Anal. Calcd. for $C_{13}H_9BrN_2$: C, 57.16; H, 3.32; Br, 29.26; N, 10.26. Found: C, 57.33; H, 3.43; Br, 29.18; N, 10.20.

The infrared spectrum (Nujol) showed bands at 2245 (C≡N), 1603, 1567, 1543 (C=C), and 735 cm^{-1} (1,2-disubstituted benzene). The ultraviolet spectrum (ethanol) had λ_{max} at 322.5 mμ (ε 16,740) and 235 mμ (ε 6830). The nmr spectrum (in DMSO-d_6) had bands at τ 7.55 (m, 2), 6.94 (m, 2), 4.36 (t, J = 3.6 cps, 1), 2.47, and 1.73 (m, 4).

The same product was obtained in 48% yield when 10 mmoles of XLI, 30 mmoles of bromomalononitrile, and 70 ml of 95% ethanol were allowed to stand at room temperature for 2 weeks. It was also obtained, in 68.4% yield, when 5.2 mmoles of XLI and 20.8 mmoles of ethyl bromocyanoacetate in 50 ml of 95% ethanol were refluxed for 10 hr.

Reaction of 2,3-Benzocyclopentylidenemalononitrile (XLII) with Bromomalononitrile.—A mixture of 1 g (5.55 mmoles) of XLII, 100 ml of 95% ethanol, and 10 ml of water was heated to effect solution. Bromomalononitrile (3 g, 20.7 mmoles) was added, and the mixture was refluxed for 6 hr, during which time a precipitate formed. Cooling and filtration gave a small (about 10%) yield of a product believed to be 5,5-dibromo-2,3-benzocyclopentylidenemalononitrile (LIV), mp 208–211° (from acetone).

Anal. Calcd for $C_{12}H_6Br_2N_2$: C, 42.64; H, 1.79; Br, 47.28; N, 8.29. Found: C, 42.72; H, 1.52; Br, 47.65; N, 8.11.

The infrared spectrum (Nujol) had bands at 2240 (C≡N), 1599, 1568 (C=C), and 790 cm^{-1} (arom). The ultraviolet spectrum (ethanol) had λ_{max} at 346 mμ (ε 15,730), 337 mμ (ε 15,860), and 236 mμ (ε 7140). A suitable solvent for an nmr spectrum could not be found.

Reaction of Bromomalononitrile with Ethanol.—A solution of 5 g (34.5 mmole) of bromomalononitrile in 15 ml of 90% ethanol was refluxed for 8 hr, then evaporated to dryness. Water (30 ml) was added to the dark residue, and the mixture was cooled in an ice bath. The crystals which separated were treated with Norit A and recrystallized from ethanol, giving 0.2 g (8.4%) of 1,1-dicyano-2-amino-2-ethoxyethene (LVI), mp 235–237°.

Anal. Calcd for $C_6H_7N_3O$: C, 52.55; H, 5.15; N, 30.64. Found: C, 52.71; H, 5.07; N, 30.73.

The infrared spectrum (Nujol) had bands at 3355, 3230 (N-H), 2248, 2205 (C≡N), 1658, 1550, and 1503 cm^{-1} (C=C and/or N-H). The ultraviolet spectrum (ethanol) had a single λ_{max} at 253 mμ (ε 18,640). The nmr spectrum (in DMSO-d_6) had bands at τ 8.71 (t, J = 7.0 cps, 3), 5.72 (q, J = 7.0 cps, 2), and 1.45 (s, 2).

Acknowledgement.—We are indebted to the National Institutes of Health for a grant (GM11775) which supported this research.

Chemistry of *gem*-Dihalocyclopropanes. V.[1] Formation of Tricyclo[4.1.0.0^{4,6}]heptane and Derivatives

LARS SKATTEBØL

Union Carbide Research Institute, P. O. Box 278, Tarrytown, New York

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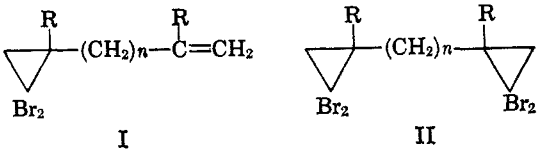
Reactions of 2-alkenyl-1,1-dibromocyclopropane (I) and bis(1,1-dibromocyclopropyl)alkane (II) with methyllithium have been studied. The corresponding allenes and diallenes were obtained from compounds I and II, respectively. In addition, from reactions of I (n = 2) and II (n = 2), the highly strained novel compound tricyclo[4.1.0.0^{4,6}]heptane and derivatives were obtained. These are probably formed by an intramolecular addition of a complexed carbene (carbenoid) intermediate.

Since the first allenic compound, *viz.*, allene itself, was synthesized one-hundred years ago[2] several methods for the preparation of this class of compounds have become available. Some of these methods are quite impractical because mixtures with the corresponding acetylenes and other isomers are frequently encountered. On the basis of prior work by Doering and LaFlamme,[3] a two-step synthesis of allenes from olefins was developed independently in this laboratory[4] and by Moore and co-workers.[5] The first step involves the preparation of *gem*-dibromocyclopropanes from olefins and dibromocarbene;[6,7] the addition of methyllithium to the bromides at temperatures between −78 and 0° gives, in a number of examples, allenes in excellent yields. This method has several advantages: olefins as starting materials, lenient reaction conditions, and the absence of acetylenic by-products being the most important. It is also the only practical method for the preparation of cyclic allenes. Hence, it was of interest to establish the generality of the reaction as a method for allene synthesis, and the present work[8] describes reactions of compounds of the general structures I and II where n >0. The expected allenes and diallenes would belong to a virtually unknown structural type.



I II

R=H or CH_3

The compounds to be studied became available by the addition of dibromocarbene to dienes,[9] and their reactions with methyllithium were carried out as already described.[4] The results from reactions of compounds of the general structure I are summarized in Table I.

As seen in Table I, all reactions afforded allenes and, except in the case of XIII, they constituted the main part of the reaction products. In those cases where the product consisted of a mixture the pure components were obtained by fractional distillation or preparative gas chromatography. Characterization of the allenes presented no difficulties. Besides elemental analysis the structures were assigned on the basis of

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[1] Part IV: L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

[2] For a comprehensive review on allenes, see A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, 1 (1964).

[3] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

[4] L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta. Chem. Scand.*, **17**, 1683 (1963).

[5] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962); W. R. Moore, H. R. Ward, and R. F. Merrit, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

[6] W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

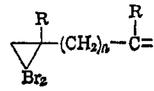
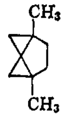
[7] For a review of this reaction, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

[8] Part of this investigation has appeared as a preliminary communication: L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

[9] L. Skattebøl, *J. Org. Chem.*, **29**, 2951 (1964).

TABLE I

REACTIONS OF *gem*-DIBROMOCYCLOPROPANE DERIVATIVES WITH METHYLLITHIUM

 (I)	Reaction temp, °C	Products (% of total product)	Structure		Yield, %
R = H, n = 1; III	−78	1,2,5-Hexatriene, IV			46[a]
R = H, n = 2; V	−78	1,2,6-Heptatriene, VI (52)		VII (48)	85
	−30	(70)		(30)	
	0	(84)		(16)	
R = H, n = 3; VIII	−78	1,2,7-Octatriene, IX (90)	 [b]	X (10)	85
R = H, n = 4; XI	−78	1,2,8-Nonatriene, XII			80
R = CH_3, n = 2; XIII	−78	3,6-Dimethyl-1,2,6-heptatriene, XIV (38)		XV (62)	88

[a] The other product was polymeric material. [b] Not obtained pure.

spectroscopic evidence and in some cases also by identification of the hydrogenation product. The infrared spectrum in each case exhibited a strong sharp band in the 1950-cm^{-1} region, characteristic of the C=C stretching vibration of an allenic system, and also a strong band in the 850-cm^{-1} region, the out-of-plane bending vibration of the allenic hydrogens. Proof for the presence of vinyl or methylene double bonds was also obtained from the infrared spectrum, and in all the allenes only end absorption was observed in the ultraviolet. The nmr spectra confirmed the assigned structures. In addition to these conventional methods the near-infrared spectra were also obtained. It is well established[10] that the first overtones of the C–H stretching vibrations of olefinic methylene, cyclopropyl methylene, and oxirane methylene groups are generally observed in the 1.62–1.64-μ region. To our knowledge the absorption of allenes in this region had not previously been studied, and it was of some interest to see whether this band would be significantly shifted from that of a normal terminal double bond.

TABLE II

NEAR-INFRARED ABSORPTION OF ALLENES[a]

Compound	λ_{max}, μ	ε
3-Methyl-1,2-butadiene	1.646	0.74
	1.654	0.47
1,2-Nonadiene	1.643	0.77
VI	1.636	0.54
	1.642	0.96
IX	1.636	0.52
	1.642	0.86
XII	1.636	0.51
	1.643	0.88
XIV	1.636	0.42
	1.647	0.80
	1.654	0.47
XXII	1.642	. . .
XXVI	1.647	1.31
	1.654	0.81

[a] CCl_4 was used as solvent; a slit opening of 0.4–0.5 mm was used.

In all the compounds of Table II the band due to the terminal allenic hydrogens appears rather constantly at 1.642–1.647 μ and in the case of disubstituted derivatives an additional band appears at 1.654 μ. The band at 1.636 μ is at the normal wavelength and intensity for a terminal double bond of a hydrocarbon.[11] It is also worth noting that the allenic absorption is of considerably higher intensity. Thus the near-infrared spectrum may serve as additional evidence for the presence of a terminal allenic grouping, and though more data are needed, it may also distinguish between mono- and disubstituted compounds of this class.

The elucidation of the structures of the nonallenic products proved considerably more difficult. The saturated hydrocarbon obtained from the reaction of 1,1-dibromo-2-(3-butenyl)cyclopropane (V) and methyllithium at −78° was assigned the structure tricyclo[4.1.0.0^{4,6}]heptane (VII) mainly on the basis of spectroscopic properties and hydrogenation results. The compound, bp 107–108°, reacted with bromine, but showed only end absorption in the ultraviolet and the absence of double-bond vibrations in the infrared spectrum. The latter, however, exhibits strong C–H stretching vibrations at 3043 and 3012 cm^{-1}, which indicate that a cyclopropane ring is present. This is further substantiated by strong bands at 1013 and 1047 cm^{-1}, the expected region for the cyclopropane ring deformation vibration, and by a near-infrared band at 1.656 μ. In Table III the latter absorption band is compared with those of a number of related cyclopropane derivatives. This absorption has been extensively studied in recent years.[12,8] The intensity of the bands is practically proportional to the number of cyclopropyl methylene groups, the same relation as found for terminal oxiranes;[11] increased ring strain seems to shift the band to higher wavelength. The nmr spectrum of the hydrocarbon is rather complex and, although in agreement with the tricyclic structure, it does not provide conclusive evidence. A triplet at τ 8.62 is assigned to the cyclopropyl methine hydrogens, whereas the other hydrogens give rise to complex multiplets centered at τ 9.04 and 8.17. The peak area ratio is 2:2:6, respectively.

The mass spectrum exhibits a parent peak at m/e 94. By far the most intense peak, however, appears at

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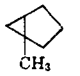
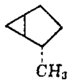
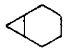
[10] For references, see R. F. Goddy in "Advances in Analytical Chemistry and Instrumentation," Vol. I, C. N. Reilley, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 347–424.

[11] S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961), and references therein.

[12] W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); P. G. Gassman, *Chem. Ind.*, 740 (1962); H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966); H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *ibid.*, **31**, 295 (1966).

TABLE III

NEAR-INFRARED ABSORPTION OF CYCLOPROPANE DERIVATIVES[a]

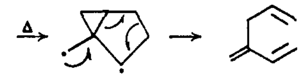
Compound	λ_{max}, μ	ε
 (XVI)	1.647	0.30
 (XVII)	1.644	0.34
	1.646	0.31
	1.644	1.20
VII	1.656	0.63
XV	1.659	0.63
XX	1.637	0.33
	1.656	0.66
XXVII	1.638	0.35
	1.656	0.70

[a] CCl_4 was used as solvent; a slit opening of 0.4–0.5 mm was used.

m/e 79, attributed to the cyclohexadienyl ion which is formed from the parent ion by loss of a methyl radical. Elimination of hydrogen from this ion leads to the phenyl cation, *m/e* 77. Another fragmentation process involves the loss of a hydrogen atom from the parent ion producing the methylcyclohexadienyl ion, *m/e* 93, which is transformed to the tropylium ion, *m/e* 91, by subsequent elimination of hydrogen. Except for the parent peak, these peaks are the most intense in the spectrum; strong peaks also appear at *m/e* 66, 53, and 40. The metastable ion corresponding to each of the fragmentation steps above has been identified, and the results are compatible with a parent ion produced by fission of the C-1–C-7 bond. In the mass spectra of the related compounds, 1- (XVI) and 2-methylbicyclo[3.1.0]hexane (XVII), the strongest peak appears at *m/e* 81, the cyclohexenyl cation; the fragmentation is almost identical with that of methylcyclohexene.

Hydrogenation of compound VII in ethanol at room temperature over a Pd–C catalyst proceeded quite rapidly until approximately 1 mole of hydrogen was absorbed. Gas chromatographic analysis of the product revealed the presence of seven compounds. These were only partly separated by preparative gas chromatography, but four of the compounds have been identified with certainty as XVI, XVII, 1-methylcyclohexene, and toluene by comparison of infrared spectra and retention times with those of authentic samples. The bicyclic compounds XVI and XVII were prepared from the corresponding olefins using the zinc–methylene iodide method.[13] The four compounds constitute about 80% of the total product. In ether solution and with PtO_2 catalyst[14] the hydrogenation gave three compounds in yields of 13, 63, and 24%. The two last components were separated and shown to be the bicyclic compounds XVI and XVII, respectively. These two compounds are expected[15] hydrogenation products of compound VII, the former probably formed by ring opening prior to hydrogenation and the latter by hydrogenolysis. As anticipated,[15] the Pd–C catalyst caused more isomerization than PtO_2; the use of ether as solvent may also play a role.[14] 1-Methylcyclohexene and toluene were both conceivably formed by initial isomerization to 1-methyl-1,3-cyclohexadiene followed by disproportionation, although the former could also have been formed directly. In any case, the hydrogenation results provide clear evidence for structure VII.

When the vapor of the hydrocarbon was passed through a tube kept at 250° one compound was formed in practically theoretical yield. It was subsequently identified as 3-methylene-1,5-hexadiene, a compound previously obtained by the thermally induced isomerization of the allene VI.[16] The formation of this triene is most readily explained on the assumption that a biradical intermediate is involved, which subsequently rearranges through other biradicals or in a concerted process to the triene.

VII 

It was now quite simple to prove the structure of the hydrocarbon obtained from 1,1-dibromo-2-methyl-2-(3-methyl-3-butenyl)cyclopropane (XIII) and methyllithium as 1,4-dimethyltricyclo[4.1.0.0^{4,6}]heptane (XV). It was separated from the allene XIV by fractional distillation. The spectral properties are similar to those of compound VII, but the nmr spectrum in this case provides conclusive structural proof. The methyl groups appear as a singlet at τ 8.98, the cyclopropyl hydrogens give rise to a quadruplet, a characteristic AB pattern at τ 8.58, and the other hydrogens show a multiplet centered at τ 8.20; the peak area ratio is 3:2:2, respectively. The minor product from 1,1-dibromo-2-(4-pentenyl)cyclopropane (VIII), however, could not be completely separated from the accompanying allene even by preparative gas chromatography. Attempts to convert the allene into higher-boiling compounds and subsequently isolate the desired compound by distillation were unsuccessful. On the basis of the infrared spectrum of enriched fractions and by analogy with the results from the reactions described above, it seems reasonable that the compound has the structure tricyclo[5.1.0.0^{5,7}]octane (X).

It is interesting to note that the relative amounts of the isomers formed are dependent on the reaction conditions. The reaction temperature, in particular, is of considerable significance; the amount of nonallenic compounds increases with decreasing temperature as demonstrated in the case of compound VII. It appears that concentrations and rate of addition also influence the isomer distribution, resulting in poor reproducibility. The isomer yields recorded in Table I represent the best as far as the nonallenic compounds are concerned, and they were generally obtained by slow addition of approximately 1 M methyllithium solutions.

The diadducts II reacted with methyllithium in a similar way. The results, recorded in Table IV, show that diallenes were in all cases the main products, and isomers were encountered only from reactions of II, $n = 2$. The diallenes, except for being considerably less stable, show normal allenic properties; very strong bands are present at 1960 and 845 cm^{-1} in the infrared

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(13) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

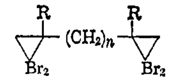
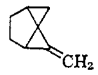
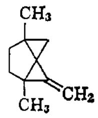
(14) G. Chiurdoglu and B. Tursch, *Bull. Soc. Chim. Belges*, **66**, 600 (1957).

(15) A. L. Liberman, *Russian Chem. Rev.*, 237 (1961).

(16) L. Skattebøl and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965).

TABLE IV

REACTIONS OF α,ω-BIS(2,2-DIBROMOCYCLOPROPYL)ALKANE WITH METHYLLITHIUM

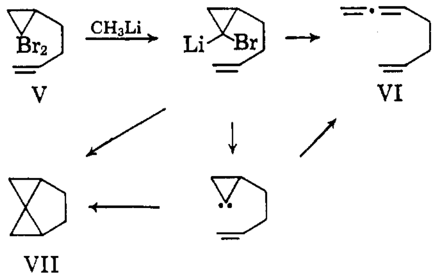
 (II)	Products, % of mixture			Yield, %
		Structure		
R = H, n = 2; XVIII	1,2,6,7-Octatetraene, XIX (68)		XX (28)[a]	71
R = H, n = 3; XXI	1,2,7,8-Nonatetraene, XXII			83
R = H, n = 4; XXIII	1,2,8,9-Decatetraene, XXIV			86
R = CH_3, n = 2; XXV	3,6-Dimethyl-1,2,6,7-octatetraene, XXVI (50)[b]		XXVII (50)[b]	78

[a] In addition 4% of a third compound was present. [b] Approximate values based on fractionation.

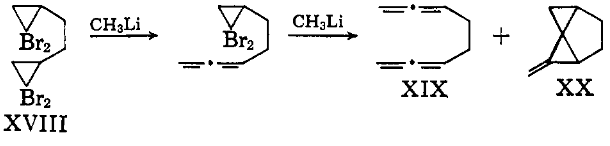
spectrum and only end absorption is observed in the ultraviolet.

The product obtained from 1,2-bis(2,2-dibromocyclopropyl)ethane (XVIII) and methyllithium consisted essentially of two compounds. The major component was obtained pure by preparative gas chromatography and subsequently identified as the diallene XIX. The other compound partially decomposed on the column and we were not able to obtain a pure sample. Knowing the infrared spectrum of the diallene, it was possible to recognize the most characteristic absorption bands. Before discussing their assignments, however, it seems advantageous to describe the products from a similar reaction of 1,2-bis(2,2-dibromo-1-methylcyclopropyl)ethane (XXV). In this case also two compounds were obtained, but separation was achieved after several fractional distillations; gas chromatography resulted in partial decomposition. One of the components was readily identified as the diallene XXVI. The other component shows infrared bands at 1760 and 855 cm^{-1}, the latter of very high intensity, which have been assigned the C=C stretching and C-H out-of-plane bending vibrations, respectively, of a methylene double bond attached to a cyclopropane ring.[17] An additional band at 1720 cm^{-1} is most probably an overtone of the bending vibration. The near-infrared maxima at 1.638 and 1.656 μ are characteristic of the CH_2 group of a methylene double bond and a strained spiropentane derivative, respectively (see Table III). These data suggested the structure 5-methylene-1,4-dimethyltricyclo[4.1.0.$0^{4,6}$]heptane (XXVII), which was confirmed by its nmr spectrum. Two singlets of equal intensity appear at τ 4.89 and 5.14, due to the olefinic protons. The methyl groups give rise to a singlet at τ 8.9 and the cyclopropyl and cyclopentyl protons show complex absorption in the τ 7.5–8.4 region. The peak area ratio is 1:1:6:6, respectively. In the ultraviolet spectrum a maximum at 206 mμ (ϵ 11,400) is present, while the parent compound methylenecyclopropane exhibits only end absorption at 200 mμ. The bathochromic shift observed could be explained on the basis of Walsh's π-electron description of cyclopropane.[18] If there exists an interaction in the ground state between the π electrons of the ring and those of a double bond,[19] it should be at its maximum in the present case since the said electrons are rigidly kept in the same plane. Unfortunately, catalytic hydrogenation gave a complex mixture from which no additional evidence could be obtained. By analogy it was thus assumed that the minor product from the reaction of XVIII would be 5-methylenetricyclo[4.1.0.$0^{4,6}$]heptane (XX), and infrared absorption at 1770, 1730, and 860 cm^{-1} strongly supports the assignment. Further evidence is provided by the near-infrared absorption (Table III).

As previously discussed,[4,5] it is probable that the reaction of *gem*-dibromocyclopropanes with methyllithium initially results in metal–halide exchange forming a 1-lithio-1-bromocyclopropane derivative. This could yield the corresponding allene either directly or through a carbene-like intermediate. The spiropentanes could also conceivably derive from either of these species as visualized in the example below.



In a similar fashion the products from the diadducts can be explained. Little is known about the reactive



intermediates besides that they must be different from a *free* carbene.[20] This is demonstrated by the fact that

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[17] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

[18] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949). Although controversial, this picture still provides the best explanation for the unsaturated nature of the cyclopropane ring.

[19] L. S. Bartell and J. P. Guillory [*J. Chem. Phys.*, **43**, 647 (1965)] have recently shown by electron diffraction that in cyclopropyl carboxaldehyde the HCO plane bisects the cyclopropane ring, the ideal conformation for maximum π-electron interaction according to Walsh's description. Similar results have also been obtained for phenylcyclopropane on the basis of nmr studies; see G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).

[20] For general reviews on carbene chemistry, see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

decomposition of 2,2-diphenylcyclopropyl-N-nitrosourea[21] in the presence of olefins, under conditions known to produce free carbenes, led to spiropentanes, while the reaction of 1,1-dibromo-2,2-diphenylcyclopropane with methyllithium in the presence of the same olefins gave no addition products.[4] Both reactions yielded 1,1-diphenylallene. Two criteria have been extensively quoted as characteristic of carbenes, *viz.*, the addition to double bonds to form cyclopropanes and insertion into σ bonds, particularly the CH bond. In the case of the *gem*-dibromocyclopropane–methyllithium reaction, these criteria found little support. Spiropentanes together with various insertion products were isolated from reactions of 7,7-dibromobicyclo[4.1.0]heptane[5] in the presence of olefins; no allenic compounds were detected. The only other example of apparent insertion was the formation of 1-methyl-1-isopropenylcyclopropane from 1,1-dibromotetramethylcyclopropane.[4] However, the addition reaction is not conclusive evidence for a carbene intermediate since it has been shown that certain metal organic compounds react with olefins yielding cyclopropanes.[13,20] Hence, the fact that spiropentanes were obtained from the present reaction does not shed any light on the mechanism. Whatever the detailed structure of the intermediate, it is most probably electrophilic since a methyl substituent on the double bond resulted in an increased amount of the spiropentane (see Tables I and IV). The influence of the reaction temperature on the product ratio can be explained on the basis of either intermediate.

Some recent work on polyhalomethane–alkyllithium reactions is interesting in this connection. Miller and Whalen[22] have shown that lithiotrichloromethane (XXVIII) is stable below −100°, but upon addition of cyclohexene at −100° dichloronorcarane was formed in high yield. They concluded that the olefin reacts concertedly and as a nucleophile with XXVIII forming the cyclopropane. Work by Köbrich and co-workers[23] does not indicate, however, that the decomposition of XXVIII is accelerated by the addition of olefins. They favor a carbenoid intermediate similar to that suggested by Closs and co-workers.[24,25]

Recently, Hoeg, Lusk, and Crumbliss reported[26] on the preparation and reactions of four α-chlorolithium derivatives, including XXVIII, in tetrahydrofuran. These compounds were stable at −100°, apparently also in the presence of olefins. However, at higher temperatures (−78°) olefins were shown to influence the stability of the α-chlorolithium derivative, as cyclopropanes were formed. A carbenoid intermediate was suggested as responsible for the cyclopropane formation.

Experimental Section[27]

General Procedure.—The 1,1-dibromocyclopropane derivative (0.1 mole) was diluted with 25 ml of dry ether and cooled in a Dry Ice–acetone bath kept at −78°. An ethereal solution of methyllithium (0.12 mole) was added dropwise with stirring during 30 min. The reaction mixture was further stirred for 30 min and then water was added. The ether layer was separated and the aqueous phase extracted with a small amount of ether. The combined ether solutions were washed with water until neutral and dried over magnesium sulfate. The ether was distilled through a spinning-band column and the residue was fractionated through the same column. The reaction was carried out both on a larger and smaller scale with practically the same results.

1,2,5-Hexatriene (IV) was prepared from 1,1-dibromo-2-(2-propenyl)cyclopropane (III)[9] and methyllithium in 46% yield, bp 74°, $n^{25}\text{D}$ 1.4497 (lit.[28] bp 73–73.5°, $n^{20}\text{D}$ 1.4480); $\nu_{\max}$ 1945, 845 cm^{-1} ($-CH{=}C{=}CH_2$) and 1640, 993, 915 cm^{-1} ($-CH{=}CH_2$). The compound is very unstable in air. The distillation residue consisted of polymeric material.

1,2,6-Heptatriene (VI) and Tricyclo[4.1.0.0^{4,6}]heptane (VII).—Reaction of 1,1-dibromo-2-(3-butenyl) cyclopropane (V)[9] and methyllithium gave a liquid in 85% yield, bp 58–60° (150 mm), $n^{24}\text{D}$ 1.4500–1.4570.

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 88.93; H, 10.78.

The liquid consisted of two compounds in almost equal amounts as shown by glpc analysis on a 3-m squalane column at 100°. The compounds were separated by preparative glpc. The lower-boiling compound was shown to be the allene VI, bp 104°, $n^{24}\text{D}$ 1.4523; $\nu_{\max}$ 1950, 845 cm^{-1} ($-CH{=}C{=}CH_2$) and 1640, 395, 913 cm^{-1} ($C{=}CH_2$); near-infrared data are recorded in Table II.

Hydrogenation of an ethanol solution of the allene VI over a 5% Pd–C catalyst gave *n*-heptane.

The higher-boiling isomer was shown to be the cyclic compound VII, bp 108°, $n^{25}\text{D}$ 1.4652.

Hydrogenation.—(a) The hydrocarbon VII (1.88 g, 20 mmoles) in 50 ml of ether was hydrogenated at 25° over 250 mg of PtO_2. The reaction stopped after 1.1 moles of hydrogen had been consumed. The catalyst was filtered, and the ether was partially distilled through a column. Analysis of the residue by glpc on a 6-ft Carbowax column at 70° revealed the presence of three components in 13, 63, and 24%, respectively. The last two compounds were trapped, and the major one was shown to be 1-methyl bicyclo[3.1.0]hexane (XVI), $n^{24}\text{D}$ 1.4310, by comparison with an authentic sample. In the same manner the other compound was identified as a stereoisomeric mixture of 2-methylbicyclo[3.1.0]hexane (XVII), $n^{24}\text{D}$ 1.4362. (b) Hydrogenation of an ethanol solution of VII over a 5% Pd–C catalyst also proceeded readily at room temperature. Analysis of the product by glpc on a 3-m squalane column at 70° showed that at least seven compounds were present; the major components, compounds XVI (43%), XVII (15%), 1-methylcyclohexene (15%), and toluene (10%), were trapped and identified by comparison with authentic samples.

Pyrolysis.—The hydrocarbon VII (0.94 g, 10 mmoles) was passed at 20-mm pressure through a tube packed with Pyrex wool and kept at 250°. After 1 hr, 0.87 g (93%) of 3-methylene-1,5-hexadiene had been collected. The compound was pure as indicated by glpc analysis on a 6-ft Carbowax column at 70°, and in all respects identical with an authentic sample.[16]

1-Methylbicyclo[3.1.0]hexane (XVI).—A mixture of 18 g of zinc-copper complex,[29] 53.6 g (0.2 mole) of methylene iodide and 0.15 g of iodine in 165 ml of dry ether was heated under reflux for 30 min. To the stirred mixture was added dropwise in the course of 30 min 28.5 g (0.35 mole) of 1-methylcyclopentene.[30] The mixture was then heated under reflux and with stirring for 58 hr. The ether solution, obtained after filtration, was washed with dilute hydrochloric acid and dried (Na_2SO_4). Fractionation through a column gave 9.6 g (50%) of (XVI), bp 95°, $n^{24}\text{D}$ 1.4310; $\nu_{\max}$ 3065, 3025, 2995 cm^{-1} (cyclopropyl CH) and 1012 cm^{-1} (cyclopropane ring deformation). The nmr spectrum shows multiplets centered at τ 9.78 and 9.17 (cyclopropyl protons),

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(21) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960); W. M. Jones, M. H. Grasley, and W. S. Brey, *ibid.*, **85**, 2754 (1963).

(22) W. T. Miller and D. M. Whalen, *ibid.*, **86**, 2089 (1964).

(23) G. Köbrich, H. R. Merkle, and H. Trapp, *Tetrahedron Letters*, 969 (1965); G. Köbrich, K. Flory, and H. R. Merkle, *ibid.*, 973 (1965).

(24) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962); G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(25) The transition state of the reaction of this intermediate with the olefin will resemble that suggested for the Simmons–Smith reaction.[13]

(26) D. G. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

(27) Boiling points and melting points are uncorrected. The infrared spectra were obtained on a Beckman IR-5A and IR-10 spectrometer. The ultraviolet spectra were measured in *n*-heptane solution, when not otherwise stated, on a Cary Model 14 spectrometer. The nmr spectra were recorded on a Varian A-60 instrument with carbon tetrachloride as solvent and tetramethylsilane as internal standard. The chemical shifts are given in τ values. Preparative-scale gas chromatographic separations were carried out with a Wilkins Autoprep Model A 700 instrument.

(28) G. Peiffer, *Bull. Soc. Chim. France*, 776 (1962).

(29) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(30) G. A. Lutz, A. E. Bearse, J. E. Leonard, and F. C. Croxton, *J. Am. Chem. Soc.*, **70**, 4139 (1948).

singlet at 8.82 ($-CH_3$), and multiplet at 8.43 ($-CH_2-$), with area ratio of 2:1:3:6, respectively. The near-infrared spectrum is recorded in Table III.

Anal. Calcd for C_6H_{12}: C, 87.42; H, 12.58. Found: C, 87.16; H, 12.45.

2-Methylbicyclo[3.1.0]hexane (XVII).—Reaction of 3-methylcyclopentene[31] with methylene iodide and zinc–copper complex, in the way described above gave XVII in 31% yield, bp 102–103°, $n^{24}D$ 1.4362; the infrared spectrum is similar to that of XVI, although two bands at 1012 and 1025 cm^{-1} suggest the presence of a mixture of stereoisomers; no separation of these by glpc was achieved. The nmr spectrum, however, confirms that the product is a mixture of stereoisomers; the methyl protons give rise to two identical doublets, $J = 6.5$ cps, centered at 9.03 and 9.10. The other protons give rise to complex absorption between 7.65 and 10.0. The near-infrared data are given in Table III.

Anal. Calcd for C_6H_{12}: C, 87.42; H, 12.58. Found: C, 87.78; H, 12.30.

1,2,7-Octatriene (IX) and Tricyclo[5.1.0.0^{5,7}]octane (X).—The reaction of 1,1-dibromo-2-(4-pentenyl)cyclopropane (VIII)[9] with methyllithium yielded 80% of a liquid, bp 64–65° (100 mm), $n^{25}D$ 1.4543.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.89; H, 11.05.

Glpc analysis on a 3-m squalane column at 130° revealed two isomers present in a 9:1 ratio. The major component was obtained pure by preparative glpc, and identified as the allene IX, bp 64° (100 mm), $n^{25}D$ 1.4540; ν_{max} 1950, 840 cm^{-1} ($-CH{=}C{=}CH_2$) and 1640, 992, 912 cm^{-1} ($-CH{=}CH_2$). Only an enriched sample of the minor component was obtained; however, the presence of strong infrared bands in the 3000–3030-cm^{-1} region, at 1025 (cyclopropane) and 762 cm^{-1} indicated that the compound had the tricyclic structure X. Not enough material was available for hydrogenation.

1,2,8-Nonatriene (XII) was prepared from 1,1-dibromo-2-(5-hexenyl)cyclopropane (XI)[9] and methyllithium in 80% yield, bp 65–66° (30 mm), $n^{24}D$ 1.4566; ν_{max} 1960, 840 cm^{-1} ($-CH{=}C{=}CH_2$) and 1640, 994, 911 cm^{-1} ($-CH{=}CH_2$); near-infrared data are given in Table II.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.25; H, 11.50.

3,6-Dimethyl-1,2,6-heptatriene (XIV) and 1,4-Dimethyltricyclo[4.1.0.0^{4,6}]heptane (XV).—Reaction of 1,1-dibromo-2-methyl-2-(3-methyl-3-butenyl)cyclopropane (XIII)[9] with methyllithium gave a liquid in 88% yield, bp 55–65° (50 mm), $n^{24}D$ 1.4497–1.4606.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 87.78; H, 11.55.

Analysis by glpc on a 6-ft Carbowax column at 77° revealed two compounds present in a 62:38 ratio. These were separated by fractional distillation through a 40-cm spinning-band column. The major component was identified as XV, bp 57° (55 mm), $n^{25}D$ 1.4490; ν_{max} 3030 (cyclopropyl hydrogens) and 1042, 1025 cm^{-1} (cyclopropane); the near-infrared data are recorded in Table III.

The minor component was the allene XIV, bp 59° (30 mm), $n^{25}D$ 1.4605; ν_{max} 1960, 845 cm^{-1} ($-C{=}C{=}CH_2$) and 1650, 886 cm^{-1} ($-C{=}CH_2$). The nmr spectrum shows a 2:5 peak area ratio of olefinic to saturated protons. The methylene protons of the double bond give rise to a weakly coupled, $J < 1$ cps, multiplet at 5.37 and the corresponding allenic protons show a multiplet at 5.47. The saturated methylene protons give rise to a doublet at 7.83 and the methyl protons exhibit a multiplet at 8.32.

1,2,6,7-Octatetraene (XIX) and 5-Methylenetricyclo[4.1.0.0^{4,6}]heptane (XX).—Reaction of 1,2-bis(2,2-dibromocyclopropyl)ethane[9] with methyllithium afforded a liquid in 71% yield, bp 48–50° (25 mm), $n^{24}D$ 1.5030–1.5055.

Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.65; H, 9.57.

Glpc analysis on a 6-ft Carbowax column at 125° revealed three components present in a 68:28:4 ratio. The major component was obtained pure by preparative glpc and proved to be the diallene XIX, $n^{25}D$ 1.4950; ν_{max} 1960, 845 cm^{-1} ($-CH{=}C{=}CH_2$). The second compound decomposed partly on the column. Infrared bands at 1770, 1730, and 860 cm^{-1}, characteristic of a methylenecyclopropane, suggest the structure XX for this compound. The near-infrared spectrum (Table II) is in agreement with this assignment. The minor compound, which may be a result of decomposition, was not isolated.

1,2,7,8-Nonatetraene (XXII) was prepared from 1,3-bis(2,2-dibromocyclopropyl)propane (XXI)[9] and methyllithium in 83% yield, bp 54–55° (10 mm), $n^{23}D$ 1.4920; ν_{max} 1960 and 840 cm^{-1} ($-CH{=}C{=}CH_2$); the near-infrared absorption is recorded in Table II.

Anal. Calcd for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.98; H, 10.00.

1,2,8,9-Decatetraene (XXIV) was prepared from 1,4-bis(2,2-dibromocyclopropyl)butane (XXIII)[9] and methyllithium in 86% yield, bp 59° (5 mm), $n^{23}D$ 1.4892; ν_{max} 1960 and 840 cm^{-1} ($CH{=}C{=}CH_2$).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.52; H, 10.16.

3,6-Dimethyl-1,2,6,7-octatetraene (XXVI) and 1,4-Dimethyl-5-methylentricyclo[4.1.0.0^{4,6}]heptane (XXVII).—Reaction of 1,2-bis(2,2-dibromo-1-methylcyclopropyl) ethane (XXV),[9] mp 128°, with methyllithium at −78° gave by fractional distillation through a 40-cm spinning-band column 32% of the tricyclic compound XXVII, bp 55–56° (35 mm), $n^{25}D$ 1.4777, and 30% of the diallene XXVI, bp 60° (10 mm), $n^{25}D$ 1.4900; ν_{max} 1960, 845 cm^{-1} ($C{=}C{=}CH_2$); the near-infrared absorption is recorded in Table II; the nmr spectrum exhibits a triplet at 8.37 (CH_3), quintet at 8.01 (CH_2), and multiplet at 5.46 ($=CH_2$) with a peak area ratio of approximately 3:2:2. Taking into account intermediate fractions, the total yield was 72%. Both compounds underwent partial decomposition on attempted glpc analysis. The other isomer of XXV,[9] mp 63°, underwent the same reaction in 78% yield and with practically the same ratio of XXVI to XXVII.

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[31] G. Crane, C. E. Boord, and A. L. Henne, *ibid.*, **67**, 1237 (1945).