peak had the same retention time as the *trans* isomer and the second peak had the same retention time as the *cis* isomer.

Photolyses Using a Filtering Solution. Procedure D.—The solution to be irradiated was placed in a 20-ml ampoule, cooled in a Dry Ice bath, evacuated, and frozen in liquid nitrogen. The ampoule was then sealed, warmed to room temperature, and immersed in the stirred filtering solution[10] contained in a 1-l. beaker. The edge of the ampoule was placed 1.1 to 1.2 cm from the edge of the beaker and the solution was irradiated. After photolysis, the ampoule was frozen in liquid nitrogen and opened. The ampoule was warmed to room temperature, the reaction mixture was removed from it, and the residue was washed with chloroform. The solutions were combined, solvent and excess olefin were evaporated, and the residue was washed with chloroform.

Photolysis in *cis*-2-Butene.—Pure I (0.054 g. 0.0023 mole) and *cis*-2-butene (8 ml) were irradiated according to procedure D. After 52 min, the mixture was worked up and analyzed by vpc (column temperature 161°, injector temperature 240°, He flow rate 300 cc/min). The *trans* peak appeared at 16.5 min and the *cis* at 21 min. The areas of the peaks were measured with a planimeter. The ratio of the isomers was obtained from calibration curves whch indicated that approximately 10% of the *trans* isomer was formed.

Photolysis in *trans*-2-Butene.—A solution of I (0.041 g. 00017 mole) and *trans*-2-butene (11 ml) were irradiated according to procedure D. After 52 min, the mixture was worked up and analyzed by vpc. There was only one component, corresponding to the *trans* isomer.

Photolysis of Tetrachlorodiazocyclopentadiene in the Presence of XI.—A solution of I (0.052 g, 0.00023 mole), pure XI (0.058 g, 0.00023 mole), and spectral grade isooctane (8 ml) was irradiated according to procedure D. The products were analyzed by vpc (column temperature 153°, injector temperature 240°, He flow rate 300 cc/min). No peak for the *trans* isomer could be detected.

Thermal Rearrangement of 1,2,3,4-Tetrachlorospiro[2.4]hepta-1,3-dienes at 180–210°. Procedure E.—Material was placed in a 50-ml round-bottomed flask which had one neck and a side arm and was fitted with a reflux condenser. The system was flushed with dry nitrogen and the flask was completely immersed in an oil bath at 180–210°.

2,3,4,5-Tetrachloro-6-methyl-6-isopropylfulvene (XIII).—1,2,3,4-Tetrachloro-6,6,7-trimethylspiro[2.4]hepta-1,3-diene (X) (1.39 g, 0.00511 mole) was heated at 190° for 20 min according to procedure E. On cooling, the mixture was chromatographed on acid-washed alumina, and hexane eluted 0.91 g of a mixture of X and XIII. Distillation gave a red oil, bp 90° (1 mm), which crystallized on standing in an icebox. Recrystallization from methanol gave 0.63 g (45%) of a red solid: mp 59–60°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 6.28 (s), 6.45 (s), 13.75 (s), and 14.35 (s) μ.

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.15; H, 3.68; Cl, 52.17. Found: C, 44.19; H, 3.88; Cl, 52.30.

2′-(3′,3′-Dimethyl-1′-butenyl)tetrachlorocyclopentadiene (XIV).—1,2,3,4-Tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1,3-diene (III) (2.0 g, 0.0070 mole) was heated for 10 min at 210° according to procedure E. Distillation of the product gave 1.02 g (52%) of yellow liquid: bp 90° (0.1 mm); $\lambda_{\max}^{\mathrm{neat}}$ 6.24 (s), 6.34 (m), 7.18 (m), 7.33 (s), 13.12 (s), 13.65 (s), 14.35 (m), and 15.06 (m) μ.

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62; mol wt, 286. Found: C, 46.28; H, 4.48; Cl, 50.00; mol wt, 290 (in benzene).

2,3,4,5-Tetrachloro-6-methyl-6-*t*-butylfulvene (XV).—A portion of III (5.42 g, 0.0190 mole) was heated for 21.5 min at 186° according to procedure E. Distillation of the product gave a red oil, bp 90° (0.07 mm), which could not be crystallized or further purified despite many varied attempts. Spectral data for the fulvene were $\lambda_{\max}^{\mathrm{neat}}$ 6.43 (s), 6.51 (s), 7.17 (m), 7.31 (s), 13.92 (s), and 15.10 (s) μ.

Procedure for Rearrangements at 435–460°. Procedure F.—The reactions were carried out in a vertical glass column packed with glass helices and heated by an electrical furnace. Material was dropped onto the column from an addition funnel attached to the top and collected in a Dry Ice cooled trap fitted with side arm. The temperature of the furnace was measured with a thermocouple. The system was flushed with nitrogen for 1 hr before the reaction *via* a three-way tap attached to the top of the addition funnel, and then was evacuated to 2.5 mm. Material was then allowed to drop on to the column over a 30-min period, the pressure difference being maintained by a small flow of nitrogen from a balloon also attached to the addition funnel.

When reaction was complete, the column was cooled, the helices were washed with chloroform, and the washings were added to the material in the trap. The chloroform was evaporated and the residue was chromatographed on acid-washed alumina.

Thermal Rearrangement of 1,2,3,4-Tetrachloro-6-methyl-7-*n*-propylspiro[2.4]hepta-1,3-diene.—The mixture of VI and VII isomers (1.67 g, 0.00588 mole), present in the *cis*:*trans* ratio of 77:23, was dropped on to the column at 460° according to procedure F. Hexane eluted 1.30 g (78%) of crude product, which was distilled and analyzed by vpc (column temperature 170°, injector temperature 245°, He flow rate 300 cc/min). The *cis*:*trans* isomer distribution was shown to be 25:75 as determined by chromatographic peak areas.

Thermal Rearrangement of 1,2,3,4-Tetrachloro-6-methyl-7-ethylspiro[2.4]hepta-1,3-diene.—The mixture of isomers of VIII and IX (2.23 g, 0.00820 mole), present in the *cis*:*trans* ratio of 80:20, was dropped onto the column at 435° according to procedure F. Hexane eluted 2.01 g (90%) of crude product, which was distilled and analyzed by vpc (column temperature 160°, injector temperature 240°, He flow rate 300 cc/min). The *cis*:*trans* isomer distribution was shown to be 25:75.

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Synthesis of Some Alkylidenecyclopropanes from Allenes[1]

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Received August 24, 1965

2,2-Dibromoalkylidenecyclopropanes have been prepared by the addition of dibromocarbene to allenes. The dibromo derivatives have been reduced successively to the monobromides and the hydrocarbons. Infrared and proton magnetic spectra of the adducts and their dehalogenation products are discussed.

Alkylidenecyclopropanes comprise a group of compounds which are of particular interest in the study of angle strain on chemical and physical properties. Early attempts to prepare the parent compound of the series, methylenecyclopropane,[4-6] met with little success. Boord and co-workers[7] obtained the compound in 17% yield by the dechlorination of 3-chloro-(2-chloromethyl)-1-propene with magnesium in dry tetrahydro-

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[2] Research associate on study leave from Muslim University, Aligarh, India.

[3] To whom correspondence should be addressed at the State University of New York at Albany.

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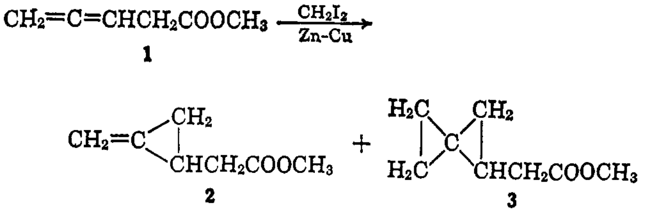
[5] I. A. D'yakanov, *J. Gen. Chem. USSR*, **10**, 402 (1940).

[6] N. J. Demjanov and M. Dojarenko, *Ber.*, **B56**, 2208 (1923).

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

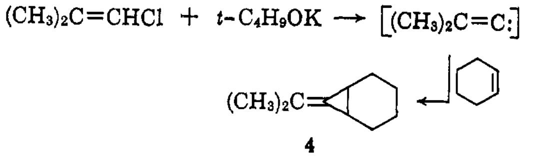
furan. The discovery by Simmons and Smith[8] of the simple general method for the synthesis of cyclopropanes from olefins by reaction with methylene iodide and zinc–copper couple provided another pathway to alkylidenecyclopropanes. This was exploited by Ullman and Franshawe,[9] who treated methyl penta-3,4-dienoate (**1**) with the Simmons–Smith reagent and obtained a 35% yield of a mixture of products containing approximately equal amounts of **2** and **3**.



$CH_2{=}C{=}CHCH_2COOCH_3 \xrightarrow[Zn\text{-}Cu]{CH_2I_2}$

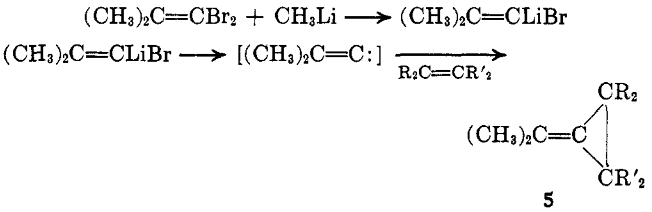
1 **2** **3**

An alternate route to alkylidenecyclopropanes was reported by Tanabe and Walsh[10] who treated 1-chloro-2-methylpropene or 3-chloro-2-methylpropene with potassium *t*-butoxide in the presence of cyclohexene and obtained **3** in yields of 8 to 25%. Isopropylidenecarbene was postulated as an intermediate. Hartzler[11] observed that treatment of aliphatic 1,1-dibromo-2-methylpropene with methyllithium in the presence of olefins leads, in yields ranging from 12 to 70%, to products which can be formulated as adducts of the alkylidenecarbene to the olefin. Another pathway to alkylidenecyclopropanes involves the addition of carbenes to allenes. This has been explored briefly by Ball and Landor,[12] who reported the synthesis of 1-alkylidene-2,2-dibromocyclopropanes in 40 to 60% yields by the addition of dibromocarbene to allenes.



$(CH_3)_2C{=}CHCl + t\text{-}C_4H_9OK \longrightarrow [(CH_3)_2C{=}C:]$

4



$(CH_3)_2C{=}CBr_2 + CH_3Li \longrightarrow (CH_3)_2C{=}CLiBr$

$(CH_3)_2C{=}CLiBr \longrightarrow [(CH_3)_2C{=}C:] \xrightarrow[R_2C=CR'_2]{}$

5

We have used the Simmons–Smith method with 2-methyl-2,3-pentadiene and 2,3-pentadiene. The reaction product mixtures were analyzed by gas–liquid partition chromatography and showed small amounts of the expected alkylidenecyclopropanes along with unreacted allene and polymeric material. Phenyl-substituted allenes appeared to undergo no reaction with the reagent.

A more promising route to the hydrocarbons appeared to be the addition of dibromocarbene to allenes, followed by hydrodehalogenation. Geminal polyhalides have been shown to undergo clean stepwise reduction by organotin hydrides.[13] This reaction has been exploited by Seyferth and co-workers for the reduction of geminal dihalocyclopropanes to the monohalides and the cyclopropane hydrocarbons.[14] Since our work was completed, Meinwald and co-workers have reported application of this method to tetramethylallene through reduction to the monobromide.[15]

3-Methyl-1,2-butadiene, 2,3-pentadiene, and 4-methyl-2,3-pentadiene were the allenes used in the present work. The addition reaction proceeded smoothly, providing yields of alkylidenedibromocyclopropanes ranging between 75 and 87%. Stepwise reductions with tri-*n*-butyltin hydride to the monobromo derivatives and to the hydrocarbons, respectively, proceeded smoothly and in satisfactory yields, attesting to the high selectivity of the reduction procedure. The structures of all products obtained are shown in Chart I. Preparative data are given in Table I. Structures of products were assigned on the basis of the nmr and infrared spectra. Each of the compounds showed the stretching frequency of a strained double bond in the range 1725–1750 cm^{-1}.

3-Methyl-1,2-butadiene underwent addition of dibromocarbene with high selectivity, yielding 1,1-dibromo-2,2-dimethyl-3-methylenecyclopropane (**6**) as the only product. Its structure was easily assigned from the nmr spectrum which showed the presence of two vinyl proton singlets at τ 4.48 and 4.15 and the methyl proton singlet at τ 8.54. The monobromide **7** obtained upon reduction showed vinyl doublets with coupling constants of 2.0 and 1.1 cps owing to splitting by the proton on the bromine-bearing carbon. The larger coupling constant is assigned to the proton which is *anti* to this carbon because the dihedral angle between the axes of these protons is about 130°, while that of C–H^e and C–H^d (Chart I) is about 50°. In the hydrocarbon **8** obtained by reduction of the monobromide the identical ring protons gave a pair of doublets with coupling constants of 2.6 and 1.7 cps owing to coupling with the vinyl protons, which gave a fairly complex multiplet.

The double bonds in 2,3-pentadiene are identical, so only one dibromocarbene adduct structure is to be expected. However, *cis–trans* isomerism about the double bond is possible. Glpc indicated only one isomer, and the nmr spectrum contained a few small peaks which might be due to a few per cent of a second isomer, but these did not show an expected pattern. Structure **9** is assigned to this product because this would represent a reaction path with the least steric interactions in the transition state. Also the vinyl protons at τ 3.77 are very near those in the major product from 3-methyl-2,3-pentadiene (see below). The spectrum yielded to a complete first-order analysis. Perhaps the most striking feature is the coupling of the ring proton with each of the others in the molecule. Coupling of 1.4 cps occurs through five bonds with the protons of the vinyl methyl group.

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

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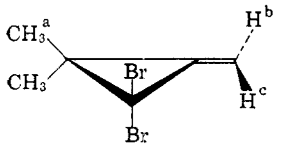
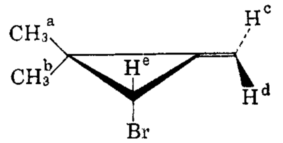
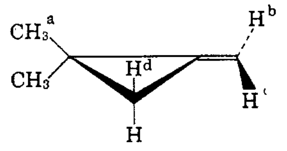
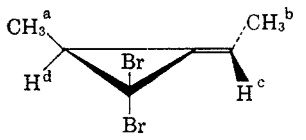
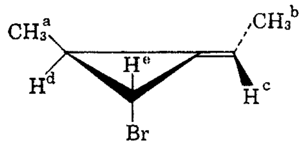
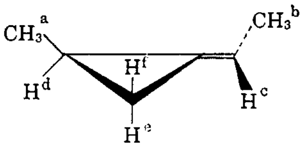
[15] J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *ibid.*, **30**, 1038 (1965).

CHART I[a,b]
ALKYLIDENE CYCLOPROPANES

 **6**	a 8.54(1)	b 4.48(1)	c 4.15(1)		
 **7**	a 8.76(1) J_{e-c} 2.0	b 8.72(1) J_{e-d} 1.1	c 4.51(2)	d 4.44(2)	e 6.66(4)
 **8**	a 9.22(1) J_{b-d} 2.6	b, c 5.07–5.30(m) J_{c-d} 1.7	d 9.50(4)		
 **9**	a 8.87(2) J_{b-c} 7.0 J_{a-d} 6.2	b 8.32(4) J_{c-d} 2.8 J_{b-d} 1.4	c 3.77(8)	d 8.34(m)	
 **10**	a 8.45–9.05(m)	b 7.87–8.47(m)	c 3.67–4.27(m)	d ∼8.4	e 6.12–6.52 (m)
 **11**	a, e, f 8.6–9.1(m) J_{b-c} 6.2 J_{a-d} 4.0	b 8.29(m) J_{d-c} or $J_{d-e,f}$ 1.8 J_{a-c} or $J_{e-e,f}$ 1.8	c 4.43(14+)	d 9.43(8)	

Reduction to the monobromide **10** could yield a pair of racemates with the ring hydrogens *cis* or *trans* to each other. It is quite likely that both were formed, for the nmr spectrum was highly complex and did not yield to analysis. Reduction to the hydrocarbon **11** provided a product with a simpler nmr spectrum, but which could not be analyzed completely because of coincidence of a coupling constant of 1.8 cps of four of the protons, a, c, d, and e or f.

The product from 4-methyl-2,3-pentadiene was a mixture containing 85% of an isomer assigned the structure **12a** and 15% of the geometrical isomer **12b**. These assignments are based on the expectation that substituents *syn* to the bromine-bearing carbon would be less shielded than those *anti* to this carbon. It would be expected on steric grounds that the isomer formed by attack by dibromocarbene from the side of the hydrogen atom of C-2 of the allene would predominate over that formed by attack from the side of the methyl group at C-2. The chemical shift difference between the vinyl proton in the isomers is 0.37 ppm and that for the methyl protons is 0.10 ppm.

Reduction of the dibromide yielded the corresponding monobromides **13a** and **13b** which we could not separate. The ring proton in **13a** produced a quintet at τ 6.60 with spacing 1.6 cps and areas 1:4:6:4:1. This could result from a quartet of adjacent identical protons, which would be unexpected, or from identical coupling with three identical protons and a fourth one which is not identical. Overlap of the expected double quartet would yield the same area ratio and spacing as that observed.

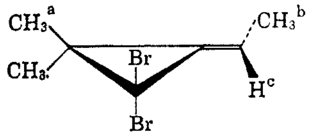
The spectrum of **13b** could not be analyzed with confidence because it was weak and overlapped with that from **13a**, but indications were that splitting patterns were similar.

Further reduction of the monobromide to the hydrocarbon yielded **14a** and **14b**. Here again the ring protons appeared as a quintet at τ 9.17 with area ratios 1:4:6:4:1 and coupling constant 2.0 cps. The vinyl proton appeared as a quartet of triplets centered at τ 4.41 with coupling constants of 6.5 and 2.0 cps. A doublet of triplets identified the vinyl methyl protons at τ 8.27, and the ring methyl protons produced a singlet. Again the spectrum of the minor component could not be completely extracted from that of the mixture.

Experimental Section

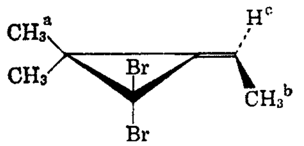
General.—All reactions were carried out under prepurified nitrogen. Melting and boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer Model 21 or 331 spectrometer equipped with

CHART I (*Continued*)



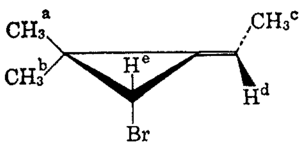
12a

a	b	c
8.55	8.17	3.72
J_{b-c} 7.0		



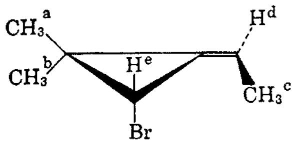
12b

a	b	c
8.60	8.07	4.09
J_{b-c} 7.0		



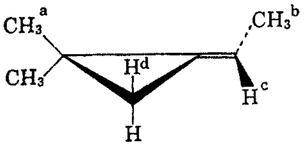
13a

a	b	c	d	e
8.77(1)	8.70(1)	8.23(4)	4.04(m)	6.67(5)
J_{c-d} 7.0	J_{c-e} 1.6	J_{d-e} 1.6		



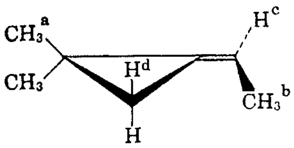
13b

a	b	c	d	e
8.83(1)	8.72(1)	8.26(4)	[4.14(m)]	6.62
J_{c-d} 7.0	J_{c-e} [1.6]	J_{d-e} [1.6]		



14a

a	b	c	d
8.83(1)	8.27(6)	4.41(12)	9.17(5)
J_{b-c} 6.5	J_{b-d} 2.0	J_{c-d} 2.0	



14b

a	b	c	d
8.88(1)	8.28(6)	?	9.23
J_{b-c} 6.5	J_{b-d} 2.0	J_{c-d} ?	

[a] Chemical shifts are in τ units, coupling constants in cycles per second. [b] Numbers in brackets are uncertain.

TABLE I

PREPARATION OF ALKYLIDENECYCLOPROPANES

Compd	Method[a]	Yield,[b] %	Bp, °C (mm)	Formula	Calcd, %			Found, %		
					C	H	Br	C	H	Br
6	A	75	62–64 (18)	$C_6H_8Br_2$	30.03	3.36	66.61	29.83	3.18	66.52
7	B	68	25–26 (18)	C_6H_9Br	44.74	5.63	49.63	44.53	5.49	49.37
8	C	53	48–48.5	C_6H_{10}	87.73	12.27		87.52	12.33	
9	A	87	30–31 (0.8)	$C_6H_8Br_2$	30.03	3.36	66.61	29.66	3.21	66.89
10	B	72	27 (0.1)	C_6H_9Br	44.74	5.63	49.63	44.48	5.62	49.53
11	C	85	66–67	C_6H_{10}	87.73	12.27		87.41	12.42	
12	A	78[c]	88–89 (10)	$C_7H_{10}Br_2$	33.09	3.96	62.93	32.86	3.83	63.13
13	B	68[d]	25–26 (18)	$C_7H_{11}Br$	44.74	5.63	49.63	44.53	5.49	49.37
14	C	60[d]	76–76.5	C_7H_{12}	87.42	12.58		87.37	12.41	

[a] A, addition of dibromocarbene to the appropriate allene; B, reduction of the dibromide with tri-*n*-butyltin hydride; and C, reduction of the monobromide with tri-*n*-butyltin hydride. [b] At least 99% pure as indicated by gas–liquid partition chromatography. [c] 85% **12a** and 15% **12b** based on glpc and nmr data. [d] Mixture of geometrical isomers, presumably 85% a and 15% b. See Chart I.

sodium chloride optics. The nmr spectra were determined with a Varian Associates A-60 instrument. Chemical shifts are given in τ units.

Materials.—The allenes were prepared from the appropriate geminal dibromocyclopropanes by reaction with methyllithium.[16–19] Trimethyltin hydride was prepared by reduction of the chloride with lithium aluminum hydride. The reaction was carried out in bis(2-ethoxyethyl) ether, and the organotin hydride distilled from the reaction mixture.

Preparation of Alkylidenedibromocyclopropanes.—The preparation of 1,1-dibromo-2,2-dimethyl-3-ethylidenecyclopropane is described as a typical example of the procedure.

Into a flask fitted with a stirrer, condenser, and dropping funnel were placed 8.2 g (0.1 mole) of 2-methyl-2,3-pentadiene and 25.3 g (0.1 mole) of bromoform in 25 ml of dry pentane. Solvent-free potassium *t*-butoxide (0.115 mole) was added during 2–3 hr while the reaction temperature was maintained at −25 to −20°. The reaction mixture was stirred for an additional 1 hr and hydrolyzed with 20 ml of water. The layers were separated, the water layer was washed with pentane, and the combined organic layers were distilled, providing 20 g (78%) of product, bp 88–89 (10 mm).

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(16) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(17) L. Skatteböl, *Tetrahedron Letters*, 167 (1961).

(18) T. L. Jacobs and D. Danker, *J. Org. Chem.*, **22**, 1424 (1957).

(19) G. F. Hennion and J. J. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).

The gas–liquid partition chromatogram showed two partially resolved peaks in area ratio of about 85:15, presumably owing to the two geometrical isomers, **12a** and **12b**.

Reduction of the Alkylidenecyclopropanes.—A typical procedure is given.

Into a flask fitted with stirrer, condenser, and dropping funnel was placed 19 g (0.074 mole) of 1,1-dibromo-2,2-dimethyl-3-ethylidenecyclopropane. The contents were cooled in an ice bath and 21.7 g (0.074 mole) of tri-*n*-butyltin hydride was added over 2 hr. The reaction mixture was then warmed to about 35° and allowed to stand until a test of an aliquot with acid indicated disappearance of the hydride (*ca.* 24 hr). Distillation provided 9.2 g (70%) of 1-bromo-2,2-dimethyl-3-ethylidenecyclopropane, bp 47° (10 mm). A residue of 27.2 g of tri-*n*-butyltin bromide remained in the distillation flask.

The reduction was also attempted with trimethyltin hydride. Although the reaction appeared to proceed more rapidly than with tri-*n*-butyltin hydride, difficulties were encountered in separating all of the trimethyltin bromide from the product. Thus, no advantage accompanied the use of this hydride.

Reduction of the Alkylidenebromocyclopropanes.—The procedure was essentially the same as that for the reduction of the dibromo derivatives with the difference that longer time was required for complete reaction.

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The Chemistry of Allene. I. Factors Governing the Orientation of Free-Radical Addition

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The kinetics of free-radical addition of benzenethiol to allene has been studied and a reaction mechanism consistent with the results is proposed. At high thiol concentrations the ratio of products (M_1/M_2) resulting from thiyl radical addition to the terminal (M_1) and the central carbon (M_2) is a measure of the corresponding rate constants k_1/k_2. The difference between the corresponding activation energies $E_{k_1} - E_{k_2} = -1100$ cal/mole. Reversibility of the initial thiyl-radical addition to the terminal carbon explains the effects of the reaction temperatures and thiol concentrations on the ratio of the terminal and central isomers.

The orientation of the addition of free radicals or electrophilic reagents to allene has been the subject of several investigations and has been reviewed recently.[1] Factors governing the point of attack and the distribution of the products of addition, however, are not well understood. For example, addition of trifluoromethyl radicals, produced photochemically from trifluoroiodomethane, occurs at the terminal carbon.[2] More recently, attack by thiyl radicals from benzenethiol, methanethiol, or ethanethiol was reported to occur with high selectivity at the terminal carbon.[3,4] In a different study[5] the products from the free-radical addition of 1-propanethiol, benzenethiol, and α-toluenethiol to allene were attributed to the indiscriminate attack of thiyl radicals on the terminal or the central carbon atoms.

Factors governing the orientation of bromine atoms to allene are equally obscure. It has been reported that bromine atoms from hydrogen bromide in the liquid[6] and in the gas[7] phase attack allene at the central carbon. The addition of hydrogen bromide at room temperature and in the liquid phase proceeds similarly and gives 2-bromopropene as the major product, but selectivity of central carbon attack decreases with a decrease in the reaction temperature.[1] Three different mechanisms were proposed to account for the observed results.

The present investigation has been undertaken to obtain quantitative analysis of the orientation of free-radical additions to allene. The kinetics of free-radical addition of benzenethiol to allene has been studied, and effects of temperatures and thiol concentrations on the proportions of the terminal and central adduct were determined. The results have been compared with those obtained from the addition of trichloromethyl radicals from bromotrichloromethane.

Results

Benzenethiol Addition to Allene.—Benzenethiol in benzene as a solvent reacted smoothly with allene in the presence of either ultraviolet light or peroxides. Unreacted allene showed no isomerization to methylacetylene under the reaction conditions. In all the runs, phenylallyl sulfide, phenylisopropenyl sulfide, 1,2- and 1,3-bisphenylthiopropane, and phenyl disulfide were the only observed reaction products. There was complete absence of 1-phenylthiopropene which would be the expected product from the free-radical addition of benzenethiol to methylacetylene.

It was reported that some ionic addition of benzenethiol to phenylallyl sulfide took place at 82°.[5] Under our experimental conditions, however, there was no evidence of ionic addition to either phenylallyl sulfide or to allene. This was supported by (1) the absence of 2,2-bisphenylthiopropane and (2) the absence of 1,2-bisphenylthiopropane from blank runs of the addition of benzenethiol to phenylallyl sulfide. For the above reasons the products of the reactions were considered throughout to be derived from the thiyl-radical

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