water, the product was isolated by extraction with ether and washed with sodium bicarbonate and water. Evaporation of the solvents gave 117 mg. of crystalline material.

B.—A solution of periodic acid (120 mg.) in water (1.0 ml.) was added to a solution of III (80 mg.) in methanol (5.0) ml., and the reaction was stored at room temperature for 2.5 hr. The mixture was diluted with water, and the steroids were dissolved in ether. After washing with sodium bicarbonate and water, and drying over sodium sulfate, the organic solvents were removed *in vacuo*. Chromatography of the residue on thin layer plates (20% ethyl acetate–chloroform) gave 65 mg. of dione VI. A mixture melting point and infrared spectrum established the identity with the material from procedure A.

Repeated recrystallization of the product from methanol gave colorless prisms: m.p. 110–115°; $\nu_{\max}^{\mathrm{KBr}}$ 1730, 1690, and 1230 cm.$^{-1}$; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1725, 1700, and 1255 cm.$^{-1}$; n.m.r., τ 7.96, 8.93 (J = 6.5 c.p.s.), 9.13; R.D. in dioxane (c 0.061) $[\phi]_{430}$ −86, $[\phi]_{400}$ −80, $[\phi]_{350}$ +6, $[\phi]_{308-309}$ +2080, $[\phi]_{302}$ +2440, $[\phi]_{300}$ +2380, $[\phi]_{285}$ −402.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.43; H, 9.24.

17β-Hydroxy-4-methylestra-1,3,5(10)-triene (Ia). **A.**—To a solution of lithium (45 mg., 6.5 equiv.) in refluxing ethylamine (30 ml.) was added a solution of 17β-hydroxy-1-methoxy-4-methylestra-1,3,5(10)-triene (Ib, 300 mg.) in ethylamine. After the addition was complete, the reaction was stirred for 5 min., then decomposed by the addition of solid ammonium chloride. The steroids were recovered by extraction with ether to give 254 mg. of crude material.

Crystallization of the residue from methanol gave 31 mg. of 17β-hydroxy-4-methylestra-1,3,5(10)-triene, identical with an authentic sample.[4] Gas chromatographic analysis[15] of the mother liquor indicated the presence of three products having retention times of 430, 480, and 600 sec. The compounds having the retention times of 430 and 600 sec. were identified as IIa and Ia by the increase in detector response when authentic material was added to the sample. The 480-sec. peak overlapped with the 430-sec. peak. Its intensity decreased upon storage of the mother liquor with a simultaneous increase in the amounts of Ia.

B.—A solution of Ia (270 mg.) in ethylamine was added dropwise to a refluxing solution of lithium (45 mg., 5 equiv.) in ethylamine (30 ml.). When the addition was complete, the reaction was stirred for 5 min., then destroyed with excess ammonium chloride. The mixture was diluted with water, and the crude material was isolated by extraction with ether. Gas chromatography[15] of a portion of the crude material gave two overlapping peaks at 430 and 480 sec. Collection of the material on the decreasing slope gave a sample enriched in the "diene": $\nu_{\max}^{\mathrm{film}}$ 3370, 1440, 1375, and 1045 cm.$^{-1}$; $\lambda_{\max}^{\mathrm{MeOH}}$ no absorption 220–320 mμ; n.m.r., τ 4.28 (impurity), 4.57 (*ca.* 2H), 6.31 (J = 6.9 c.p.s.), 8.36 (4 methyl), 9.29 (18 methyl).

Again Ia was recovered from the mixture upon storage of the material. Occasional gas chromatographic analysis of the mixture showed decrease of the 480-sec. peak with a concomitant increase of the 600-sec. signal (Ia).

1-Methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one (Ic).—A mixture of 1-hydroxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one[12] (Id, 500 mg.), barium oxide (1.0 g.), barium hydroxide (1.0 g.), dimethylformamide (5 ml.), and dimethylsulfoxide (5 ml.) was stirred at 0°. Dimethylsulfate (3 ml.) was added, and the mixture was stirred overnight. The excess dimethylsulfate was destroyed with ammonium hydroxide (*ca.* 3 ml.), and the mixture was diluted with ether. The organic layer was washed with water, dried over sodium sulfate, and evaporated to give crystalline material.

A portion was recrystallized repeatedly from acetone to give an analytical sample: m.p. 160–163°; $\nu_{\max}$ 1700, 1580, and 800 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.74; H, 9.06.

4-Methyl-19-norpregna-1,3,5(10)-trien-20-one (Ie).—A solution of 1-methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one (Ic, 440 mg.) in ethylamine (20 ml.) was added to a stirred solution of lithium (40 mg.) in ethylamine (50 ml.). At the end of 5 min. ammonium chloride was introduced and the mixture was diluted with water. The steroids were isolated by extraction with ether.

The residue was a complex mixture, from which three major products were isolated by t.l.c. (chloroform). The most mobile substance was starting material. The other two components (180 mg.) were combined and oxidized with chromium trioxide (120 mg.) in pyridine (4.0 ml.) to give 4-methyl-19-norpregna-1,3,5(10)-trien-20-one (170 mg.). Recrystallization from acetone gave an analytical sample: m.p. 153–155°; $\nu_{\max}$ 1700, 1580, 780, and 740 cm.$^{-1}$; n.m.r., τ 7.78 (C-4 methyl), 7.83 (CH_3CO), 9.35 (18 Me).

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 84.77; H, 9.35.

Chemistry of *gem*-Dihalocyclopropanes.
II.[1] The Reaction of Dienes with Dibromocarbene

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The reaction of dibromocarbene with dienes generally gave a mixture of monoadducts and diadducts, *i.e.*, compounds derived from the addition of dibromocarbene to one or both double bonds of the diene, respectively. No 1,4-addition to a conjugated diene has been observed. The use of an excess of dibromocarbene increased the yield of diadduct, but it still became in only one case (XVIII) the main product of the reaction. The physical properties of these *gem*-dibromocyclopropane derivatives, particularly their ultraviolet spectra, are discussed.

The reaction of dihalocarbenes with olefins yielding the corresponding dihalocyclopropanes has been thoroughly studied[2] since its discovery by Doering and Hoffmann.[3] The additions of dihalocarbenes to dienes and polyenes, however, have not received the same attention. The reactions of 1,3-butadiene with dichloro- and dibromocarbene, as reported by Woodworth and Skell,[4] gave the corresponding monoadducts, 1,1-dihalo-2-vinylcyclopropanes, and Orchin and Herrick[5] also obtained the diadduct, 2,2,2′,2′-tetrachlorobicyclopropyl from the same reaction involving dichlorocarbene. Since this original work only a number of scattered examples of the addition of dihalocarbenes to dienes and polyenes have been reported.[2,6,7]

We want to report an extensive study on the reactions of dibromocarbene with conjugated as well as nonconjugated dienes. We were interested in the expected products, *i.e.*, the monoadducts A and the di-

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(1) Part I: L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

(2) For a review of the chemistry of halocarbenes, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

(3) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(4) R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

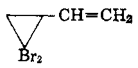
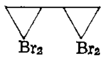
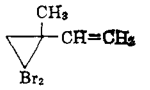
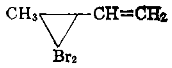
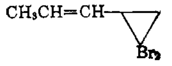
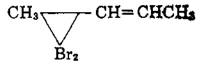
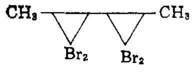
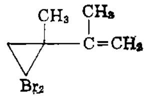
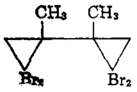
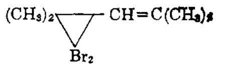
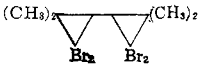
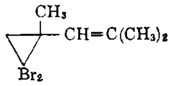
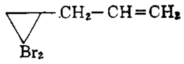
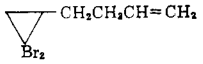
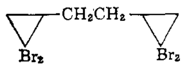
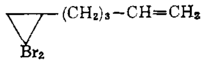
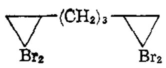
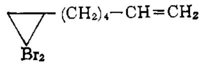
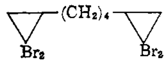
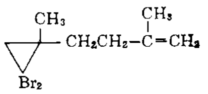
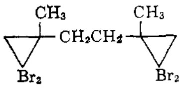
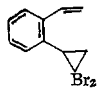
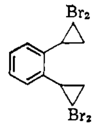
(5) M. Orchin and E. C. Herrick, *J. Org. Chem.*, **24**, 139 (1959).

(6) H. Komrsová and J. Farkaš, *Collection Czech. Chem. Commun.*, **25**, 1977 (1960).

(7) A. J. Birch and J. M. H. Graves, *Proc. Chem. Soc.*, 282 (1962).

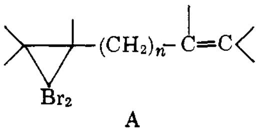
TABLE 1

REACTIONS OF DIENES WITH DIBROMOCARBENE

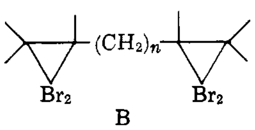
Diene	Molar ratio, $CHBr_3$–diene	Monoadduct	No.	Yield,[a] %	Diadduct	No.	Yield,[a] %
1,3-Butadiene	3		I	40		XV	9
	<1			58[b]			. . .
2-Methyl-1,3-butadiene	<1		II	60[b]	. . .		
1,3-Pentadiene	1		III	64[c,d]	. . .		
			IV				
2,4-Hexadiene[c]	1		V	74[c]		XVI	4[c]
	2.1			41[c]			21[c]
2,3-Dimethyl-1,3-butadiene	1		VI	77		XVII	. . .
	2.5			55			32
2,5-Dimethyl-2,4-hexadiene	1		VII	7		XVIII	20
	2.6			. . .			92
2,4-Dimethyl-1,3-pentadiene	1		VIII	62	. . .		
1,4-Pentadiene	1		IX	34	. . .		
1,5-Hexadiene	1		X	44		XIX	1
	2			32			12
1,6-Heptadiene	1.25		XI	47		XX	11
1,7-Octadiene	1.25		XII	46		XXI	12
2,5-Dimethyl-1,5-hexadiene	1		XIII	44		XXII	14
o-Divinylbenzene	1		XIV	27		XXIII	8

[a] The yields are, where not otherwise stated, based on the olefin. [b] The yield is based on bromoform. [c] Mixture of stereoisomers. [d] Yield of total mixture of III and IV.

adducts B, in order to study their reactions with alkyllithium. We had previously shown that alkyl- and aryl-substituted *gem*-dibromocyclopropanes reacted readily with methyl- or *n*-butyllithium to give, in most cases, good yields of allenes.[8] Similar results were also independently obtained by Moore and Ward.[9]



A



B

The reactions described here were carried out by adding bromoform to a stirred and cooled slurry of dry potassium *t*-butoxide, the respective diene, and pentane.[3,8] A small excess of the theoretical amount of base was always used. The results are summarized in Table I. Using equimolar amounts of the diene and bromoform, the monoadduct was the predominant product although some diadduct was usually formed. As expected, the amount of the latter was increased by increasing the ratio of bromoform to diene, but despite a considerable excess of dibromocarbene the diadduct remained, except for one case (XVIII), the minor product of the reaction.

The monoadducts were all liquids. The compounds with the double bond adjacent to the cyclopropane ring

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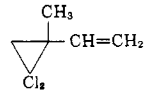
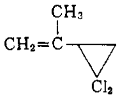
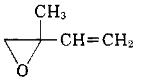
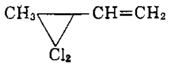
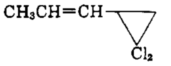
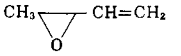
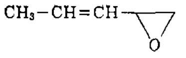
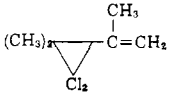
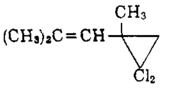
[8] L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

[9] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962).

Table II

Reactions of Dienes with Dichlorocarbene or Peracetic Acid

Diene	CCl_2 addition product (%)				CH_3CO_3H oxidation product (%)			
2-Methyl-1,3-butadiene		(98)		(2)				(100)
1,3-Pentadiene		(42)		(58)		(57)		(43)
2,4-Dimethyl-1,3-pentadiene		(12)		(88)			*a*	

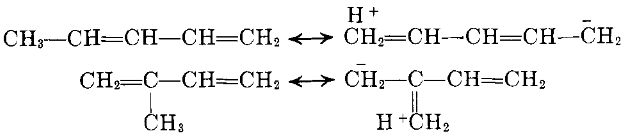
[a] The epoxidation of this diene gave a complex mixture of products. The infrared spectrum of the mixture showed no band in the 900-cm.$^{-1}$ region characteristic of a methylene double bond.

were quite unstable, gradually turning colored even on standing at 0°. The structural assignments were generally based on elemental analysis and spectroscopic evidence including nuclear magnetic resonance data. The product from 2-methyl-1,3-butadiene was found to consist principally of 1,1-dibromo-2-methyl-2-vinylcyclopropane (II), in agreement with results previously obtained from this[10] and similar[5,11] reactions. 2,4-Hexadiene, the starting material for another reaction described in Table I, was prepared by acid-catalyzed dehydration of 2-hexanol-4.[12] Gas chromatographic analysis showed that 10% of the product consisted of 1,3-hexadiene, which was separated by fractional distillation, and that the 2,4-hexadiene fraction was a mixture of stereoisomers.[13] These could not be separated by fractional distillation. The mixture was used in the subsequent reaction with dibromocarbene, and the monoadduct obtained, *viz.*, 1,1-dibromo-2-methyl-3-(1-propenyl)cyclopropane (V), was therefore a mixture of stereoisomers.

A good deal of information about the nature of the reaction of dichloro- and dibromocarbene with olefins has been accumulated in recent years.[2,14,15] It has been shown that the rate of addition to double bonds is enhanced by methyl substitution, and furthermore that the reaction compares well with peracid oxidation, a well-established electrophilic reaction.

In the case of methyl-substituted conjugated dienes one might perhaps expect addition to take place preferentially at the most substituted double bond. The results of Table I show that this is not always the case. In contrast with the selective addition of dibromocarbene to isoprene, the addition to 1,3-pentadiene gave a mixture consisting of 40% III and 60% IV. The reaction of 2,4-dimethyl-1,3-pentadiene with dibromocarbene gave mainly VIII; *i.e.*, addition occurred essentially at the double bond bearing the smallest number of methyl groups.

Since these *gem*-dibromocyclopropanes could not successfully be analyzed by gas chromatography the more stable dichloro analogs were prepared. The total reaction products were analyzed by gas chromatography and the results compared with those obtained by peracetic acid oxidation of the same dienes.[16] As can been seen from Table II, the results of these two reactions compare quite well and therefore the products are those expected for an electrophilic reaction.[14,15] The results can be rationalized on the basis of the two effects a methyl group will have on the electron density of double bonds, *i.e.*, the inductive and the hyperconjugative effects. A terminal methyl group will increase the electron density of both double bonds of a conjugated diene, but at a nonterminal position only the double bond bearing the methyl substituent will be effected. This is visualized below in the cases of 1,3-pentadiene and isoprene. This does not exclude the possibility of



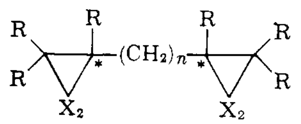
$$CH_3{-}CH{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{H^+}{CH_2}{=}CH{-}CH{=}CH{-}\overset{-}{C}H_2$$

$$\underset{CH_3}{CH_2{=}C}{-}CH{=}CH_2 \longleftrightarrow \overset{-}{C}H_2{-}\underset{H^+CH_2}{\overset{}{C}}{-}CH{=}CH_2$$

a certain steric effect in the dihalocarbene addition reactions, particularly with the bulky dibromocarbene. The data on this reaction[2] do not indicate, however, that such an effect would generally be significant.[17]

Our present knowledge of the mechanism of the dihalocarbene addition reaction indicates a three-center attack of the carbene to the unsaturated bond.[2] If an intermediate[4] were involved, a certain amount of 1,4-addition to a conjugated system might be expected. None of the reactions described here, however, gave products which even suggested that 1,4-addition had occurred.

The diadducts, which were formed in varying amounts in most of these reactions, were all stable compounds. Their structures were generally proven by elemental analysis and spectroscopic evidence. Compounds of the general structure shown below have two equivalent asymmetric centers (marked with



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[10] A. Ledwith and R. M. Bell, *Chem. Ind* (London), 459 (1959).

[11] I. A. Dyakonov and V. F. Myznikova, *Sb. Statei Obshch. Khim. Akad. Nauk, SSSR*, **1**, 489 (1953); *Chem. Abstr.*, **49**, 883 (1955).

[12] R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **61**, 2083 (1939).

[13] The mixture consisted of 54% *trans,trans*, 40% *cis,trans*, and 6% *cis,cis* isomers in good agreement with the results reported by Bartlett at the 18th National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June, 1963.

[14] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

[15] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[16] A. N. Pudovik and B. E. Ivanov, *J. Gen. Chem. USSR*, **26**, 3087 (1956).

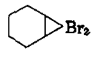
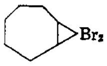
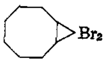
[17] Doering and Henderson[15] have found that in the addition to olefins the relative rate increase is smaller for dibromocarbene than for dichlorocarbene the greater the degree of methyl substitution, which may indicate that a steric factor is operating. A comparison of the relative rates of addition of chloro- and dichlorocarbene to olefins also points to the presence of a steric effect; see G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960).

asterisks), so that both *meso* and *d* and *l* forms would be expected. We have been able to confirm this in two cases. 2,2,2′,2′-Tetrabromobicyclopropyl (XV) was separated by fractional crystallization from methanol into a higher melting (128°) and a lower melting (81°) form, the former being the least soluble. The two forms show identical ultraviolet spectra, but both their infrared and n.m.r. spectra are different. Similar results were obtained in the case of 1,2-bis(2,2-dibromo-1-methylcyclopropyl)ethane (XXII). On the basis of the n.m.r. spectrum, XVIII also appears to be formed in both isomers. We assume that the higher melting isomer in each case has the *meso* configuration.

The ultraviolet absorption of these compounds was quite interesting in that all showed medium-intensity absorption in the 195–215-mμ region. Subsequently, we found that this absorption is not characteristic of the diadducts since a number of simple alkyl-substituted *gem*-dibromocyclopropanes also absorbed in this region. Kimura and Nagakura[18] have recently studied the near-ultraviolet absorption spectra of alkyl iodides and bromides. This absorption was assigned to an n → σ* transition in which one of the lone-pair electrons on the bromine atom became excited. We assume that the absorption of the *gem*-dibromocyclopropanes is due to the same type of transition.[19] The above authors furthermore observed that methyl substituents on the carbon bonded to the halogen atom caused bathochromic shifts of the absorption maxima. As can be seen from the data collected in Table III, a similar substituent effect was also observed in the present work and the question arose as to whether this effect was steric or polar by nature. By comparing the maxima of the bicyclopropyl compounds XV–XVII and also the cyclopropane derivatives, 1,1-dibromo-2-*n*-hexylcyclopropane and XII, it became clear that the substituent effect could not be essentially steric. The shifts may, however, be explained by a polar effect in which the alkyl groups cause bathochromic shifts and the alkenyl groups hypsochromic shifts.[20] This appears to be a reasonable assumption since any change in the electron density distribution of the carbon–halogen bond would be expected to change correspondingly the ionization potential of the lone-pair electrons of the halogen atom. Accordingly, electron-releasing substituents should lower this energy causing a bathochromic shift of the maxima and the opposite should be true for electron-attracting groups. Since the substituents are always attached to the carbon adjacent to the one bearing the bromine atoms, the present results can be regarded as further evidence for the ability of the cyclopropane ring to transmit electronic effects.[21]

TABLE III

THE ULTRAVIOLET ABSORPTION OF *gem*-DIBROMOCYCLOPROPANE DERIVATIVES

Derivative	λmax, mμ *n*-Hexane	 Methanol	ε[a]
Diadducts			
XV	204		5400
XVI	208.5	208.5	5400
XVII	202		5000
XVIII	213	211.5	6200
XIX	199.5		4500
XX	199.5		4700
XXI	199.5		4700
XXII	203		4700
Monoadducts			
I–XIII	End absorption[b]		
Cyclopropane, dibromo-			
-2-*n*-hexyl-	199.5		2400
-*cis*-2,3-dimethyl-	202.5		3000
-2,2-dimethyl-	202.5		2600
-trimethyl-	206	205	2500
-tetramethyl-	208	208	3400
	203.5		3000
	206[c]	206	3500
	206[c]		3100

[a] These values refer to measurements in *n*-hexane (*n*-heptane). [b] VII shows a maximum at 199 mμ (ε 12,600), but this is probably due to a π → π* transition. Since the spectra were not recorded under an inert atmosphere, maxima below 200 mμ are of questionable accuracy. [c] Measured in *n*-heptane as solvent.

The *gem*-dibromocyclopropane ring caused a bathochromic shift in magnitude practically equivalent to or more than that of a methyl group. This electron-repelling property of the cyclopropyl group is well established,[21] and particularly striking in this respect is the kinetic study by Hart and Sandri[22] on the solvolysis of *p*-nitrobenzoates of cyclopropylcarbinols and the stability of the tricyclopropylcarbonium ion.[23] It is clearly not an inductive electron release because this has been shown to be less than that of a methyl group.[24] Several authors have suggested a hyperconjugative effect,[21] but a really satisfactory explanation is still missing. The maxima of all the *gem*-dibromocyclopropane derivatives were at lower wave lengths and of higher intensity than the corresponding values for methylene bromide.[18] Accepting the unsaturated picture[25] of the cyclopropane ring, this could perhaps be explained by a weak overlap of the lone-pair electrons of the bromine with the ring which would increase the ionization potential of the said electrons. The electric dipole moments of the following dichlorides indicate that such an interaction is probably present: 2,2-dichloropropane, 2.25 D.[26]; 1,1-dichlorocyclopropane, 1.59 D.[27]; and 1,1-dichloroethylene, 1.30 D.[28] This interaction is probably even stronger in the correspond-

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(18) K. Kimura and S. Nagakura, *Spectrochim. Acta*, **17**, 166 (1961).

(19) In a recent paper, H. Weitkamp, U. Hasserodt, and F. Korte [*Chem. Ber.*, **95**, 2280 (1962)] report the ultraviolet absorption maxima of two *gem*-dibromocyclopropanes. One of the compounds, *viz.*, 1,1-dibromo-2-methyl-3-isopropylcyclopropane, shows a bathochromic shift (4.5 mμ) of its maximum changing the solvent from cyclohexane to methanol. In the present work, however, essentially no shift or a small hypsochromic shift was invariably observed which is not inconsistent with an n → σ* transition.

(20) It is possible that the end absorption caused by the double bonds of the monoadducts will tend to blur any maximum due to the n → σ* transition of these compounds. Hence, the present results do not conclusively establish the hypsochromic effect of the double bond on this transition.

(21) For a comprehensive review, see M. Y. Lukina, *Usp. Khim.*, **31**, 901 (1962); *Russ. Chem. Rev.*, 419 (1962).

(22) H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).

(23) N. C. Deno, H. G Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

(24) T. L. Brown, J. M. Sandri, and H. Hart, *J. Phys. Chem.*, **61**, 698 (1957).

(25) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(26) A. A. Maryott, M. E. Hobbs, and P. M. Gross, *J. Am. Chem. Soc.*, **63**, 659 (1941).

(27) W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962).

(28) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 1243 (1947).

ing bromides, but the pertinent data are unfortunately not available.

The reactions of the *gem*-dibromocyclopropane derivatives described in this paper (Table I) with methyllithium have in part been published[29] as a preliminary communication. A full account of that investigation will be reported in subsequent papers.

Experimental

General.—Boiling points and melting points are uncorrected. All reactions were carried out under nitrogen.

The dienes were either commercial products or samples prepared by conventional methods. The purity as determined by analytical gas chromatography was in no case less than 98%. Reagent grade bromoform and commercial grade anhyrous *t*-butyl alcohol were used without further purification. The pentane was a 99+ % grade, dried over sodium.

The analytical gas chromatograms were obtained on a Perkin-Elmer vapor fractometer with helium as carrier gas. The infrared spectra were recorded on Perkin-Elmer Model 21 and Beckman IR 5 spectrometers. The ultraviolet spectra were recorded on a Cary Model 14 spectrometer and, when not otherwise stated, *n*-hexane was used as solvent. With this solvent the slit was fully open at 192 mμ, and no appreciable solvent absorption was noted above 195 mμ. The n.m.r. spectra were measured on a Varian A 60 instrument. Carbon tetrachloride was used as solvent and tetramethylsilane as internal standard.

Reactions of Dienes with Dibromocarbene. General Procedure.—The method employed was essentially that described by Doering and Hoffmann.[3] Bromoform was slowly added to a stirred slurry of potassium *t*-butoxide, the diene, and dry pentane, surrounded by an ice–salt bath. The amount of pentane is not critical and varied between 200 and 280 ml./mole of bromoform. The addition time was usually 6–8 hr. The reaction mixture was left stirring at room temperature overnight. Water was added, and the product was extracted with ether and worked up in the ordinary way. Table I summarizes the results. The yields are, if not otherwise stated, based on the diene.

1,1-Dibromo-2-vinylcyclopropane (I) and 2,2,2′,2′-Tetrabromobicyclopropyl (XV).—1,3-Butadiene reacted with dibromocarbene giving a 40% yield of I: b.p. 76–82° (50 mm.), $n^{22}\text{D}$ 1.5462; lit.[4] b.p. 69.5–70 (26 mm.), $n^{25}\text{D}$ 1.5420. The distillation residue was dissolved in benzene and passed through a column of alumina. Evaporation of the solvent and crystallization of the residue from methanol gave XV in 9% yield, m.p. 75–110°.

Anal. Calcd. for $C_6H_6Br_4$: C, 18.12; H, 1.52. Found: C, 17.94; H, 1.64.

By fractional crystallization from methanol, crystals, m.p. 121–122° and m.p. 81–82°, were obtained, the former being the least soluble. The ultraviolet spectra (Table III) of the two forms are identical, while the infrared spectra are different as solids as well as in carbon tetrachloride and carbon disulfide. The n.m.r. spectrum of the lower melting isomer shows two multiplets at τ 8.14 and 8.62 with relative peak areas 2:1. The other isomer shows very complex absorption at τ 7.7–8.6. In a run with an excess of 1,3-butadiene, a 58% yield of I and no XV was obtained.

1,1-Dibromo-2-methyl-2-vinylcyclopropane (II).—The reaction between 2-methyl-1,3-butadiene and dibromocarbene yielded 60% of a liquid, b.p. 69–72° (13 mm.), which by gas chromatography was shown to consist of >98% of II. Refractionation gave pure II: b.p. 68–69° (10 mm.); $n^{23}\text{D}$ 1.5395; lit.[4] b.p. 70° (12 mm.); ν_{max} 1630, 988, and 913 cm.$^{-1}$ (-CH=CH$_2$). A detailed discussion of the n.m.r. spectrum has recently been published.[30]

Reaction of 1,3-Pentadiene with Dibromocarbene.—The 1,3-pentadiene used consisted of a mixture of 71% *trans* and 29% *cis* isomers. The addition of dibromocarbene to this mixture gave a liquid in 64% yield: b.p. 64–70° (8 mm.), $n^{24}\text{D}$ 1.5383.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.21; H, 3.47.

The liquid was shown by gas chromatography and infrared spectroscopy to consist of 40% 1,1-dibromo-2-methyl-3-vinylcyclopropane (III) and 60% 1,1-dibromo-2-(1-propenyl)cyclopropane (IV).

Reaction of 1,3-Pentadiene with Dichlorocarbene.—The same isomeric mixture of 1,3-pentadiene was used. The reaction gave 54% of a mixture of monoadducts: b.p. 64–66° (40 mm.), $n^{24}\text{D}$ 1.4771. No separation of these was achieved by fractional distillation.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.71; H, 5.34. Found: C, 47.99; H, 5.58.

The mixture was found by gas chromatography and infrared spectroscopy to consist of 42% 1,1-dichloro-2-methyl-3-vinylcyclopropane and 58% 1,1-dichloro-2-(1-propenyl)cyclopropane.

1,1-Dibromo-2-methyl-3-(1-propenyl)cyclopropane (V) and 2,2,2′,2′-Tetrabromo-3,3′-dimethylbicyclopropyl (XVI).—The reaction of 2,4-hexadiene with dibromocarbene yielded 74% of V: b.p. 60–62° (2 mm.), $n^{22.5}\text{D}$ 1.5349. The presence of strong bands at 960 and 735 cm.$^{-1}$ in the infrared spectrum, characteristic of *trans* and *cis* double bonds, respectively, indicates a stereoisomeric mixture.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 32.84; H, 4.00.

Digestion of the distillation residue gave a solid which after recrystallization from methanol yielded 4% of XVI, m.p. 87°.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37. Found: C, 22.95; H, 2.32.

From another run, using an excess of 2 molar equiv. of dibromocarbene, V was obtained in 41% yield together with 21% yield of the diadduct XVI as a viscous liquid, b.p. 96–105° (0.1 mm.), $n^{24}\text{D}$ 1.5808.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37. Found: C, 22.49; H, 2.25.

By standing, the liquid partly crystallized, and the above isomer, m.p. 87°, was separated. The n.m.r. spectrum of the crystalline XVI shows a strong singlet at τ 8.57 which is assigned to the methyl groups. Almost covered by this peak is a doublet due to the cyclopropyl proton adjacent to the methyl group. This proton and the methyl protons show no evidence of coupling because of their nearly identical chemical shifts. Finally, a multiplet at τ 8.95 represents the other cyclopropyl hydrogens.

1,1-Dibromo-2-methyl-2-isopropenylcyclopropane (VI).—The reaction between equimolar amounts of dibromocarbene and 2,3-dimethyl-1,3-butadiene gave a 77% yield of VI: b.p. 68–70° (9 mm.), $n^{26}\text{D}$ 1.5250, ν_{max} 1670 and 898 cm.$^{-1}$ (>C=CH$_2$).

The isopropenyl group shows a clear ABX$_3$ pattern in the n.m.r. spectrum with multiplets at τ 5.05 and 5.20 and a triplet at 8.05. The cyclopropyl protons form an AB pattern with a quadruplet centered at τ 8.24 and $|J|$ = 6.7 c.p.s. The methyl group attached to the cyclopropane ring shows a single peak at τ 8.53. The peak area ratio is 2:3:2:3.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 33.31; H, 3.91.

2,2,2′2′-Tetrabromo-1,1′-dimethylbicyclopropyl (XVII).—The reaction of 2,3-dimethyl-1,3-butadiene with an excess of dibromocarbene gave 55% yield of VI and 32% of XVII, m.p. 96–99°. Pure XVII was obtained by sublimation, m.p. 100°. The n.m.r. spectrum in CCl$_4$ solution shows only two singlets at τ 8.33 (CH$_3$) and 8.48 (cyclopropyl CH$_2$). In acetone solution, however, the latter forms a quadruplet. The peak area ratio is 3:2.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.56; H, 2.37. Found: C, 22.73; H, 2.48.

1,1-Dibromo-2,2-dimethyl-3-isobutenylcyclopropane (VII).—The addition of dibromocarbene to 2,5-dimethyl-2,4-hexadiene. using equimolar amounts, gave a crystalline product. The main part (20%) was the diadduct XVIII, described below, but by fractional crystallization and final sublimation a small amount (7%) of VII was obtained: m.p. 40-41°; ν_{max} 1625 and 842 cm.$^{-1}$ (C=CH—); n.m.r. (τ), multiplets at 5.10 (C=CH) and 8.07 (cyclopropyl hydrogen), doublets at 8.20 and 8.26 [=C-(CH$_3$)$_2$], and singlets at 8.53 and 8.81 (–CH$_3$). The peak area ratio is 1:1:6:3:3.

Anal. Calcd. for $C_9H_{14}Br_2$: C, 38.33; H, 5.00. Found: C, 37.77; H, 5.24.

The compound is very unstable. A considerable amount of the diene was recovered.

2,2,2′,2′-Tetrabromo-3,3,3′,3′-tetramethylbicyclopropyl (XVIII).—The reaction of 2,5-dimethyl-2,4-hexadiene with an excess of 2 molar equiv. of dibromocarbene yielded 92% of XVIII, m.p. 107–109°.

Recrystallization from ethanol raised the melting point to 109°. The n.m.r. spectrum shows four singlets at τ 8.83, 8.80, 8.72, and

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(29) L. Skattebøl. *Chem. Ind.* (London), 2146 (1962).

(30) E. B. Whipple and Y. Chiang. *J. Chem. Phys.*, **40**, 713 (1964).

8.47, respectively, and a weakly split doublet at 8.55. This strongly indicates that the sample is a mixture of *meso* and *d* and *l*, forms.

Anal. Calcd. for $C_{10}H_{14}Br_4$: C, 26.46; H, 3.11. Found: C, 26.70; H, 3.09.

1,1-Dibromo-2-methyl-2-isobutenylcyclopropane (VIII).—The addition of dibromocarbene to 2,4-dimethyl-1,3-pentadiene gave a liquid in 62% yield, b.p. 60–62° (2 mm.). The infrared spectrum showed that the liquid consisted mainly of VIII. Some of the isomeric compound, *i.e.*, 1,1-dibromo-2,2-dimethyl-3-isopropenylcyclopropane, was present as indicated by a weak band at 900 cm.$^{-1}$. Gas chromatographic analysis was unsuccessful because of decomposition. VIII was obtained free of the isomer by careful fractional distillation: b.p. 62° (2 mm.); $n^{23}\mathrm{D}$ 1.5232; n.m.r. (τ), multiplet centered at 4.62 (—CH=C), doublet at 8.28 [$C{=}C(CH_3)_2$] and singlets at 8.41 (cyclopropyl H) and 8.58 ($-CH_3$). The peak area ratio is 1:6:2:3.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51. Found: C, 35.77; H, 4.67.

Reaction of 2,4-Dimethyl-1,3-pentadiene with Dichlorocarbene.—The reaction was carried out as for the dibromocarbene reaction but using chloroform. A liquid was obtained in 46% yield: b.p. 67–69° (12 mm.), $n^{23.5}\mathrm{D}$ 1.4741. The infrared spectrum shows a medium to weak band at 900 cm.$^{-1}$ ($C{=}CH_2$).

Anal. Calcd. for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75. Found: C, 53.58; H, 6.89.

Gas chromatographic analysis shows that the liquid consists of 88% 1,1-dichloro-2-methyl-2-isobutenylcyclopropane and 12% 1,1-dichloro-2,2-dimethyl-3-isopropenylcyclopropane.

1,1-Dibromo-2-(2-propenyl)cyclopropane (IX).—The reaction of equimolar amounts of dibromocarbene and 1,4-pentadiene yielded 34% of IX: b.p. 61–62° (8 mm.); $n^{24}\mathrm{D}$ 1.5230; $\nu_{\max}$ 1645, 995, and 918 cm.$^{-1}$ ($—CH{=}CH_2$).

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.33; H, 3.33.

1,1-Dibromo-2-(3-butenyl)cyclopropane (X) and 1,2-Bis(2,2-dibromocyclopropyl)ethane (XIX).—1,5-Hexadiene reacted with a molar excess of dibromocarbene yielding 32% of X: b.p. 78–79° (8 mm.); $n^{20}\mathrm{D}$ 1.5180; $\nu_{\max}$ 1640, 992, and 913 cm.$^{-1}$ ($—CH{=}CH_2$).

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 32.98; H, 3.91.

The residue was digested with some methanol, and, by cooling, a solid was obtained. Recrystallization from methanol gave 6% of XIX, m.p. 68–70°.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.57; H, 2.37. Found: C, 22.80; H, 2.57.

Distillation of the mother liquor gave 6% of liquid XIX: b.p. 140-150° (bath temperature) (0.05 mm.), $n^{25}\mathrm{D}$ 1.5737.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.57; H, 2.37. Found: C, 22.78; H, 2.33.

With equimolar amounts of 1,5-hexadiene and dibromocarbene 44% of X and only 1% of crystalline XIX were obtained.

1,1-Dibromo-2(4-pentenyl)cyclopropane (XI) and 1,3-Bis(2,2-dibromocyclopropyl)propane (XX).—The reaction between 1,6-heptadiene and a slight excess of dibromocarbene gave XI in 47% yield: b.p. 58–59° (1 mm.); $n^{24}\mathrm{D}$ 1.5124; $\nu_{\max}$ 1640, 992 and 914 cm.$^{-1}$ ($—CH{=}CH_2$).

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51. Found: C, 35.72; H, 4.35.

The residue was distilled to yield 11% of XX: b.p. 90–100° (0.05 mm.), $n^{24}\mathrm{D}$ 1.5684.

Anal. Calcd. for $C_9H_{12}Br_4$: C, 24.58; H, 2.75. Found: C, 24.60; H, 2.84.

1,1-Dibromo-2-(5-hexenyl)cyclopropane (XII) and 1,4-Bis(2,2-dibromocyclopropyl)butane (XXI).—The addition of dibromocarbene to 1,7-octadiene gave 46% of XII: b.p. 55° (0.2 mm.); $n^{24}\mathrm{D}$ 1.5085; $\nu_{\max}$ 1640, 993, and 910 cm.$^{-1}$ ($—CH{=}CH_2$).

Anal. Calcd. for $C_9H_{14}Br_2$: C, 38.33; H, 5.00. Found: C, 38.15; H, 5.15.

The residue was distilled to yield 12% of XXI: b.p. 100–110° (0.03 mm.), $n^{23}\mathrm{D}$ 1.5604.

Anal. Calcd. for $C_{10}H_{14}Br_4$: C, 26.46; H, 3.11. Found: C, 26.61; H, 3.43.

1,1-Dibromo-2-methyl-2-(3-methyl-3-butenyl)cyclopropane (XIII) and 1,2-Bis(2,2-dibromo-1-methylcyclopropyl)ethane (XXII).—The reaction of 2,5-dimethyl-1,5-hexadiene with an equimolar amount of dibromocarbene gave XIII in 44% yield: b.p. 65° (0.4 mm.), $n^{20}\mathrm{D}$ 1.5180, $\nu_{\max}$ 1650 and 887 cm.$^{-1}$ ($C{=}CH_2$).

Anal. Calcd. for $C_9H_{14}Br_2$: C, 38.33; H, 5.00. Found: C, 38.25; H, 5.21.

During the work-up of this reaction some solid was filtered and recrystallized from methanol to give 5.5% of the diadduct XXII: m.p. 128°; n.m.r. (τ), quadruplet at 8.12 ($-CH_2-$), doublet at 8.57 (cyclopropyl CH_2), and a singlet at 8.65 with the peak area ratio 2:2:3.

Anal. Calcd. for $C_{10}H_{14}Br_4$: C, 26.46; H, 3.11. Found: C, 26.66; H, 3.05.

The distillation residue solidified and was recrystallized from methanol to give 8.5% yield of XXII: m.p. 65°, n.m.r. (τ), quadruplet at 8.15 and singlets at 8.60 and 8.62. The infrared spectra of the two solids are similar but not identical in carbon tetrachloride or carbon disulfide solutions and as KBr pellets.

***o*-(2,2-Dibromocyclopropyl)styrene (XIV) and *o*-Bis(2,2-dibromocyclopropyl)benzene (XXIII).**—The reaction between *o*-divinylbenzene and dibromocarbene produced a 27% yield of XIV: b.p. 92–94° (0.2 mm.); $n^{25}\mathrm{D}$ 1.6044; $\nu_{\max}$ 1625, 990, and 920 ($—CH{=}CH_2$), 1600, 1485, and 765 cm.$^{-1}$ (Ph).

Anal. Calcd. for $C_{11}H_{10}Br_2$: C, 43.74; H, 3.33. Found: C, 44.03; H, 3.23.

Some solid material was sublimed and recrystallized from *n*-heptane to give (8%) of XXIII: m.p. 153–154°; n.m.r. (τ), multiplet at 1.85 (Ph-H), triplet at 6.73, and quadruplet at 7.80 with relative peak areas 2:1:2, respectively; $\lambda_{\max}$ (*n*-heptane) 200.5 mμ (ϵ 3200).

Anal. Calcd. for $C_{12}H_{10}Br_4$: C, 30.42; H, 2.13. Found: C, 30.22; H, 2.46.

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