4-(β,β-Dichlorocyclopropyl)cyclohexene showed infrared (pure liquid) 3025 (s), 2915 (s), 2840 (s), 1650 (m), 1605 (sh), 1450 (m), 1440 (s), 1390 (m), 1340 (w), 1292 (w), 1271 (w), 1248 (w), 1227 (m), 1211 (m), 1190 (w), 1139 (m), 1123 (m), 1109 (s), 1042 (s), 1008 (m), 957 (m), 932 (w), 910 (m), 895 (w), 872 (m), 841 (w), 793 (w), 752 (s), 723 (w), 650 (s), and 555 (w) cm.$^{-1}$; n.m.r. (CCl$_4$) triplet at 5.62 (2 H) and multiplets at 2.05 (6 H), 1.5 (3 H), and 1.05 p.p.m. (1 H).

1,1-Dichloro-2-ethoxymethylcyclopropane gave infrared (pure liquid) 3075 (w), 3000 (sh), 2975 (s), 2925 (w), 2865 (s), 2805 (w), 1480 (m), 1450 (m), 1385 (s), 1370 (w), 1345 (w), 1270 (w), 1247 (w), 1220 (m), 1153 (m), 1105 (s), 1069 (w), 1059 (w), 1035 (w), 975 (m), 942 (w), 891 (w), 871 (w), 850 (w), 817 (w), and 750 (s) cm.$^{-1}$; n.m.r. (CCl$_4$) multiplet at 3.6 (4 H), triplet at 1.25, and a multiplet centered at 1.4 p.p.m. (6 H total).

4,4-Dichloro-3-ethoxy-1-butene had infrared (pure liquid) 3075 (m), 3010 (sh), 2975 (s), 2925 (w), 2890 (m), 2865 (s), 2775 (w), 1875 (w), 1650 (m), 1480 (m), 1450 (m), 1425 (m), 1400 (m), 1315 (sh), 1310 (m), 1215 (m), 1175 (m), 1120 (s), 1098 (s), 1070 (m), 1022 (w), 993 (m), 940 (s), 892 (m), 779 (s), 705 (w), and 680 (m) cm.$^{-1}$; n.m.r. (CCl$_4$) multiplet centered at 5.6 (4 H, includes dichloromethyl proton), doublet at 3.8 quartet at 3.4 (3 H total), and triplet at 1.25 p.p.m. (3 H).

The Halogenation of Diazomethane. Study of the Reactivities of Carbenes Derived from Halodiazomethanes[1-3]

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Halogenation of diazomethane with less than molar amounts of t-butyl hypohalites at −100° gives halodiazomethanes in good yields. Thermolysis at −10° and photolysis of chloro- and bromodiazomethane yield free halocarbenes with undergo insertion reactions and additions to olefins. Halocarbenes from halodiazomethanes are less reactive than methylene but more reactive than the chlorocarbenoid generated from methylene chloride by α-elimination. Halogenation of diazomethane with 2 equiv. of t-butyl hypohalite probably leads to dihalodiazomethanes which are too unstable to be characterized. Product analysis of reactions carried out in olefins as solvent suggests that dihalodiazomethanes decompose instantaneously to nitrogen and dihalomethylenes.

Ever since the pioneering studies by Hine and Doering halocarbenes have been postulated as intermediates in a great variety of reactions.[5] Comparison of the reactivities of these carbenes with that established for methylene generated from diazomethane or ketene revealed significant differences between the parent carbene and its halogen derivatives. Perhaps the most

striking discrepancy in the behavior of the postulated intermediates is the fact that methylene inserts into the carbon–hydrogen bond with great ease, while its halogen derivatives undergo this reaction only under very special conditions.[6] Considering only conventional structure–reactivity relationships, this behavior can be attributed to resonance stabilization in halocarbenes.[10,11] Although this conclusion is probably qualitatively correct, it does not take into account that the two types of carbenes were generated by two entirely different reactions and under otherwise incomparable conditions. Justification for this reservation is found in the observation that other methylene transfer reagents when produced by α-elimination processes are also considerably more selective and frequently do not give the insertion reaction either.[12,13] Recently severe doubt has been cast on the notion that any α-elimination necessarily proceeds through a carbene, even when trapping experiments seem to indicate the intermediacy of such species.[14,15]

(1) Supported by a grant from the Petroleum Research Fund and by an unrestricted grant from Shell Development Co.

(2) This paper is taken from the Ph.D. Thesis of J. J. Coyle, University of Chicago, 1965.

(3) A part of this work was published as preliminary communication, G. L. Closs and J. J. Coyle, J. Am. Chem. Soc., 84, 4350 (1962).

(4) A. P. Sloan Foundation Fellow, 1962–1966.

(5) For recent summaries of carbene chemistry see: (a) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; (b) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (c) W. E. Parham and E. E. Schweizer, Org. Reactions, 13, 55 (1963).

(6) Dichloromethylene, for example, will not insert into the C–H bonds of hydrocarbons in the presence of alkoxides.[7] Only if less nucleophilic reagents such as sodium trichloroacetate[8] or bromodichloromethylphenylmercury[9] are used for the formation of dichloromethylene, have C–H bond insertions been observed.

(7) W. v. E. Doering and A. K. Hoffmann, J. Am. Chem. Soc., 76, 6162 (1954).

(8) E. K. Fields, ibid., 84, 1744 (1962).

(9) D. Seyferth and J. M. Burlitch, ibid., 85, 2667 (1963).

(10) P. S. Skell and A. Y. Garner, ibid., 78, 5430 (1956).

(11) G. L. Closs and G. M. Schwartz, ibid., 82, 5729 (1960).

(12) Cf. H. E. Simmons and R. D. Smith, ibid., 80, 5323 (1958).

(13) L. Friedman and J. G. Berger, ibid., 82, 5758 (1960).

(14) G. L. Closs and R. A. Moss, ibid., 86, 4042 (1964).

(15) For a recent review on the mechanism of α-elimination see W. Kirmse, Angew. Chem., 77, 1 (1965); Angew. Chem. Intern. Ed. Engl., 4, 1 (1965).

Since the pyrolysis or photolysis of diazocompounds is the least ambiguous route to divalent carbon intermediates, we found it highly desirable to prepare and study the decomposition of halodiazomethanes. The immediate goals of this research were (a) to study the influence of halogen substitution on the reactivity of methylene and (b) to learn whether product distributions from the diazo compound decompositions deviate substantially from those observed in α-elimination reactions where formally identical intermediates had been postulated.

Among the many possible approaches to the synthesis of the hitherto unknown halogen derivatives of diazomethane,[16] halogenation of diazomethane appeared to us the most promising. The reaction of elemental halogen with diazomethane produces methylene halides,[17] and must therefore be discarded as a feasible synthesis. However, mechanistic speculations led us to try *t*-butyl hypohalites as halogenation reagents.

Results

When *t*-butyl hypochlorite in trichlorofluoromethane (Freon 11) was added dropwise to a solution of diazomethane in *n*-pentane, instantaneous violent reaction was observed. By lowering the temperature to −100° it was possible to control the reaction to the extent that little nitrogen evolution took place during the addition. Simultaneous with the addition of the reagent the color of the solution changed to deep red. Use of less than a molar amount of *t*-butyl hypochlorite (usually 70%) was found to optimize yields and purity of products in subsequent reactions. On warming the solution to −40° slow nitrogen evolution set in which became quite rapid at −10° and led to decolorization of the solution. Evidence that the reaction mixture at low temperature indeed contained the desired chlorodiazomethane is based on physical and chemical properties of the solution. The infrared spectrum, recorded at approximately −60°, indicates the presence of a diazo group with a strong stretching vibration at 2066 cm.$^{-1}$. The corresponding vibration of diazomethane appeared at 2097 cm.$^{-1}$ under identical conditions. The visible spectrum of the solution resembles that of diazomethane with a considerable red shift. Absorption maxima of nearly equal intensities were found at 485, 518, and 545 mμ, probably originating from one electronic transition with vibrational fine structure. Chemical evidence for the presence of chlorodiazomethane was provided by reaction with acetic and propionic acid. Chloromethyl acetate and chloromethyl propionate were isolated in modest yields. Additional chemical evidence for the presence of chlorodiazomethane in solution comes from the reactions with olefins to be discussed below.

Reaction of diazomethane solutions with somewhat less than 1 equiv. of *t*-butyl hypobromite proceeded essentially in the same manner. The spectral characteristics of bromodiazomethane were found to be very similar to those of the chloro analog (infrared, 2069 cm.$^{-1}$; visible, broad maximum at 540 mμ).

Because of the intrinsic instabilities of chloro- and bromodiazomethane neither of the compounds was amenable to further purification. Therefore all reactions were carried out with the crude reaction mixture containing besides solvent and substrate *t*-butyl alcohol and small amounts of unreacted diazomethane. Furthermore, for the study of reactions of halodiazomethanes with olefins it was found advantageous to generate the diazomethane in the olefin and to carry out the halogenation in the same medium. The well-known halogenation of olefins with *t*-butyl hypohalites[18] introduced no further complication when less than 1 equiv. of *t*-butyl hypohalite was used. Presumably olefin halogenation cannot compete with the extremely rapid reaction of diazomethane with hypohalites.

Thermolysis of chloro- and bromodiazomethane at −10° in *n*-pentane gave rise to the three isomeric chloro- and bromohexanes (II–IV). The products were isolated by gas–liquid partition chromatography (g.l.p.c.) and were characterized by comparison with authentic samples. Difficulties were encountered with the g.l.p.c. separation of III and IV. However, the infrared spectra showed that both isomers were present. The ratios of the branched (III + IV) *vs.* the unbranched (II) products were 20:1 from chlorodiazomethane and 25:1 from bromodiazomethane. No significant change from this ratio was found when chlorodiazomethane was photolyzed at −50°.[19] Although the yields of insertion products II–IV did not exceed 9% in the thermolysis and 11% in the photolysis, they comprised the major fraction of volatile products obtained in the reaction.

$$XCH_2(CH_2)_4CH_3$$
$$IIa, X = Cl$$
$$IIb, X = Br$$

$$XCHN_2 + n\text{-}C_5H_{12} \xrightarrow{\Delta} CH_3\text{—}CH\text{—}(CH_2)_2CH_3$$
$$\underset{CH_2X}{|}$$

Ia, X = Cl IIIa, X = Cl
Ib, X = Br IIIb, X = Br

$$CH_3CH_2\text{—}CH\text{—}CH_2CH_3$$
$$\underset{CH_2X}{|}$$
IVa, X = Cl
IVb, X = Br

Thermolysis of chloro- and bromodiazomethane in various olefins gave the corresponding halocyclopropanes in yields ranging from 40 to 60%. Adducts were prepared from cyclohexene and from the olefins listed in Table II. The chlorocyclopropanes were known compounds, synthesized earlier in our laboratory *via* the reaction of methylene chloride with alkyllithium in olefins.[20] Three of the bromocyclopropanes have been reported previously,[21] and the remaining unknown compounds were characterized by their elemental analysis and infrared and n.m.r. spectra. In all those

(16) Recently the first well-characterized halogen derivative of an isomer of diazomethane, difluorodiazirine, has been described: R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).
(17) H. v. Pechmann, *Ber.*, **31**, 2640 (1889).

(18) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).
(19) Although thermolysis of chlorodiazomethane proceeds with measurable rate at this temperature, the rate of nitrogen evolution in this experiment showed that the major decomposition path was photolytic.
(20) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); **82**, 5723 (1960).
(21) D. Seyferth, H. Yamazaki, and D. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

cases where the symmetry of the olefin dictates the formation of two epimers, the isomers were formed in almost equal yields. Table I shows the lack of stereoselectivity of halocyclopropane formation from halodiazomethanes in comparison with the results obtained previously on α-elimination on methylene chloride.[20] Assignment of the *syn* and *anti* configurations[22] to the individual compounds was made on the basis of the n.m.r. spectra. It is now well established that *cis*-vicinal protons in cyclopropanes are stronger coupled than *trans* protons.[23] Since the signal originating from the proton situated at the same carbon atom as the halogen atom (α-proton) is well separated from other resonances, it is usually possible to determine which of the epimers has the larger vicinal coupling constants, although the complete analysis of the spectrum may not be possible because of considerable overlap of the remaining signals. Additional support for the configuration assignment can be found in the chemical shift parameters of the α-protons. In the *anti* series these protons are substantially more shielded than in the corresponding *syn* compounds. Qualitatively, this behavior is expected if one considers the anisotropies introduced by the alkyl substituents on the cyclopropane ring.[24]

Table I. Isomer Ratios (*syn/anti*) of Halocyclopropanes as Obtained from Methylene Chloride–Butyllithium and from Thermolysis of Halodiazomethanes at $-30°$

| Olefin substrate | Reactants | | |
	CH_2Cl_2 + RLi^a	$ClCHN_2$	$BrCHN_2$
2-Methyl-2-butene	1.6	1.0	. . .
Cyclohexene	3.2	1.0	1.0
cis-2-Butene	5.5	1.0	1.0
1-Butene	3.4	1.0	1.0

^{a} Data are taken from ref. 11.

One more check on the validity of the n.m.r. arguments was made by synthesizing the two 1-chloro-2-ethylcyclopropanes by an independent, stereospecific route. Both *cis*- and *trans*-1-chloro-1-butene were treated with Simmons–Smith reagent[12] and were converted in very low yield to the corresponding *syn*- and *anti*-1-chloro-2-ethylcyclopropanes. Comparison

(22) The geometrical relationship of the chlorine atom and the *largest* number of alkyl groups defines the classification of the compounds as either *syn* or *anti*.
(23) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, 84, 2249 (1962); D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, 85, 3218 (1963), and references cited therein.
(24) The contribution of this effect to the chemical shift difference of the α-protons in the geometrical isomers can be calculated using the simple dipole approximation

$$\Delta\delta = -\Delta\chi/3 \left[\sum_{i_{syn}} \frac{3\cos^2\theta_i - 1}{r_i^3} - \sum_{i_{anti}} \frac{3\cos^2\theta_i - 1}{r_i^3} \right]$$

where the r_i terms are are the length of the vectors extending from the center of the ring-alkyl bonds to the α-proton, and the θ_i terms are the angles between these vectors and the alkyl bonds. If one uses the normally accepted value of 5.5×10^{-30} cm.^{3} for $\Delta\chi^{25}$ and molecular parameters derived from closely related compounds[28] the calculated difference in chemical shifts for the α-protons of *syn*- and *anti*-1-chloro-*cis*-2,3-dimethylcyclopropanes has the correct sign but is too small by a factor of 2.5 ($\Delta\delta_{exp}$ 0.64 p.p.m. *vs.* $\Delta\delta_{calcd}$ 0.26 p.p.m.). Apparently, some of the approximations and assumptions inherent in this treatment, such as the use of identical bond length and bond angles in both epimers and the neglect of carbon–hydrogen bond anisotropies, are not permissible.
(25) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, 70, 833 (1958).
(26) E. Goldish, *J. Chem. Educ.*, 36, 408 (1959).

of these products with the adducts obtained from the carbene reactions confirmed the assignment. Although we have done so at previous occasion,[27] it should be pointed out again that the original assignment of the configuration to the chlorocyclopropanes obtained *via* the α-elimination route were in error.[20]

The halocyclopropanes were the only major products obtained in the reactions of halodiazomethanes with olefins. Any insertion products into the allylic C–H bonds of the olefins, if formed at all, were present in amounts too small to identify. In one run chlorodiazomethane was decomposed in a mixture of *n*-pentane and *cis*-2-butene present in a ratio of 100:1. The two epimeric chlorocyclopropanes were formed in a ratio unchanged from the one obtained in the pure olefin as solvent. However, approximately equal amounts of cyclopropanes and *n*-pentane insertion products (II–IV) were formed.

Additions to *cis*- and *trans*-2-butene were stereospecific within the limits of detection, giving only products in which the relative configurations of the methyl groups were identical with that of the starting olefins.

Table II shows the relative rates of halocyclopropane formation from thermolysis of chloro- and bromodiazomethane as determined by competition experiments with large excess of olefin pairs present in known ratios. A small spread of relative rates is observed with variation of the degree of alkyl substitution of the double bond, and within experimental uncertainty, the discriminating abilities of chloro- and bromocarbene are the same. For comparison the substantially different ratios obtained from α-elimination on methylene chloride are included in the table.

Table II. Relative Rates of Halocyclopropane Formation from Olefins

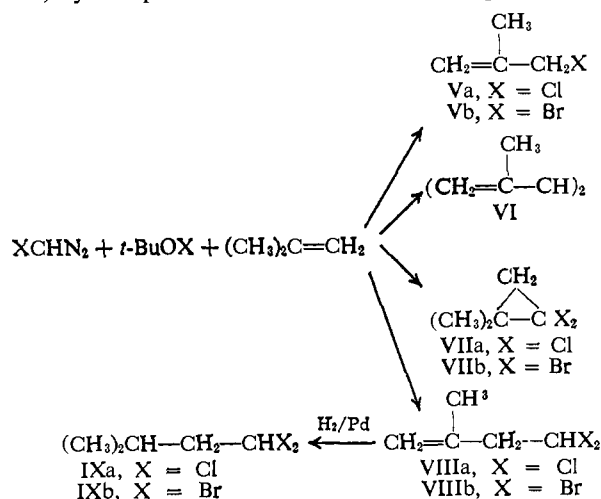| Olefins | Reagents | | |
	CH_2Cl_2 + RLi^a	$ClCHN_2{}^b$	$BrCHN_2{}^b$
2,3-Dimethyl-2-butene	2.81	1.20	1.18 (1.21)^c
2-Methyl-2-butene	1.78	1.18	. . .
trans-2-Butene	0.45	1.09	1.10
cis-2-Butene	0.91	0.99	1.02
Isobutene	1.00	1.00	1.00
1-Butene	0.23^d	0.74 (0.77)^c	0.75

^{a} These data taken from ref. 11. Reaction temperature $-35°$. ^{b} Thermolysis of halodiazomethane at $-30°$. ^{c} Measured in competition with *trans*-2-butene. ^{d} Relative rate of addition to 1-pentene.

Several attempts were made to prepare dihalodiazomethanes by halogenation of diazomethane with 2 equiv. of hypohalite. However, addition of the second mole of *t*-butyl hypochlorite to diazomethane at $-100°$ led to rapid nitrogen evolution and to complete decolorization of the reaction mixture. Similar results were obtained with *t*-butyl hypobromite. When the halogenation with 2 equiv. of *t*-butyl hypochlorite was carried out in isobutene as solvent, methallyl chloride (Va) was the major reaction product. A C_8 hydrocarbon, formed in lower yield, was identified by comparison with an authentic sample as 2,5-dimethyl-1,5-hexadiene (VI). In addition two C_5 products

(27) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, 84, 4985 (1962).

were isolated in low yield. The structure of 1,1-dichloro-3-methyl-3-butene (VIIIa) was assigned to the predominantly formed C_5 product on the basis of spectral evidence. The n.m.r. spectrum of this product shows a triplet at τ 4.27 (6.4 c.p.s. separation), a multiplet at 5.14, a doublet at 7.14 (6.4 c.p.s. separation), and a narrow multiplet at 8.23. The observed signal intensities have the correct ratios for signals arising from protons at C-1, the terminal methylene group, the methylene group at C-2, and the methyl group, respectively. The infrared spectrum is also in agreement with structure VIIIa, since it clearly indicates the presence of a terminal methylene function (1652 and 905 cm.$^{-1}$). Hydrogenation of VIIIa gave the saturated derivative XIa which was identical in all properties with a sample prepared from isovaleraldehyde with phosphorus pentachloride. The other C_5 product was identified as the known 1,1-dichloro-2,2-dimethylcyclopropane (VIIa) by comparison with an authentic sample.

$$CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2X$$
Va, X = Cl
Vb, X = Br

$$(CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH)_2$$
VI

$$(CH_3)_2\underset{\triangle}{C}{-}\overset{CH_2}{C}\;X_2$$
VIIa, X = Cl
VIIb, X = Br

$$XCHN_2 + t\text{-}BuOX + (CH_3)_2C{=}CH_2$$

$$CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2{-}CHX_2$$
VIIIa, X = Cl
VIIIb, X = Br

$$(CH_3)_2CH{-}CH_2{-}CHX_2 \xleftarrow{\;H_2/Pd\;} CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2{-}CHX_2$$
IXa, X = Cl
IXb, X = Br

The reaction of diazomethane with 2 moles of t-butyl hypobromite in isobutene gave the corresponding products Vb, VI, VIIb, and VIIIb. It was found that the yield of cyclopropane formation could be increased somewhat (to 10% of VIIb) by addition of 2 mole % of 2,6-di-t-butylphenol.

The relative rates of dihalocyclopropane formation with isobutene and 2,3-dimethyl-2-butene were determined by competition experiments. The adduct of the tetraalkyl-substituted olefin is formed 16 times faster than the isobutene adduct in the chlorination reaction, while the corresponding ratio is 1:1 in the bromination.

Discussion

Although no mechanistic studies of the halogenation of diazomethane were carried out, the rapidity of reaction combined with the lack of an observable induction period appear to exclude a free-radical halogenation of the type usually observed with t-butyl hypohalites.[28] This view is supported by the observation that free-radical inhibitors such as 2,6-di-t-butylphenol do not change the course of the reaction and in some experiments were shown to have a beneficial effect by inhibiting formation of side products. Reaction sequence 1, in which the initial step is a nucleophilic displacement by diazomethane on the halogen atom to give the

(28) Cf. C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108, 6113 (1960).

halomethyldiazonium-t-butoxide ion pair, with subsequent proton transfer, represents a likely pathway.

$$t\text{-}BuOX + CH_2N_2 \longrightarrow t\text{-}BuO^- \; XCH_2N_2^+$$
$$t\text{-}BuO^- \; XCH_2N_2^+ \longrightarrow t\text{-}BuOH + XCNH_2 \qquad (1)$$
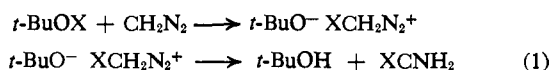
Because of the inductive effect of the halogen atom, monohalodiazomethanes should exhibit a somewhat reduced nucleophilicity relative to that of diazomethane. This effect is noted in the reaction with carboxylic acids which proceeds visibly slower than with diazomethane. The reduced nucleophilicity is probably of some benefit in the preparation of halodiazomethanes because it prevents attack by a second hypohalite molecule.

Thermolysis or photolysis of halodiazomethanes can reasonably be expected to give rise to free halocarbenes which may add to olefins or insert into C–H bonds. While both reaction types have been observed, quantitative product analysis shows that halocarbenes are indeed considerably less reactive than methylene. Thus, halocarbenes exhibit a very great preference for olefin addition which completely predominates when there is a choice. In contrast, insertion competes successfully with addition in methylene reactions.[29] Similarly, halocarbene insertion into secondary C–H bonds is greatly favored over attack at the less reactive primary carbon, while methylene shows no discrimination between different C–H bond types. On the other hand, halocarbenes have little ability to distinguish among differently substituted olefins. The total spread of relative addition rates between the least and most reactive olefins is only a factor of 1.6. There appears to be little, if any, difference in the reactivities of bromo- and chlorocarbene, as judged from the product distribution in both insertion and addition reactions.

It is interesting to compare the reactivities of halocarbenes with those reported for other monosubstituted methylenes generated from their diazo precursors.[5b] An examination of relevant data for three substituent types, halogen, aryl, and carbethoxy, reveals that all these carbenes exhibit a mildly electrophilic behavior in their additions to olefins. However, the response of relative rates to changes in nucleophilicity of the olefins are small, and no distinct difference in the discriminating abilities of these carbenes exist. One must conclude then that at least for the more reactive carbenes, olefin addition is a poor reactivity criterion. Somewhat more revealing are the ratios of relative rates of attack on primary vs. secondary carbon atoms in the insertion reaction.[30–32] Another useful measure of the reactivities of highly reactive methylene derivatives are the relative rates of olefin addition and C–H insertion.[14,29,32] On the basis of the latter two criteria the following series of increasing reactivities can be established: HCCl = HCBr < HCC$_6$H$_5$ < HCCOOR < HCH. The low thermostability of halodiazomethanes as compared to diazomethane may be interpreted as additional evidence for the stabilizing influence that halogen exerts on the divalent carbon atom. It is of course possible

(29) Cf. H. M. Frey, Proc. Roy. Soc. (London), A250, 409 (1959).
(30) W. v. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, J. Am. Chem. Soc., 78, 3224 (1956).
(31) W. v. E. Doering and L. H. Knox, ibid., 83, 1989 (1961).
(32) C. D. Gutche, G. L. Bachman, and R. S. Coffey, Tetrahedron, 18, 617 (1962).

that in addition to lowering the transition state energy, some destabilization of the reactant by halogen substitution will be responsible for the low activation energy.
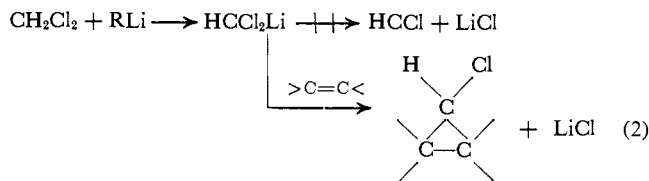
Chlorocarbene has previously been postulated as the intermediate in lithium alkyl induced α-elimination on methylene chloride.[20] This view was supported by product analysis in several reactions. Furthermore, the electrophilic sequence of addition to olefins with varying degree of alkyl substitution was found to be intermediate between those of methylene and dichloromethylene.[11] Comparison of the data summarized in Tables I and II shows that significant discrepancies exist in the reactivities of the intermediates formed from chlorodiazomethane and α-elimination on methylene chloride. While both reactions produce chlorocyclopropanes with olefins, the pronounced stereoselectivity observed in the α-elimination reaction giving rise to relatively large $syn/anti$ ratios, is reduced to random addition, when halocarbenes are generated from the diazo precursors. Similarly the competition data with different olefins show that a considerably less reactive intermediate is formed in the α-elimination. In line with these observations is the fact that thermolysis of chlorodiazomethane gives products of insertion while the intermediate in the α-elimination reaction is inert toward C–H bonds. It has been suggested that both reactions proceed through free halomethylenes, but that thermolysis or photolysis of the diazo compound produce excited species, whereas α-elimination gives the intermediate in the thermal equilibrium with its environment.[15,33] Although there is ample precedent for reactions of "hot" methylenes in the gas phase, it is our opinion that this hypothesis cannot be upheld. The observation that addition of chloromethylene to a double bond is favored over C–H insertion by at least a factor of 100 implies many unsuccessful collisions before insertion occurs. A more quantitative estimate is derived from the observation that reaction with n-pentane is 100 times as slow as addition to the double bond in cis-2-butene. Per bond type, the ratio of addition to insertion into the secondary C–H bonds is approximately 600, and into the primary C–H bonds approximately 12,000. Furthermore from the nonzero activation barrier for addition it must be concluded that the number of collisions necessary for insertion is much greater than the values quoted for the relative rates of reaction with the C–H and double bonds. Certainly, translational and vibrational relaxation is much more efficient. Electronic relaxation should also be complete unless the molecule is kept in a long-lived, metastable state. These considerations are supported by the observation that 100-fold dilution of the cis-2-butene with pentane produces no change in the $syn/anti$ isomer ratio of the resulting cyclopropanes.[34]

It would appear therefore, that the observed differences between the two reaction types should be attributed to the intermediacy of free carbenes from halodiazomethanes and to that of dichloromethyllithium in the α-elimination reaction (eq. 2). A

number of reactions have been reported recently suggesting that α-haloorganometallics (carbenoids)[14] can give carbene-like reactions without actually dissociating into free carbenes.[12,14,15,35—37]

$$CH_2Cl_2 + RLi \longrightarrow HCCl_2Li \overset{|}{\longrightarrow} HCCl + LiCl$$

$$+ \text{LiCl} \quad (2)$$

Dichloromethyllithium has recently been shown to have a considerable lifetime at $-60°$ in tetrahydrofuran,[38] and trichloromethyllithium can be attacked by olefins under conditions where it is stable in the presence of saturated hydrocarbons.[39] As has been pointed out by several workers[12,14,35—37] nucleophilic attack by the olefinic double bond on carbenoids can be visualized to proceed through a transition state as depicted schematically in X.[40,41]
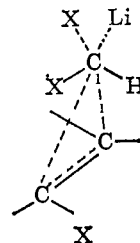
The problem of assigning spin multiplicities to the free halocarbenes is of considerable theoretical interest. Application of the Skell criterion,[42] that of stereospecificity of the addition reaction to cis- and $trans$-2-butene, would point to a singlet state of chloro- and bromocarbene. Because of the apparent insensitivity of stereospecificity as a diagnostic, and because the interplay of factors which determine the over-all stereochemical result can be expected to be greatly affected by the presence of substituents, its use as a criterion for the multiplicities of substituted methylenes is of uncertain value.[43] Furthermore, chemical reactivity arguments do not necessarily give any information about the ground state. Electron spin resonance experiments in which halodiazomethanes were photolyzed in various matrixes at 77°K. have

(33) *Cf.* ref. 5b, p. 192.

(34) Very recently tritiochlorocarbene has been produced in the vapor phase by Y. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 1625 (1965). The reactivities found for this species compare well with those of chlorocarbene generated from chlorodiazomethane.

(35) G. Wittig and K. Schwarzenbach, *Ann. Chem.*, **650**, 1 (1961).

(36) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962); *Angew. Chem., Intern. Ed. Engl.*, **1**, 334 (1962).

(37) H. E. Simmons and E. P. Blanchard, *J. Am. Chem. Soc.*, **86**, 1337 (1964).

(38) G. Köbrich and W. Drischel, *Angew. Chem. Intern. Ed. Engl.*, **3**, 513 (1964).

(39) W. T. Miller and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

(40) Formulations in which the α-halocarbanion is thought to add to the double bond followed by displacement of halide ion have been proposed as alternative reaction path: H. Hoberg, *Ann. Chem.*, **656**, 15 (1962). However, such schemes do not take into consideration the observed electrophilic behavior of carbenoid additions, nor do they account for the complete stereospecificity of the reaction.

(41) Very recently G. Köbrich, K. Flory, and H. R. Merkle, *Tetrahedron Letters*, No. 15, 972 (1965), found that the decomposition of dichloromethyllithium in tetrahydrofuran at $-60°$ is not accelerated by the addition of olefins to the reaction mixture. Contrary to these workers' claim, this finding is not in disagreement with our suggested mechanism because chlorocyclopropanes were formed only as minor side-products under these conditions.

(42) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(43) For a detailed discussion of this point see P. P. Gaspar and G. S. Hammond, Chapter 12 of ref. 5b.

failed to give any spectra attributable to triplet states. Unfortunately, this can only be regarded as negative evidence since methylene itself has so far evaded e.s.r. detection and yet there can be little doubt that it possesses a triplet ground state. At present then, the multiplicities of chloro- and bromomethylene are still open to question.
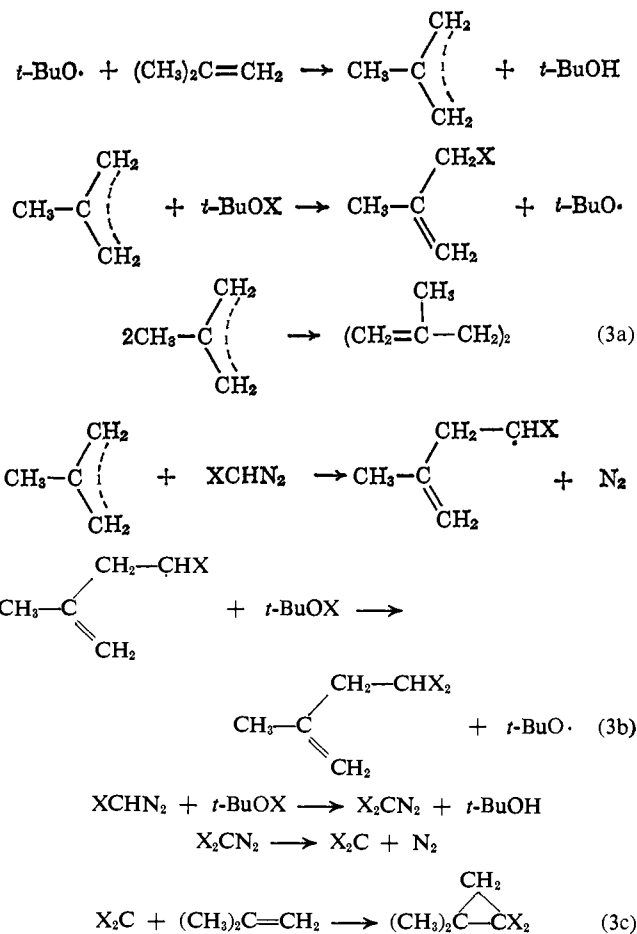
In view of the extreme instability of monohalodiazomethanes it is hardly surprising that dihalodiazomethanes evaded characterization. Of considerable interest, however, is the question whether dihalodiazomethanes are actually formed upon further halogenation and immediately decompose to dihalocarbenes and nitrogen, or whether the second halogenation step deviates sufficiently from the first that dihalodiazomethanes are bypassed. It was hoped that halogenation in the presence of olefins would provide an answer to this problem. The formation of small amounts (up to 10%) of dihalocyclopropanes in this reaction seems to support the former alternative. The predominant C_5 product VIII, isolated from the reaction with isobutene, and formally identical with an insertion product of dihalomethylene into the allylic C–H bond of isobutene, however, almost certainly does not arise from dihalomethylene. This conclusion is strongly supported by the abnormally high ratio of "insertion" to addition product which would necessitate the intermediacy of an extremely reactive carbene.[44] Furthermore this ratio can be decreased significantly by free-radical inhibitors. Both observations are incompatible with a dihalocarbene precursor for both products. Finally, the formation of methallyl halides as major products, and the isolation of the dimer of isobutenyl radical VI indicate the intervention of a radical-chain reaction. A very attractive reaction sequence (3a–c) can be written for the formation of all the major products. Because of the reduced nucleophilicity of monohalodiazomethane, allylic halogenation of the olefin can become a competing reaction. After an unknown initiation step, the radical-chain process described by the first two equations of (3a) leads to the formation of methallyl halide.[18] Reaction of the intermediate methallyl radical with monohalodiazomethane will lead to 1-halo-3-methallyl radical. Abstraction of halogen by this intermediate from t-butyl hypohalite will give the dihalide VIII according to reaction scheme 3b.[45] Competing with this radical-chain process is the halogenation of monohalodiazomethane as described in reaction scheme 3c. Radical inhibitors will slow down reactions 3a and 3b, prevent the depletion of monohalodiazomethane, and lead to an increase of dihalodiazomethane formation.

The hypothesis that the dihalocyclopropanes are formed from dihalocarbenes is supported to some extent by the competition experiments involving tetramethylene and isobutene. The observed relative addition rates of 16:1 and 1:1 for the chloro and bromo derivatives, respectively, are compatible with the intervention of carbene intermediates.[46] It is possible, how-

(44) The most reactive carbene, methylene, gives an insertion to addition ratio of 0.7 with isobutene: H. M. Frey, *Proc. Roy. Soc.* (London), A250, 409 (1959).

(45) The reaction of the intermediate radical with halodiazomethane may be written either as a displacement, or perhaps more reasonably, as an addition–elimination process.

(46) Values of 6.5:1 and 1.8:1 have been reported for the relative addition rates of dichloro- and dibromocarbene, respectively, when

$t\text{-BuO·} + (CH_3)_2C=CH_2 \rightarrow CH_3-C(CH_2)(CH_2) + t\text{-BuOH}$

$CH_3-C(CH_2)(CH_2) + t\text{-BuOX} \rightarrow CH_3-C(CH_2X)=CH_2 + t\text{-BuO·}$

$2CH_3-C(CH_2)(CH_2) \rightarrow (CH_2=C(CH_3)-CH_2)_2$ (3a)

$CH_3-C(CH_2)(CH_2) + XCHN_2 \rightarrow CH_3-C(CH_2-CHX)=CH_2 + N_2$

$CH_3-C(CH_2-CHX)=CH_2 + t\text{-BuOX} \rightarrow$

$CH_3-C(CH_2-CHX_2)=CH_2 + t\text{-BuO·}$ (3b)

$XCHN_2 + t\text{-BuOX} \rightarrow X_2CN_2 + t\text{-BuOH}$

$X_2CN_2 \rightarrow X_2C + N_2$

$X_2C + (CH_3)_2C=CH_2 \rightarrow (CH_3)_2C\overset{CH_2}{\triangle}CX_2$ (3c)

ever, to write mechanisms for dihalocyclopropane formation without invoking either dihalodiazomethane nor dihalocarbenes as intermediates. We must therefore conclude that while it is likely that dihalodiazomethanes are formed in modest yields by halogenation of diazomethane, no definite proof can be advanced for this hypothesis at the present time.

Experimental Section

Boiling points are uncorrected. Infrared spectra were recorded with a Beckman IR-7 spectrophotometer; n.m.r. spectra were recorded with a Varian DP-60 or A-60 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane using carbon tetrachloride as solvent. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Vapor phase chromatograms were obtained with a Wilkens Instrument and Research, Inc., Aerograph 90-P, and were recorded with a Brown recorder equipped with a disk integrator.

Preparation of Chlorodiazomethane (General Procedure). Chlorodiazomethane was prepared in a variety of solvents; n-pentane is used to illustrate the general method. A mixture of n-pentane (150 ml.) and 50% aqueous potassium hydroxide (30 ml.) was cooled to 0° in a 250-ml. flask equipped with a magnetic stirrer and nitrogen inlet. N-Methyl-N-nitrosourea[47] (8.00 g., 0.0775 mole) was introduced, and the mixture was allowed to stir at this temperature for 45

generated by α-elimination at −10°: W. v. E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, 80, 5274 (1958).

(47) F. Arndt, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

min. The diazomethane solution was freeze dried by cooling to $-75°$ and after a period of 1 hr. at this temperature, the organic phase was transferred through a short length of glass tubing to a second 250-ml. flask by decantation and application of a small, positive nitrogen pressure. The second flask was equipped with a magnetic stirrer, low-temperature thermometer, and an addition funnel fitted with a drying tube. The diazomethane solution was standardized by the benzoic acid method,[47] and found to be 0.36 M. t-Butyl hypochlorite[48] (4.34 g., 0.040 mole), using trichlorofluoromethane (30 ml.) as a diluent, was added dropwise over a period of 30 min. to the diazomethane solution at $-100°$. This temperature was maintained during the addition by employing a liquid nitrogen–diethyl ether slush mixture in an insulated, double-walled bath.

This procedure was modified slightly using the C_4 olefin as solvents by equipping the flask used for the generation of diazomethane with a Dry Ice–acetone reflux condenser. The olefin was then condensed directly in the Dry Ice–acetone-cooled flask. A slightly lowered temperature was also required to avoid loss of diazomethane and solvent. Lightly greased ground glass joints were used throughout the apparatus.

Upon warming the solution to $-40°$, nitrogen evolution could be observed and at $-10°$, total decomposition of the diazo compound occurred over a period of approximately 30 min., as evidenced by decolorization of the red solution.

Both the infrared and electronic spectra of chlorodiazomethane were measured in pentane solutions using low-temperature cells. The infrared spectrum exhibited a strong band at 2066 cm.$^{-1}$ which disappeared upon warming of the solution. The visible absorption spectrum showed three maxima of about equal intensity at 485, 518, and 545 mμ. An approximate extinction coefficient can be calculated assuming a 65–75% yield of chlorodiazomethane, based on t-butyl hypochlorite, resulting in a value of 5–8. The above conversion is most consistent with the yields of chlorocyclopropanes obtained in the olefin addition reactions. Diazomethane showed an absorption maximum under identical conditions at approximately 420 mμ (ϵ 3).

Preparation of Bromodiazomethane. Solutions of bromodiazomethane in various solvents were prepared in a manner identical in all respects with that described for chlorodiazomethane, employing t-butyl hypobromite as the halogenating agent. Following the general procedure of Walling and Padwa, t-butyl hypobromite in trichlorofluoromethane was prepared from t-butyl alcohol and hypobromous acid.[49]

The thermal stability of bromodiazomethane was found to be quite similar to that of chlorodiazomethane; an approximately 0.25 M solution decolorized completely at $-10°$ over a period of 35–40 min.

Both the infrared and visible spectra of bromodiazomethane were measured in n-pentane solutions. Characteristic absorptions were observed at 2069 cm.$^{-1}$ and 540 mμ (ϵ 5–10).

Reactions of Chlorodiazomethane with Carboxylic Acids. Chlorodiazomethane was prepared as outlined above from diazomethane (3.1 g., 0.074 mole)

and t-butyl hypochlorite (4.86 g., 0.045 mole) in pentane (250 ml.). Propionic acid (3.35 g., 0.045 mole) in trichlorofluoromethane (10 ml.) was added dropwise at $-60°$. The solution was stirred for 5 hr., at which time almost complete decolorization had occurred. The reaction mixture was warmed to room temperature, most of the pentane was removed by distillation, and the residue was fractionated *in vacuo*. The product (2.9 g., 53%) was collected at 42–45° (39 mm.). A small sample of the product was purified by g.l.p.c. on a 10-ft. silicone 710 column operating at 110°. The n.m.r. spectrum of the purified product showed resonances at τ 8.82 (t), 7.63 (q), and 4.33 (s) with intensity ratios of 3:2:2. The infrared spectrum strong absorption at 1773, 1180, 1086, and 1037 cm.$^{-1}$.

Chloromethyl acetate (1.08 g., 22%) was prepared in an identical fashion from acetic acid (2.6 g., 0.045 mole) and chlorodiazomethane prepared from diazomethane (3.1 g., 0.074 mole) and t-butyl hypochlorite (4.86 g., 0.045 mole). Comparison of the g.l.p.c. retention times and n.m.r. spectra showed this material to be identical with chloromethyl acetate prepared by the method of Ulich and Adams.[50]

Thermolysis of Chlorodiazomethane in n-Pentane. A solution of chlorodiazomethane in n-pentane (250 ml.), prepared as indicated above from diazomethane (3.1 g., 0.074 mole), was allowed to decompose at $-10°$. The reaction mixture was washed with water (three 100-ml. portions) and dried over sodium sulfate. Most of the pentane was removed by distillation over a 3-ft. tantalum spiral column and the remainder was subjected to g.l.p.c. analysis. 1-Chloro-2-methylpentane (IIIa) and 1-chloro-2-ethylbutane (IVa) had a shorter retention time and were easily separated from 1-chlorohexane (IIa) on a 6-ft. column with 20% TCP on firebrick, operating at 90°. Because of poor separation IIIa and IVa were collected together and the infrared spectrum of the mixture was compared with the infrared spectrum of a 1:1 mixture of IIIa and IVa which were prepared by authentic methods.[51] A quantitative g.l.p.c. analysis gave the product ratio (IIIa + IVa)/IIa = 20. On the basis of g.l.p.c. analysis, the combined yield of IIa, IIIa, and IVa was 9%.

Photolysis of Chlorodiazomethane in n-Pentane. Photolysis of a solution of chlorodiazomethane in n-pentane was carried out in a three-necked flask equipped with mechanical stirrer, thermometer, and drying tube. The flask was immersed in a double-walled, Pyrex cooling bath. Methanol was used as coolant and circulated through a copper heat exchanger immersed in a dewar flask containing a Dry Ice–acetone mixture. The temperature was controlled by a variable speed pump. The flask was illuminated by a General Electric, Photoflood, PH/RFL-2 500-w. lamp, which was positioned directly beneath the cold bath. The temperature inside the flask was held at $-50°$, and decolorization occurred after 45 min. G.l.p.c. analysis and product identification was carried out as described above for the thermolysis. The product ratio (IIIa + IVa)/IIa was 25. The combined yield of these products was 11% as determined by g.l.p.c. analysis.

(48) H. M. Teeter and E. W. Bell, *Org. Syn.*, 32, 20 (1952).
(49) C. Walling and A. Padwa, *J. Org. Chem.*, 27, 2976 (1962).

(50) L. H. Ulich and R. Adams, *J. Am. Chem. Soc.*, 43, 660 (1921).
(51) F. S. Prout and J. Cason, *J. Org. Chem.*, 14, 132 (1949).

Thermolysis of Bromodiazomethane in n-Pentane. A solution of bromodiazomethane (approximately 0.035 mole) in *n*-pentane (300 ml.) was allowed to decompose at −10°. The reaction mixture was washed with water (three 100-ml. portions) and dried over sodium sulfate, and the pentane was distilled off over a 3-ft. tantalum spiral column. The remainder was subjected to g.l.p.c. analysis, using a 10-ft. Carbowax 20 M (20% on firebrick) column operating at 100°. The isomeric bromohexanes, IIb, IIIb, and IVb, were trapped in the conventional manner. Separation of IIIb and IVb was incomplete and both compounds were trapped together. Product identity was shown by comparison of the g.l.p.c. retention times infrared spectra with those of samples of IIb and IIIb and IVb prepared by authentic methods.[51,52] Because of the incomplete separation of IIIb and IVb the infrared spectrum of the trapped material was compared with that of a 1:1 mixture of the corresponding synthetic samples. The ratio of (IIIb + IVb)/IIb was determined to be 25.

Chlorocyclopropanes from Chlorodiazomethane. Cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were washed with ferrous sulfate–sulfuric acid solution, dried, and fractionally distilled before use. Isobutene, *cis*- and *trans*-2-butene, and 1-butene (Philips Hydrocarbons, pure grade) were used without further purification. Diazomethane, generated from N-methyl-N-nitrosourea (4.0 g., 0.039 mole) in 90–100 ml. of the olefin, was standardized and chlorinated using 70% of the stoichiometric amount of *t*-butyl hypochlorite (2.2 g., 0.02 mole) as described in the general procedure.

In the thermolytic decomposition of chlorodiazomethane the solutions were brought to −30°. Maintenance of this temperature for 2–3 hr. effected complete decolorization.

In the photolysis experiments the chlorodiazomethane solutions were kept at −45° with the aid of the cooling bath described above. The flask was illuminated by a General Electric, Photoflood, PH RFL-2 500-w. lamp, which was positioned directly beneath the cooling bath. Normally, less than 45 min. of irradiation were required to effect decolorization.

The reaction mixtures were washed with ice water and dried over sodium sulfate, and the excess olefin was removed by distillation. The residue was fractionally distilled and the chlorocyclopropanes were collected at the boiling points previously reported.[20] In those cases where epimeric chlorocyclopropanes were formed, the isomer ratios were determined by g.l.p.c. analysis on the crude reaction mixture to prevent product fractionation. Separation of all epimeric pairs was accomplished on a 10-ft. TCP (20% on firebrick) column operating between 70 and 112° with helium flow rates of 60–100 ml./min. The isomer ratios found are listed in Table I.

All chlorocyclopropanes were purified by g.l.p.c. and were identified by comparison of their infrared and n.m.r. spectra with those of samples prepared previously.[20] Yields of chlorocyclopropanes ranged from 45 to 55%, based on *t*-butyl hypochlorite, as determined by g.l.p.c. calibration using pure samples.

In one run chlorodiazomethane (approximately 0.01 mole) was decomposed thermolytically at −30° in *n*-pentane (300 ml.) containing 1% (by volume) of *cis*-2-butene. G.l.p.c. analysis of the crude reaction mixture showed that the two epimeric 1-chloro-*cis*-2,3-dimethylcyclopropanes were produced in equal amounts. In addition, with longer retention times, a peak originating from a mixture of IIIa and IVa was present. Comparison of the areas of the cyclopropane peak and the peak from chlorohexanes showed these compounds to be present in equal quantities.

Bromocyclopropanes from Bromodiazomethane. Procedure, amounts of starting materials, and work-up were identical with those described for the preparation of chlorocyclopropanes from chlorodiazomethane. The olefins employed as solvents were 2,3-dimethyl-2-butene, 2-methyl-2-butene, isobutene, *cis*- and *trans*-2-butene, and 1-butene. In typical cases approximately 50% yields of bromocyclopropanes were obtained as indicated by g.l.p.c. calibration using purified samples. Resolution of the epimeric bromocyclopropanes in the *cis*-2-butene and 1-butene reaction was effected on a 5-ft. column with SF-96 (20% on firebrick) as stationary phase, with the column operating at 75° with a flow rate of 45 ml./min. The isomer ratios were experimentally indistinguishable from unity. Under conditions necessary to resolve the isomeric 1-bromo-2,2,3-trimethylcyclopropanes, a significant amount of decomposition occurred on g.l.p.c. analysis and the isomer ratio was not obtainable in this instance. No 1-bromo-*trans*-2,3-dimethylcyclopropane could be detected using *cis*-2-butene as solvent. Similarly, no 1-bromo-*cis*-2,3-dimethylcyclopropane was formed when *trans*-2-butene was used as substrate.

All bromocyclopropanes were purified by g.l.p.c. and trapping in the conventional manner. 1-Bromo-2,2,3,3-tetramethylcyclopropane, 1-bromo-2,2,3-trimethylcyclopropane, and 1-bromo-2,2-dimethylcyclopropane were compared with samples prepared by the method of Seyferth, Yamazaki, and Alleston.[21]

1-Bromo-*cis*-2,3-dimethylcyclopropane gave the following analysis. *Anal.* Calcd. for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62. Found: C, 40.40; H, 6.30; Br, 53.68.

1-Bromo-*trans*-2,3-dimethylcyclopropane gave the following analysis. *Anal.* Calcd. for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62. Found: C, 40.13; H, 5.95; Br, 53.71.

1-Bromo-2-ethylcyclopropane gave the following analysis. *Anal.* Calcd. for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62. Found: C, 40.42; H, 6.01; Br, 53.72.

The n.m.r. data of the bromocyclopropanes are summarized in Table III.

1-Bromo-cis-2,3-dimethylcyclopropane. 1,1-Dibromo-*cis*-2,3-dimethylcyclopropane was prepared from *cis*-2-butene, potassium *t*-butoxide, and bromoform following the procedure of Skell and Garner[53] in 87% yield, b.p. 74–75° (28 mm.). The dibromide (10 g. 0.044 mole) was reduced with tri-*n*-butyltin hydride (13 g., 0.04 mole) following the procedure of Seyferth, Yamazaki, and Alleston.[21] Fractionation of the reaction mixture gave the desired bromide (5.0 g., 77%),

(52) H. A. Shonle, J. H. Waldo, A. K. Keltch, and H. W. Coles, *J. Am. Chem. Soc.*, **58**, 585 (1936).

(53) P. S. Skell and A. V. Garner, *ibid.*, **78**, 5430 (1956).

	Chemical shifts in τ-units	
	α-CH	CH$_3$ groups
1-Bromo-2,2,3,3-tetra-methylcyclopropane	7.34 (s)	8.87 (s), 8.91 (s)
1-Bromo-2,2,3-trimethyl-cyclopropane (syn)	7.12 (d) (7.3 c.p.s.)[a]	8.85–9.0 (m)
1-Bromo-2,2,3-trimethyl-cyclopropane (anti)	7.58 (d) (4.0 c.p.s.)[a]	8.75–8.95 (m)
1-Bromo-2,2-dimethyl-cyclopropane	7.25 (q)[b]	8.72 (s), 8.86 (s)
1-Bromo-trans-2,3-di-methylcyclopropane	7.31 (m) (13 c.p.s.)[c]	8.7–8.9 (m)
1-Bromo-cis-2,3-di-methyl cyclopropane (syn)	6.82 (m) (16 c.p.s.)[c]	8.95–9.05 (m)
1-Bromo-cis-2,3-di-methylcyclopropane (anti)	7.86 (m) (8 c.p.s.)[c]	8.8–9.0 (m)
1-Bromo-2-ethylcyclo-propane (syn)	7.0 (m) (20 c.p.s.)[c]	. . .
1-Bromo-2-ethylcyclo-propane (anti)	7.5 (m) (14 c.p.s.)[c]	. . .

[a] Spacing of doublet $\simeq J_{vic}$. [b] Complete analysis of the ring protons as ABX system gave the following parameters: J_{cis} 7.68 c.p.s.; J_{trans} 4.12 c.p.s., and J_{gem} 5.8 c.p.s.; τ 9.39 for proton trans to Br; τ 9.05 for proton cis to Br. [c] Spacings refer to the total width of the multiplet. Because of virtual coupling with methyl groups some of these signals are very complex.

b.p. 119–120°. G.l.p.c. analysis on a silicon oil SF-96 column indicated the syn/anti ratio of 30:1.

1-Bromo-2-ethylcyclopropane. 1,1-Dibromo-2-ethylcyclopropane was prepared from 1-butene, potassium butoxide, and bromoform following the procedure of Skell and Garner[53] in 63% yield, b.p. 68–69° (30 mm.). The dibromide (10 g., 0.44 mole) was prepared according to the procedure of Seyferth, Yamazaki, and Allerston.[21] Fractionation of the reaction mixture under reduced pressure gave the epimeric bromides (3.9 g., 60%), b.p. 47–52° (66 mm.). G.l.p.c. analysis on a 14-ft. column with silicon oil QF-1, operating at 70° gave a syn/anti isomer ratio of 1.5:1.

Olefin Competition Experiments with Chloro- and Bromodiazomethane. The procedure used in these experiments is analogous to that used in the runs involving a single olefin. The olefins (0.75 mole of each) were distilled into the reaction flask from a cold trap. The trap was differentially weighed to determine the quantities of olefin introduced. The diazomethane (approximately 0.05 mole) was generated and halogenated in the olefin solvent as described above. Thermolysis of the halodiazomethane was effected at −30°. After the solution was decolorized, the excess olefin was allowed to distil and the product mixture was subjected to flask-to-flask distillation which was shown not to alter the product ratios. Product analysis was carried out by g.l.p.c. A 10-ft. TCP column (20% on firebrick) operating at 50–70° with flow rates of 60–100 ml. of helium per minute resolved all chlorocyclopropanes studied. For the analysis of the bromocyclopropanes a 6-ft. column with Carbowax 20 M (20% on firebrick) operating at 90–100° with helium flow rates of 50–80 ml./min. was used. In the run involving 2,3-dimethyl-2-butene a 5-ft. column with silicon oil SF-96 on firebrick, operating at 90°, was used. In all cases product

identities were established by comparison of g.l.p.c. retention times and infrared spectra of trapped samples with authentic samples. Thermal conductivity corrections were applied for the quantitative analyses. Relative addition rates were determined using the expression $k_1/k_2 = [P_1/P_2][O_2/O_1]$ where $[P_1/P_2]$ represents the mole ratio of the cyclopropanes as determined by g.l.p.c. and $[O_2/O_1]$ represents the olefin mole ratios.

Reaction of Diazomethane with 2 Equiv. of t-Butyl Hypochlorite in Isobutene. To a solution of diazomethane (0.034 mole) in isobutene (100 ml.) was added dropwise a solution of t-butyl hypochlorite (7.05 g., 0.065 mole) in trichlorofluoromethane (30 ml.). The first half of the addition was carried out at 100° over a period of 30 min., the second half at −60° over a period of 1 hr. (in another run the total addition was completed at −100°, with essentially the same results). After the addition was completed, the reaction mixture was colorless. The excess olefin was allowed to distil and the residue was washed with water, dried over sodium sulfate, and subjected to g.l.p.c. analysis on a 6-ft. R.C.A. polyadipate column (35% on firebrick), operating at 95°. Only the major components of the complex reaction mixture were identified by trapping and comparison of the n.m.r. and infrared spectra with those of authentic samples. These were, in the order of emergence from the column: methallyl chloride (45%), 2,5-dimethyl-1,5-hexadiene (8%), 1,1-dichloro-2,2-dimethylcyclopropane (VIIa, 2%), and 1,1-dichloro-3-methylbutene (VIIIa, 8%).

Hydrogenation of 1,1-Dichloro-3-methyl-3-butene (VIIIa). A solution of VIIIa (105 mg., 0.75 mmole) in methanol (20 ml.) was hydrogenated over 5% palladium on charcoal (75 mg.). After 35 min. the hydrogen uptake was complete (17 ml., 95%). The catalyst was filtered off and water was added followed by extraction with ether. After evaporation of the solvent the hydrogenated material was purified by g.l.p.c. on a Carbowax 20 M column, operating at 138°, and was found to have identical infrared and n.m.r. spectra and g.l.p.c. retention time to that of 1,1-dichloro-3-methylbutane (IXa) prepared as described by Schmerling.[54]

Reaction of Diazomethane with 2 Equiv. of t-Butyl Hypobromite in Isobutene. To a solution of diazomethane (0.036 mole) in isobutene (100 ml.) was added dropwise a solution of t-butyl hypobromite (10.1 g., 0.066 mole) in trichlorofluoromethane at −100°. After 2.5 hr., the addition was completed and the red color of the bromodiazomethane, which had reached a maximum intensity after approximately one-half of the reagent had been added, disappeared completely. The olefin was allowed to evaporate and the residue was washed with water, dried over sodium sulfate, and subjected to g.l.p.c. analysis on a 6-ft. Carbowax 20 M column operating at 150°. Only the major components of the complex reaction mixture were identified by trapping and comparison of the n.m.r. and infrared spectra with those of authentic samples. These were, in order of emergence from the column: methallyl bromide, 2,5-dimethyl-1,5-hexadiene, methylene bromide (4%), 1,1-dibromo-2,2-dimethylcyclopropane

(54) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 1652 (1946).

(4%), 1,1-dibromo-3-methyl-3-butene (10%), and bromoform (4%). The structure of the olefinic product (VIIIb) was assigned on the basis of its spectral properties and its hydrogenation to 1,1-dibromo-3-methylbutane. The n.m.r. spectrum showed a triplet at τ 4.33 ($J = 7.02$ c.p.s.), multiplet at 5.10, doublet at 6.78 ($J = 7.02$ c.p.s.), and a narrow multiplet at 8.24 in the correct intensity ratios for the assigned structure. The infrared spectrum of VIIIb shows double bond vibrations at 1655 and 3085 cm.$^{-1}$.

When the reaction was carried out in the presence of 2,6-di-t-butylphenol (0.5 mole %, based on t-butyl hypobromite) the yield of VIIb was 5% and of VIIIb 12%. When the 2,6-di-t-butylphenyl concentration was increased to 2 mole %, the yield of VIIb went up to 10% and the yield of VIIIb went up to 19%.

Reaction of Diazomethane with 2 Equiv. of t-Butyl Hypohalite in Mixtures of Isobutene and 2,3-Dimethyl-2-butene. The competition runs were carried out in identical manner as described for the halogenations involving isobutene only, except that mixtures of isobutene and 2,3-dimethyl-2-butene were used as solvent. Free-radical inhibitors (2,6-di-t-butylphenol and diphenylamine) were used on concentrations of 2 mole %, based on t-butyl hypohalite. The reaction mixtures were analyzed by g.l.p.c. on 6-ft. polyadipate and 6-ft. Carbowax 20 M columns. The product ratios were determined by using thermoconductivity corrections for the cyclopropanes. The relative rates were derived from the expression $k_1/k_2 = [P_1/P_2][O_2/O_1]$, where $[P_i]$ and $[O_i]$ are the number of moles of product and olefin, respectively.

Hydrogenation of 4,4-Dibromo-2-methylbutene-1. The olefin (86 mg., 0.38 mmole), dissolved in 20 ml. of methanol was hydrogenated over 5% palladium on charcoal (60 mg.). After 20 min., the correct amount of hydrogen was absorbed, water was added, and the reaction mixture was extracted with ether, dried, most of the ether was removed, and the residue was submitted to g.l.p.c. analysis on a 6-ft. SF-96 column operating at 105°. The analysis indicated the presence of a single product. The n.m.r. and infrared spectra of the trapped material proved to be identical with that of 1,1-dibromo-3-methylbutane, as prepared below.

Preparation of 1,1-Dibromo-3-methylbutane. A. 2-Bromo-4-methylpentanoic Acid. Following the procedure described by Clarke and Taylor for the bromination of n-caproic acid,[55] 2-bromo-4-methylpentanoic acid was prepared from 4-methylpentanoic acid in 83% yield, b.p. 125–135° (9 mm.).

B. Following the general procedure of Conly,[56] 2-bromo-4-methylpentanoic acid was converted to its silver salt, dried for 16 hr. at 0.025 mm., and reacted with bromine in carbon tetrachloride at 0°. Distil-

lation afforded 1,1-dibromo-3-methylbutane (30.7%), b.p. 65–67° (25 mm.).

Anal. Calcd. for $C_5H_{10}Br_2$: C, 26.11; H, 4.38; Br, 69.50. Found: C, 26.18; H, 4.45; Br, 69.49.

Synthesis of cis- and trans-1-Chloro-2-ethylcyclopropane. A. cis- and trans-1-Chloro-1-butene. The chloroolefins were prepared following the procedure of Henne and Hinkamp.[57] To a solution of potassium hydroxide (73.0 g., 1.30 moles) in n-butyl alcohol (250 ml.) at reflux temperature, the dichloride (151 g., 1.17 moles) was added dropwise over a period of 2 hr. The chloroolefins were allowed to distil from the mixture through a short column as the addition progressed. The crude chloroolefins (71.0 g., 66.9%) were washed with water, dried over calcium chloride, and carefully fractionated on a 3-ft. helix-packed column employing reflux ratios of 20–30:1. This procedure afforded cis-1-chloro-1-butene (17.1 g., b.p. 63.0–63.6°), and $trans$-1-chloro-1-butene (35.2 g., b.p. 68.0–68.4°). G.l.p.c. analysis on a 10-ft. TCP column operating at 80° showed the isomers to be free of each other.

B. Simmons–Smith Reaction on cis- and trans-1-Chloro-1-butene. Zinc–copper couple was prepared as described by Shank and Shechter.[58] To a suspension of the couple (14.3 g.) in ether (115 ml.) was added dropwise methylene iodide (47.0 g., 0.176 mole) containing iodine (0.1 g.) at reflux temperature over a period of 1 hr. After refluxing for an additional 0.5 hr., $trans$-1-chloro-1-butene (35.1 g., 0.39 mole) was added dropwise over a period of 2 hr. The reaction mixture was refluxed for 24 hr., filtered through Super-Cel, washed with 3% hydrochloric acid, water, and bicarbonate solution, and dried over calcium chloride. Most of the ether was removed and the residue was subjected to g.l.p.c. analysis. The analysis indicated only a very low conversion of olefin to chlorocyclopropane. In order to increase the conversion the residue was submitted and resubmitted to the above reaction conditions. G.l.p.c. analysis showed the presence of only one of the isomeric chlorocyclopropanes and in a sufficient amount for trapping. Trapping of the single component and infrared spectra comparison showed it to be identical with the *minor* isomer from the reaction of methylene chloride, methyllithium, and butene-1.[20]

When the reaction was carried out using cis-1-chloro-1-butene (17.1 g., 0.19 mole) in an identical fashion, g.l.p.c. analysis again showed conversion to chlorocyclopropane to be very low. After repeating the reaction on the residue, sufficient material was present for characterization. The single chlorocyclopropane present was trapped from the g.l.p.c. and exhibited an identical infrared spectra with that of the major isomer in the reaction of methylene chloride, methyllithium, and butene-1.[20]

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