ACTA CHEMICA SCANDINAVICA 17 (1963) 1683–1693

The Synthesis of Allenes from 1,1-Dihalocyclopropane Derivatives and Alkyllithium

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A number of 1,1-dibromocyclopropane derivatives react with either butyllithium or methyllithium to give allenes in good yields. The dichloro analogs react similarly with butyllithium but no reaction has been observed with methyllithium under the same conditions. In some cases when the product consists of a mixture of isomers, this can readily be explained by assuming a carbene intermediate in the reaction.

Despite the fact that compounds containing cumulated double bonds, *viz.* allenes and cumulenes, have been known for several decades, until recently comparatively little was known about their chemical behaviour. In the case of the allenes this may partly be explained by the fact that no convenient general method for their preparation has been found[1]. The best route so far is probably that starting from the readily available α-acetylenic alcohols which by halogenation and subsequent reduction with zinc[2] or lithium aluminum hydride[3] yield allenes usually contaminated with acetylenic derivatives. We have for some time been interested in the synthesis and reactions of compounds with cumulated double bonds and the present work constitutes a way of preparing allenes starting from the corresponding ethylenic derivatives[4].

Recently Doering and La Flamme[5] reported a reaction of 1,1-dibromocyclopropanes with magnesium or highly dispersed sodium which leads to allenes in reasonable yields, contaminated with acetylenes and cyclopropanes[6]. With this interesting work in view it seemed promising to try reactions of these halides with alkyllithium compounds, and we actually found that 1,1-dibromocyclopropanes react rapidly with both butyl- and methyllithium even at $-78°$. The characteristic infrared absorption of the product in the 1950 cm^{-1} region showed that allenes had been formed.

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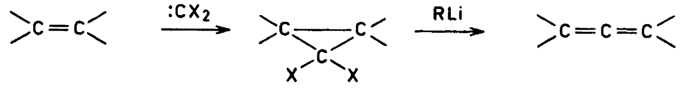


X = Cl or Br

I

gem. Dihalocyclopropanes (I) are readily available from olefins and dihalocarbenes [7]. We prepared these compounds essentially as described by Doering and Hoffmann [7a]. No excess of olefin was used and dry pentane was added in order to obtain an easily stirred slurry. The yields were generally good, varying between 50 and 80 % in most cases (see experimental part, Table 2). From dienes a mixture of the mono- and bicyclopropane derivatives was formed as expected, the former being the predominant product. Reasonable yields of the bicyclopropanes are obtained, however, when more than twice the equimolar amount of haloform and base relative to the diene is employed. Thus cycloocta-1,5-diene gave 29 % of 9,9-dibromobicyclo[6,1,0]non-4-ene and 34 % of 5,5,10,10-tetrabromotricyclo[7,1,0,0^{4,6}]decane (II), and from cyclotetradeca-1,8-diene only 8,8,16,16-tetrabromotricyclo[13,1,0,0^{7,9}]-hexadecane (III) was isolated. In the case of 2,5-dimethylhexa-2,4-diene the corresponding bicyclopropane derivative was obtained in more than 90 % yield in this way [8].

The 1,1-dibromocyclopropane derivatives were treated with an ethereal solution of either methyl- or butyllithium usually at −30° to −40°C. The reaction products were analyzed by gas chromatography and infrared spectroscopy. Allenes were practically the sole products in most cases, but occasionally small amounts of acetylenic compounds were detected, particularly when butyllithium was used. These are probably formed by the base-catalyzed allene-acetylene rearrangement. The phenylallenes appear to be particularly sensitive to bases, which is in accordance with the fact that aryl groups greatly facilitate this rearrangement [9]. Generally methyllithium proved to be the most convenient lithium reagent since difficulties were occasionally encountered in separating completely butylbromide from the allene when

Table 1. The reaction between 1,1-dibromocyclopropanes and alkyllithium.

1,1-Dibromocyclopropane derived from:	Alkyl lithium	Allene	Yield (%)
Isobutylene	MeLi	3-methylbuta-1,2-diene	92[a]
Trimethylethylene	»	2-methylpenta-2,3-diene	69
	BuLi	»	68
Oct-1-ene	MeLi	nona-1,2-diene	86
1-Ethoxy-2-methylprop-2-ene	»	1-ethoxy-2-methylbuta-2,3-diene	71
Styrene	»	1-phenylpropa-1,2-diene	82
1,1-Diphenylethylene	»	1,1-diphenylpropa-1,2-diene	43
Cyclooctene	»	cyclonona-1,2-diene	93
Cycloocta-1,5-diene	»	cyclonona-1,2,6-triene	80

[a] Determined by gas chromatographic analysis.

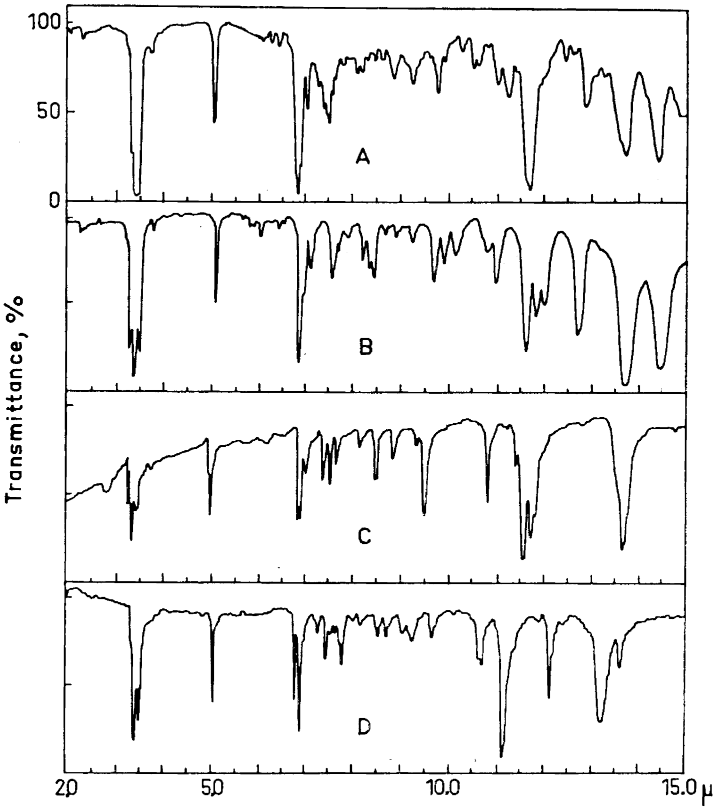
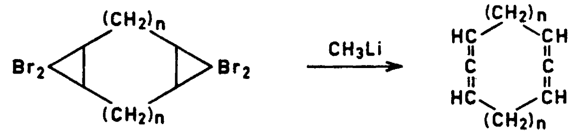


Fig. 1. I.R.-spectra of A: Cyclonona-1,2-diene (liq.; 0.023 mm); B: Cyclonona-1,2,6-triene (liq.; 0.023 mm); C: Cyclodeca-1,2,6,7-tetraene (KBr); D: Cyclohexadeca-1,2,9,10-tetraene (KBr).

butyllithium was used. 1,1-Dichlorocyclopropane derivatives react with butyllithium under similar conditions to yield a mixture of products including allenes, which we found to be the main product.

In Table 1 some of the results are summarized. Unless otherwise stated the yields are based on fractionated products. The initial yield of 1,1-diphenylpropa-1,2-diene (IV) was actually higher than that given in Table 1. Apparently a reaction took place during the distillation (bath temperature: 140°), and from the residue a colourless crystalline product, m.p. 192—193°, was obtained by chromatography on Al_2O_3. This solid, the analysis of which gave the formula $(C_{15}H_{12})_3$, was not thoroughly studied. IV is also formed by decomposition of diphenyldiazocyclopropane [10].

The high yields of cyclic allenes obtainable by this reaction are particularly interesting since these compounds are not conveniently available by other methods. Blomquist *et al.*[11] obtained the nine- and ten-membered cyclic allenes only as mixtures with the corresponding acetylenic isomers. Recently, the work of Faworskii and Domnin[12] on the preparation of cyclohepta-1,2-diene has been shown to be incorrect, the product of the reaction actually being cycloheptene and polymers[13]. We have not been able to detect any allenic compounds in the products from the reactions of either 7,7-dibromobicyclo[4,1,0]-heptene or 8,8-dibromobicyclo[5,1,0] octane with methyllithium. These reactions gave a number of interesting compounds which have already been described by Moore *et al.*[14,15] Cyclonona-1,2-diene is the smallest cyclic allene which can be represented by a strainless model, and it is therefore perhaps not so astonishing that the lower homologues are not formed. Treatment of the tricyclic compound II with methyllithium gave a small yield of the diallene cyclodeca-1,2,6,7-tetraene (V), m.p. 36°. The structure V has been assigned on the basis of analysis and spectroscopic results. The infrared spectrum (Fig. 1) shows strong bands at 1960 and 856 cm^{-1}, characteristic of the allenic groupings, and the absence of bands in the triple and double bond regions. Only end absorption is observed in the ultraviolet. Substantial information was obtained from the n.m.r. spectrum. Two multiplets are observed at τ : 5.17 ($C=C=CH$) and 7.92 (CH_2) with relative peak areas 1:2. The main product of the reaction is a polymeric substance. The reaction of III with methyllithium yielded 52 % of cyclohexadeca-1,2,9,10-tetraene (VI), m.p. 80°; the assignment is based on similar evidence as for V. An attempt to rearrange V to cyclodeca-1,6-diyne with potassium *t*-butoxide resulted in recovery of the starting material.



II, n = 2
III, n = 5

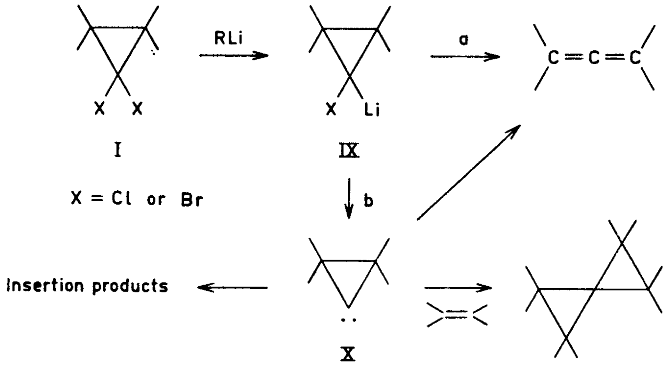
V, n = 2
VI, n = 5

As already mentioned above, allenes are not always the sole product of the reaction. In some cases considerable amounts of isomeric products are obtained. These cannot possibly have been formed by a subsequent reaction of the allene[16]. Thus 1,1-dibromotetramethylcyclopropane gave a liquid, b.p. 83—85°, n_D^{20} 1.4253 in about 70 % yield which has been erroneously reported as tetramethylallene (VII)[4]. The physical properties of VII given in the literature show considerable discrepancies and it seems that the products so far recorded as VII have all been impure[17]. Our product is invariably a mixture of isomers as shown by gas chromatography, but the main constituent usually represents about 95 % of the total mixture. This compound was obtained pure by preparative gas chromatography, and on the basis of chemical and spectroscopic evidence is assigned the structure 1-methyl-1-isopropenyl-cyclopropane (VIII). This has been confirmed by an independent synthesis of VIII. We have not been able to isolate any tetramethylallene from the reaction mixture. A plausible mechanism for the formation of VIII is discussed below.

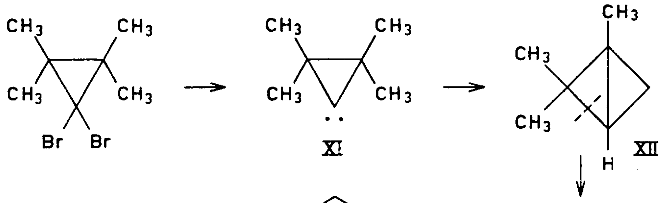
Mechanism

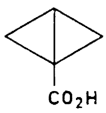
The first step in the reaction of *gem.* dihalocyclopropanes (I) with alkyllithium can be depicted as a halogen-lithium interconversion with formation of a 1-lithio-1-halocyclopropane derivative (IX). The reaction is dependent on the nature of both the halide and the lithium reagent [18], but its mechanism is not fully understood. Bromides react more readily than the corresponding chlorides and butyllithium is generally much more reactive than methyllithium. This is also in accordance with our findings.

It is expected that the intermediate IX would readily eliminate lithium halide. As already discussed by Doering and LaFlamme [5] this may occur by two different mechanisms: (*a*) concerted elimination and ring opening to an allene, or (*b*) α-elimination to the carbene intermediate (cyclopropylidene) X. Path *a* may well be the way by which the allenic product is formed, although it appears that cyclopropyl anions have considerable stability [19]. However, the formation of non-allenic isomers [14,16] in a number of these reactions is difficult to explain either as resulting from a direct reaction of IX or as a further rearrangement product of the allene. In this respect, path *b*, involving a carbene intermediate X, seems promising. This is expected to undergo ring opening with formation of the corresponding allene and to show the typical reactions of alkyl carbenes.

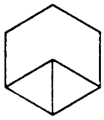


The first assumption has recently been rendered likely [10,21] by the isolation of 1,1-diphenylallene from the treatment of N-nitroso-N-(2,2-diphenyl)-cyclopropyl urea under conditions expected to produce carbenes. Addition to double bonds with formation of cyclopropanes and particularly insertion at carbon-hydrogen bonds are the most characteristic carbene reactions. Hence, the isolation of spiropentanes from reactions carried out in the presence of olefins would indicate such an intermediate. Accordingly, a number of the 1,1-dibromocyclopropanes were treated with methyllithium in the presence of isobutylene or tetramethylethylene, but no spiropentanes were detected. Moore *et al.* obtained spiropentanes from the reaction of 7,7-dibromonorcarane with methyllithium in the presence of isobutylene, cyclohexene [14] and *cis*- and *trans*-but-2-ene [15], respectively. In the last case they were also able to demonstrate the stereospecificity of the addition. Furthermore, the other products of the reaction could be explained as resulting from both intra- and intermolecular insertion reactions of an intermediate carbene. The formation of 1-methyl-1-isopropenylcyclopropane (VIII) may also be explained by assuming a carbene intermediate.

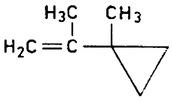




XIII



XIV



VIII

Insertion of the carbene (XI) at one of the methyl hydrogens yields the bicyclobutane derivative XII, which by subsequent ring opening at the bond indicated leads to VIII. The bicyclobutane derivatives XIII [20] and XIV [15] are described in the literature. The former is reported as being much less stable than the latter. We have so far no evidence for the presence of XII in our reaction product, but the increased "crowding" in this compound as compared with XIII and XIV is expected to reduce its thermal stability considerably.

It is at present impossible to choose between the two reaction paths, *a* and *b*, which both might lead to allenes. It is indeed reasonable to assume that both mechanisms are operating [21]. The non-allenic products can be explained on the basis of a carbene intermediate (X). The absence in all but one case of the expected addition reaction with olefins is somewhat surprising. It is, however, quite possible that in the present reaction the rate of concerted ring opening of IX (path *a*) in most cases is much higher than that of α-elimination (path *b*). Hence, a carbene intermediate is only formed in a reaction where path *a* for some reason is unfavorable. Furthermore, there are reasons [22] to believe that X, if formed, will not be a free carbene intermediate. The above argument is certainly only valid on the assumption that IX can neither react with olefins to form spiropentanes nor undergo insertion reactions.

It is hoped that future work will shed some light on the mechanism of this reaction.

I am indebted to Dr. J. F. M. Oth for the n.m.r. spectra and to Dr. J. H. Block for the mass spectrometric determination. Acknowledgement is also due to Mr. I. Litvin and Mr. G. G. Vrambout for technical assistance.

EXPERIMENTAL

General

Boiling points are uncorrected. All reactions were carried out under nitrogen. The olefins used were either commercial products or samples prepared by known procedures. Their purity was determined by analytical gas chromatography and infrared spectroscopy. Reagent grade chloroform and bromoform were used without further purification.

The analytical gas chromatograms were obtained on a Beckman GC2 instrument with helium as carrier gas. When not otherwise stated a 8.5 ft. column of squalane on Chromosorb W was used. The preparative scale gas chromatographic separations were carried out on a Beckman Megachrom with nitrogen or helium as carrier gas. A column of Apiezon J on firebrick was used.

The infrared spectra were recorded on Perkin Elmer Model 21 and Beckman IR 5 spectrophotometers. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer and when not otherwise stated, hexane was used as solvent. The n.m.r. spectra were measured at 60 Mc with a Varian dual purpose high-resolution spectrometer equipped with superstabilizer. The samples were dissolved in carbon disulfide. Chemical shifts were measured by the side-band technique, and are reported relative to tetramethylsilane as internal standard.

1,1-Dihalocyclopropanes. General Procedure

The method employed was essentially that described by Doering and Hoffmann [7a]. Equimolar amounts of olefin and haloform were generally used.

Haloform was slowly added to a stirred slurry of potassium *t*-butoxide, the olefin and dry pentane (50—100 ml per mole olefin), kept at 0° to —10°. The addition time was usually 6—8 h. The reaction mixture was left with stirring at room temperature overnight. Water was added, the product extracted with ether and worked up in the ordinary way. Table 2 summarizes the results. The yields recorded are in some cases the best of several runs, and if not otherwise stated, they are based on the olefin.

Reaction between cycloocta-1,5-diene and dibromocarbene

A mixture of potassium *t*-butoxide (from 23 g potassium), 27 g cycloocta-1,5-diene and 100 ml dry pentane was cooled in an ice-salt bath. 127 g of bromoform was added dropwise with stirring during 7 h. The reaction mixture was left overnight at room temperature. Water was added and some solid material filtered and washed with a little ether. The aqueous phase was extracted with ether and the extract washed with water until neutral and dried over sodium sulphate. Evaporation of the solvent and fractionation gave 21 g (29 %) of *9,9-dibromobicyclo*[*6,1,0*]*non-4-ene*, b.p. 86° (0.3 mm), n_D^{17} 1.5727. (Found: C 38.74; H 4.13. Calc. for $C_9H_{12}Br_2$: C 38.60; H 4.32). The crystalline distillation residue was combined with the filtered material and recrystallized from methylene chloride. 38 g (34 %) of *5,5,10,10-tetrabromotricyclo*[*7,1,0,0*^{4,6}]*decane* (II) was obtained, m.p. 174—180 . (Found: C 26.69; H 2.62. Calc. for $C_{10}H_{12}Br_4$: C 26.58; H 2.68).

8,8,16,16-Tetrabromotricyclo[13,1,0,0^{7,9}] hexadecane (III)

A mixture of potassium *t*-butoxide (from 13 g potassium), 17.5 g cyclotetradeca-1,8-diene and 60 ml pentane was cooled in an ice-salt bath. 46.5 g of bromoform was added dropwise with stirring during 5 h. The reaction mixture was then left at room temperature overnight. Water was added and some solid material was filtered and washed with a small amount of ether. Recrystallization from methylene chloride gave 10.4 g (21 %) of (III); m.p. 200—204°. (Found: C 35.68; H 4.38. Calc. for $C_{16}H_{24}Br_4$; C 35.85; H 4.51).

Table 2. Products of the reactions of olefins with haloform and potassium tert butoxide.

Cyclopropane derivative	b.p. °(mm)	m.p.°	n_D(t°)	Analysis C Found	C Calc.	H Found	H Calc.	Yield (%)	Ref.
1,1-Dibromo-2,2-dimethyl	51–52(16)		1.5156(20)					80[a]	23
1,1-Dibromo-2,2,3-trimethyl	65–74(18)		1.5130(27)					84	23
1,1-Dichloro-2,2,3-trimethyl	63(45)		1.4545(28)					70	7a
1,1-Dibromo-2,2,3,3-tetramethyl		81						80	7b
1,1-Dichloro-2,2-3,3-tetramethyl		52						78	7g
1,1-Dibromo-2-hexyl	70(0.1)		1.4940(23)	38.32	38.06	5.44	5.67	44	
1,1-Dichloro-2-hexyl	85(11)		1.4515(24)	55.85	55.40	8.19	8.26	15[b]	
7,7-Dibromobicyclo[4,1,0]heptane	110(12)		1.5577(22)					73	7a
8,8-Dibromobicyclo [5,1,0]octane	60–61 (0.1)		1.5521(23)	35.83	35.85	4.55	4.51	58	
9,9-Dibromobicyclo [6,1,0]nonane	80–82 (0.1)		1.5520(20)	38.47	38.33	5.01	5.00	65	
1,1-Dibromo-2-phenyl	90–91 (0.1)		1.6001(22)	39.16	39.16	2.94	2.92	37	7b
1,1-Dibromo-2,2-diphenyl		154–156		51.15	51.17	3.53	3.44	54	7b
1,1-Dichloro-2,2-diphenyl		115–116		68.50	68.46	4.76	4.60	60	
1,1-Dibromo-2-methyl-2-(ethoxymethyl)	52–53(2)		1.5024(26)	31.08	30.82	4.35	4.40	68	

[a] Excess of isobutylene was used and the yield is based on bromoform

[b] The low yield is partly due to accidental loss of product during work-up.

The reaction between 1,1-dihalocyclopropane derivatives and alkyllithium. General procedure

0.1 mole of the 1,1-dibromo- or 1,1-dichlorocyclopropane derivative was diluted with 25 ml of dry ether and cooled in a dry ice/acetone bath kept at −30 to −40°. An ethereal solution of alkyllithium (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 sodium sulphate. When low-boiling products were expected, the ether was distilled through a 50 cm Dixon ring-packed column. The residue was then fractionated either through a 25 cm column packed with Dixon rings or a 100 cm spinning-band column. The reaction has been carried out both on a larger and smaller scale with practically the same result.

3-Methylbuta-1,2-diene was prepared from 1,1-dibromo-2,2-dimethylcyclopropane and methyllithium. The yield was 92 % as estimated by gas chromatography. A sample was obtained by preparative gas chromatography, b.p. 40°, n_D^{24} 1.4152 (reported[3], b.p.

40°, n_D^{25} 1.4148). The infrared spectrum shows strong bands at 1930 and 845 cm^{-1} and the absence of bands in the 3300 and 2100—2300 cm^{-1} regions characteristic of acetylenic bonds.

2-Methylpenta-2,3-diene was obtained in 69 % yield from 1,1-dibromo-2,2,3-trimethylcyclopropane and methyllithium, b.p. 72°, n_D^{25} 1.4340 (reported [5], b.p. 72.5°, n_D^{25} 1.4350). Gas chromatography indicates a purity of at least 99 %. The infrared spectrum shows a medium strong band at 1965 cm^{-1}. With butyllithium a 68 % yield of the allene was obtained.

Nona-1,2-diene. A liquid was obtained from 1,1-dibromo-2-hexylcyclopropane and methyllithium in 89 % yield, b.p. 45° (15 mm), n_D^{23} 1.4432 (Found: C 86.65; H 13.21. Calc. for C_9H_{16} : C 87.02; H 12.98). Gas chromatographic analysis shows the presence of 3 % impurities. The infrared spectrum shows strong bands at 1950 and 842 cm^{-1}.

1-Ethoxy-2-methylbuta-2,3-diene was obtained in 71 % yield from 1,1-dibromo-2-methyl-2(ethoxymethyl)cyclopropane and methyllithium, b.p. 112°, n_D^{21} 1.4260. (Found: C 74.92; H 10.83. Calc. for $C_7H_{12}O$: C 74.96 ; H 10.78). A weak band is observed at 1955 cm^{-1} and strong bands at 850 and 870 cm^{-1} in the infrared. Gas-chromatographic analysis on a 2 m column of dinonylphthalate on Embacel indicates at least 99 % purity.

1-Phenylpropa-1,2-diene was obtained in 82 % yield from 1,1-dibromo-2-phenylcyclopropane and methyllithium at —60°, b.p. 64—65° (11 mm), n_D^{24} 1.5809 (reported [24], b.p. 68° (16 mm), n_D^{17} 1.5830). UV λ_{max} (in ethanol) : 284 mμ (ε = 16 300). The infrared spectrum shows strong bands at 1940 and 860 cm^{-1}. The product was at least 99 % pure as shown by gas chromatography. It is important that the reaction is carried out at low temperature and that contact of the product with base is as short as possible. The latter is achieved by fast addition of the lithium compound and subsequently adding dilute hydrochloric acid to the reaction mixture. When this was not observed as much as 10 % of isomeric acetylenes have been detected in the reaction product.

The allene is rapidly oxidized in air. However, redistillation of a sample, kept over hydroquinone at 0° for more than 1 year, recovered about 70 % of the allene.

1,1-Diphenylpropa-1,2-diene (IV) was prepared in 43 % yield from 1,1-dibromo-2,2-diphenylcyclopropane and methyllithium, b.p. 80° (0.01 mm), n_D^{20} 1.6301. (Found: C 92.88; H 6.23. Calc. for $C_{15}H_{12}$: C 93.71 ; H 6.29). The infrared spectrum shows strong bands at 1940 and 855 cm^{-1}. A small amount of 1,1-diphenylprop-2-yne is probably present as indicated by a weak band at 3300 cm^{-1}. A reaction apparently occurred during the distillation. The residue was dissolved in benzene, and a solid precipitated by addition of petroleum-ether. Recrystallization from cyclohexane afforded colourless crystals, m.p. 192—193°. (Found: C 93.43; H 6.21 ; mol. wt. 559. Clac. for $C_{45}H_{36}$: C 93.71 ; H 6.29 ; mol. wt. 577).

Cyclonona-1,2-diene was obtained in 93 % yield from 9,9-dibromobicyclo[6,1,0]nonane and methyllithium, b.p. 62—63° (16 mm), n_D^{20} 1.5060. (Found: C 88.43; H 11.44. Calc. for C_9H_{14} : C 88.45 ; H 11.55). The infrared spectrum is given in Fig. 1. Gas-chromatographic analysis indicates at least 99 % purity.

Ozonolysis of 1 g of the allene in ethyl acetate and subsequent oxidation of the product with peracetic acid yielded suberic acid (0.35 g), m.p. 138—140°, undepressed on admixture with an authentic sample.

Cyclonona-1,2,6-triene was formed in 80 % yield from 9,9-dibromobicyclo[6,1,0]non-4-ene and methyllithium, b.p. 61—62° (13 mm), n_D^{24} 1.5218. (Found: C 89.60 ; H 9.84. Calc. for C_9H_{12} : C 89.94 ; H 10.06). The infrared spectrum is given in Fig. 1. Only end-absorption is observed in ultraviolet light. The compound is unstable.

Ozonolysis of 1 g of the allene in ethyl acetate at 0° with subsequent oxidation of the reaction product with peracetic acid gave succinic acid (0.3 g), m.p. 185—186°, undepressed on admixture with an authentic sample.

Cyclodeca-1,2,6,7-tetraene (V). 22.6 g (0.05 mole) of the tetrabromide (II) was suspended in 25 ml of dry ether and cooled to —40°. An ethereal solution of methyllithium (80 ml ; 1.5 M) was added dropwise with stirring during 30 min. The reaction mixture was further stirred for 30 min and water was added. Some ether insoluble material was formed. The ether layer was separated, washed until neutral with water and dried over sodium sulphate. The ether was evaporated under vacuum and the residue extracted with pentane, leaving behind a considerable residue. The pentane was evaporated under vacuum and the residue distilled at 80° bath temperature (0.05 mm) into a cooled flask. A liquid distilled which crystallized partly in the receiver. Recrystallization from a little pentane gave 800 mg (5 %) of (V), m.p. 36°. (Found: C 90.74; H 9.31; mol. wt. 132*. Calc. for $C_{10}H_{12}$: C 90.85; H 9.15; mol. wt. 132). The infrared spectrum is reproduced in Fig. 1. Only end absorption is observed in ultraviolet light.

Cyclohexadeca-1,2,9,10-tetraene (VI). 7.7 g of the tetrabromide (III) was suspended in 10 ml of dry ether and cooled to −40°. An ethereal solution of methyllithium (30 ml; 1.15 M) was added dropwise with stirring during 30 min. The reaction mixture was further stirred for 1 h while the bath temperature rose to 0°. Water was added, the ether phase separated, washed until neutral with water and dried over sodium sulphate. Evaporation of the ether under vacuum gave a crystalline residue. Recrystallization from ethanol and subsequently from pentane gave 1.6 g (52 %) of (VI); m.p. 80°. (Found: C 88.75; H 11.13. Calc. for $C_{16}H_{12}$: C 88.82; H 11).18. The infrared spectrum is shown in Fig. 1. In the ultraviolet spectrum only end absorption is observed.

The reaction between 1,1-dibromotetramethylcyclopropane and methyllithium.

25.6 g of the bromide in 50 ml of dry ether, where it was only partly dissolved, was cooled to −40 . To the stirred suspension was added dropwise during 1 h an ethereal solution of methyllithium (80 ml; 1.5 M). The reaction mixture was further stirred for 30 min and water was added. The ether phase was separated and the aqueous phase extracted with a small amount of ether. The combined ether solutions were washed until neutral with water and dried over calcium chloride. Fractionation through a column gave 6.7 g of a liquid, b.p. 83−85°, n_D^{20} 1.4253. (Found: C 87.25; H 12.32. Calc. for C_7H_{12}: C 87.42; H 12.58). The liquid was shown to consist of three compounds by gas chromatography. The main component which, represented about 95 % of the total mixture, was obtained pure by preparative gas chromatography and subsequently proved to be 1-methyl-1-isopropenylcyclopropane (VIII), b.p. 84°, n_D^{25} 1.4223. Only end absorption is observed in the ultraviolet. The infrared spectrum shows the characteristic absorption of a methylene double bond at 3080, 1650 and 892 cm^{-1}. A strong band at 1022 cm^{-1} indicates the presence of a cyclopropane ring. The spectrum is identical with that of a synthetic sample of VIII. The n.m.r. spectrum shows five bands with relative peak areas 2:3:3:2:2. The chemical shifts and assignments are as follows: τ = 5.30 (multiplet) $H_2C{=}C$; 8.37 (quadruplet) $C{=}C{-}CH_3$; 8.88 (singlet) CH_3 on cyclopropane; 9.40 and 9.62 (multiplets) cyclopropane CH_2.

Ozonolysis of VIII gave formaldehyde characterized as the 2,4-dinitrophenylhydrazone and a ketone $C_6H_{10}O$ also characterized as the 2,4-dinitrophenylhydrazone derivative, m.p. 164−168°. (Found: C 51.85; H 4.99; N 19.98. Calc. for $C_{12}H_{14}O_4N_4$: C 51.79; H 5.07; N 20.14).

Variation of the reaction temperature between −78° and 0°, or the use of dioxane, tetrahydrofuran, diglyme or benzene as solvents for the bromide did not effect the course of the reaction. In all the reactions VIII was practically the sole product. Furthermore, the same result was obtained using butyllithium instead of methyllithium, and the reaction of 1,1-dichlorotetramethylcyclopropane and butyllithium, carried out as above, yielded practically only VIII.

1-Methyl-1-isopropenylcyclopropane (VIII)

A mixture of Zn-Cu couple (prepared from 42 g of zinc) 134 g of methylene iodide, 300 mg of iodine and 400 ml of dry ether was heated under reflux for 30 min. 77 g of 2,3-dimethylbuta-1,3-diene was added dropwise during 3/4 h. The reaction mixture was finally heated under reflux for 62 h and then filtered. The filtrate was washed subsequently with dilute hydrochloric acid and aqueous sodium bicarbonate and dried over sodium sulphate. Fractionation gave 9.8 g of a liquid, b.p. 85−92°, n_D^{24} 1.4245. This was shown by gas chromatography to consist of two compounds in 60 and 40 %, respectively, which

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* Determined by mass spectrometry.

were separated by preparative gas chromatography. The main product was VIII, b.p. 84°, n_D^{25} 1.4223. (Found: C 87.24; H 12.34. Calc. for C_7H_{12}: C 87.42; H 12.58). The other constituent was probably 1,1-dimethylbicyclopropane, n_D^{25} 1.4228. (Found: C 86.59; H 12.49. Calc. for C_8H_{14}: C 87.19; H 12.81). The infrared spectrum shows strong bands at 3020 and 1012 cm^{-1} characteristic of a cyclopropane ring.

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Received March 16, 1963.