-2-methyl-3-methylenecyclopropane (22 g., 58%), b. p. 49-50°/2 mm. (Found: C, 32·4; H, 4.3; Br, 63.2. C<sub>7</sub>H<sub>10</sub>Br<sub>2</sub> requires C, 33.0; H, 3.9; Br, 63.0%;  $\nu_{max.}$  1820w, 1750w, 1040m (cyclopropane), 905s (>C=CH<sub>2</sub>), and 800s cm.<sup>-1</sup>;  $\lambda_{max}$  207 ( $\epsilon$  5300), 225sh mµ ( $\varepsilon$  3000). G.l.c. on 30% dinonyl phthalate on Celite at 140° (nitrogen flow of 1.81. hr.) showed one component only.

The product (0.9 g.) in ethyl acetate (20 ml.) with Adams platinum oxide catalyst (0.042 g.) absorbed 77 ml. of hydrogen at 21°/760 mm. (1 mole required 79 ml.) in 8 min. Filtration of the catalyst and evaporation of the solvent gave a residue,  $\nu_{max.}$  905m, 800m, and 755s cm  $^{-1}.$ 

Ozonolysis of the product (0.8 g.) in dry ethyl acetate and working up as described above, gave formaldehyde as the dimedone derivative (0.3 g.), m. p. 189.5°.

1,1-Dichloro-2-methyl-3-methylene-2-pentylcyclopropane.---To a rapidly stirred mixture of potassium t-butoxide from t-butyl alcohol (150 ml.) and potassium (4 g., 0.1 g.-atom) and 3-methyl-octa-1,2-diene \* (12.5 g., 0.1 mole) in dry pentane (10 ml.) in an ice-salt bath, chloroform (12 g., 0.1 mole) was added dropwise during 1 hr. The mixture was stirred or 1 hr. at 0°, and 1 hr. at room temperature, after which it was poured into ice-water and extracted with pentane  $(3 \times 50 \text{ ml.})$ , dried (MgSO<sub>4</sub>), filtered, and twice distilled to give 1,1-dichloro-2-methyl-3-methylene-2-pentylcyclopropane (14.5 g., 36%) (Found: C, 57.7; H, 7.6; Cl, 34.2%. C<sub>10</sub>H<sub>16</sub>Cl<sub>2</sub> requires C, 58.0; H, 7.8; Cl,  $34\cdot3\%$ ;  $\nu_{max}$  1820w, 1730w (overtone), 1640w, 1012m (cyclopropane), 910s (>C=CH<sub>2</sub>), and 865s cm.<sup>-1</sup>.

1,1-Dibromo-2-methylene-3-propylcyclopropane.—To dry potassium t-butoxide (from potassium 4.4 g., 0.11 g.-atom and t-butyl alcohol) and hexa-1,2-diene 9 (9 g., 0.11 mole) at 0°, bromoform (25 g., 0·1 mole) was added dropwise with vigorous stirring during 20 min. Stirring was continued for 1 hr. after which time the mixture was poured on to ice, extracted with ether  $(3 \times 50 \text{ ml.})$ , dried (MgSO<sub>4</sub>), and distilled to give 1,1-dibromo-2-methylene-3-propylcyclopropane (11.6 g. 43%), b. p. 46-50°/3.5 mm. (Found: C, 33.1; H, 3.0; Br, 62.9. C<sub>7</sub>H<sub>10</sub>Br<sub>2</sub> requires C, 33.0; H, 3.9; Br, 63.0%);  $\nu_{max.}$  1750w, 1070s (cyclopropane), 900s (>C=CH<sub>2</sub>), and 795s cm.<sup>-1</sup>. G.l.c. on 30% dinonyl phthalate on Celite at 140°, showed only one component. The product (0.96)g.) in ethyl acetate (30 ml.) with a suspended catalyst (PtO<sub>2</sub>, 0.045 g.) absorbed 89 ml. of hydrogen at  $18^{\circ}/754$ mm. (1 mole requires 90.5 ml.).

Ozonolysis of the product (1 g.) in dry ethyl acetate (30 ml.) and hydrogenolysis (PtO<sub>2</sub>, 0.036 g.) gave formaldehyde as its dimedone derivative (0.16 g.), m. p. 189°.

1,1-Dibromo-3-ethylidene-2,2-dimethylcyclopropene.-To 2-methylpenta-2,3-diene 9 (8.2 g., 0.1 mole) and dry potassium t-butoxide [prepared from potassium (4 g., 0.1 g.-atom) and t-butyl alcohol (200 ml.)] at 0° bromoform (25.3 g., 0.1 mole) was added dropwise over 30 min. with stirring. The mixture was stirred for a further 2 hr., poured on to ice, extracted with ether  $(3 \times 50 \text{ ml.})$ , dried (MgSO<sub>4</sub>), and fractionated to give 1,1-dibromo-3-ethylidene-2,2-dimethylcyclopropane (12.7 g., 50%), b. p. 39-40°/4 mm. (Found:

\* Prepared from 3-chloro-3-methyloct-1-yne in 71% yield by the Zn-Cu couple method.<sup>9</sup>

C, 33.0; H, 3.9; Br, 62.9.  $C_7H_{10}Br_2$  requires C, 33.0; H, 3.9; Br, 63.0%);  $v_{max}$  1750m, 1000m (cyclopropane ring), 840m ( $\supset$ C=CH-), and 730s cm.<sup>-1</sup>; g.l.c. on dinonyl phthalate on Celite at 120° (nitrogen flow of 1.8 l./hr.) showed one main band (95%) and a small band (5%). The product (0.8 g.) in ethyl acetate (30 ml.) over catalyst (PtO<sub>2</sub>, 0.043 g.) absorbed 92 ml. of hydrogen at 21°/756 mm. (1 mole requires 97 ml.).

Ozonolysis of the product (1.6 g.) in dry ethyl acetate (50 ml.), hydrogenolysis (PtO<sub>2</sub>, 0.051 g.), and distillation gave acetaldehyde as the 2,4-dinitrophenylhydrazone (0.2 g.), m. p. 168°.

4-Methylpenta-1,2-3-triene.—(a) To n-butyl lithium [from lithium wire (0.6 g., 0.1 g.-atom), n-butyl bromide (6.8 g., 0.05 mole)] at  $-40^{\circ}$  a solution of 1,1-dibromo-2,2-dimethyl-3-methylenecyclopropane (12.0 g., 0.05 mole) in ether (25 ml.) was added dropwise over 15 min., the temperature being maintained below  $-30^{\circ}$ . The mixture was stirred for 15 min. at  $-30^{\circ}$ , and then slowly allowed to warm to 30°. Distillation in vacuo gave a product which was collected in a cold trap  $(-\,40^\circ)$  and then redistilled under nitrogen at atmospheric pressure to give 4-methylpenta-1,2,3-triene b. p. 56-58° in ether; g.l.c. on 10% silicone-Celite at 21° (hydrogen at a pressure of 9 atmosphere) gave two peaks  $t \ 3 \ \min$ . (50%) ether,  $t \ 9 \ \min$ . (50%) cumulene. The yield of cumulene by g.l.c. was *ca*. 3 g. (75%);  $\nu_{max}$  2080s (C=C=C=C), 820 (broad) cm.<sup>-1</sup>;  $\lambda_{max}$ . (n-hexane) 220 (ε 3500), 254 (ε 13,000), 294 mµ (ε 700). The product (ca. 0.5 g., 0.006 mole) in ether over a catalyst (PtO<sub>2</sub>, 0.158 g.) absorbed hydrogen (530 ml. 0.023 mole). Distillation gave 2-methylpentane (b. p. 60°) in ether identified by comparing with an authentic sample on g.l.c. [silicone oil, 16° (nitrogen flow 2 l./hr.), t 9 min.] and infrared spectra.

(b) Using the same procedure 1,1-dichloro-2,2-dimethyl-3-methylenecyclopropane (3.8 g., 0.025 mole) gave 4-methylpenta-1,2,3-triene (1.4 g., 70%).

4-Methylhexa-1,2,3-triene.—(a) To n-butyl lithium [from lithium wire (0.6 g., 0.1 g.-atom) and dry n-butyl bromide (6.9 g., 0.05 mole)] in ether (10 ml.) at  $-40^{\circ}$  a solution of 1,1-dibromo-2-ethyl-2-methyl-2-methylenecyclopropane (12.7 g., 0.05 mole) in ether (25 ml.) was added dropwise over 15 min. the temperature being maintained below  $-30^{\circ}$ . The mixture was stirred for 15 min. at  $-30^{\circ}$  then slowly allowed to warm up to 30°, distilled in vacuo and the product collected in a cold trap (at  $-40^{\circ}$ ). Redistillation under nitrogen at atmospheric pressure gave 4-methylhexa-1,2,3-triene, b. p. 65-68° containing ether; g.l.c. on 10% silicone-Celite at 22° (nitrogen flow of 21./hr.) gave two components t 3 min. (60%) ether, and t 28 min. (40%) cumulene. The yield by g.l.c. was ca. 3.7 g., 75%;  $v_{max}$ . 2080 (C=C=C), 820 (broad) cm.<sup>-1</sup>;  $\lambda_{max}$ . 218 ( $\epsilon$  7700), 256 ( $\epsilon$  16,000), 294 m $\mu$  ( $\epsilon$  900). The product (1 g., 0.012 mole) in ether over a catalyst (PtO<sub>2</sub>, 0.140 g.) absorbed hydrogen (595 ml., 0.27 mole). Distillation gave 3-methylhexane identified by comparison with an authentic sample on g.l.c. [silicone oil, 16° (nitrogen flow 21./hr.), t 27 min.] and infrared spectra.

(b) Using the same procedure, 1,1-dichloro-2-ethyl-2-methyl-3-methylenecyclopropane (4·1 g., 0·025 mole) and n-butyl lithium [from lithium wire (0·3 g., 0·05 g.-atom) and n-butyl bromide (3·4 g., 0·025 mole)] gave 4-methylhexa-1,2,3-triene (1·8 g., 73%).

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