bulbous part of a peyote cactus with a Hamilton microliter syringe. Three weeks later the cactus was macerated in a Waring blendor with 300 ml of methanol. The methanol extract was filtered and evaporated to dryness, and the residue was extracted with 100 ml of 1% hydrochloric acid. The aqueous acidic extract (4.9×10^6 dpm) was basified with ammonium hydroxide and extracted with chloroform (6×50 ml). The pooled chloroform extract (5.1×10^6 dpm) was fractionated[27] into the phenolic and nonphenolic alkaloids, and the radioactive anhalonidine (19.8 mg, 6.01×10^6 dpm) was isolated by preparative tlc as its hydrochloride from the phenolic fraction.

Administration of [1,9-^{14}*C*]Peyoxylic Acid (XXVII) to Peyote Cactus and Isolation of Radioactive Anhalamine (I). A 15.5-mg quantity of [1,9-^{14}*C*]peyoxylic acid (1.32×10^9 dpm/mmol) was administered to a peyote cactus as described above. The plant was harvested after 3 weeks and the isolation of anhalamine hydrochloride (6.8 mg, 8.92×10^7 dpm/mmol) from the phenolic alkaloid fraction was carried out as in the case of II (above).

Degradation of Anhalonidine (II) Derived from [1-^{14}*C*]Peyoruvic Acid (XXVI). Kuhn–Roth oxidation of anhalonidine (19.8 mg, 6.01×10^6 dpm/mmol) gave acetic acid which was collected as sodium acetate (5.95×10^6 dpm/mmol). Schmidt[40] degradation of acetic acid gave carbon dioxide having an activity of 5.93×10^6 dpm/mmol.

Degradation of Anhalamine (I) Derived from [1,9-^{14}*C*]Peyoxylic Acid (XXVII). The radioactive anhalamine (6.8 mg, 8.92×10^7 dpm/mmol) was diluted with 35 mg of cold anhalamine and converted to *O*-methyl pellotine (XXX, 8.81×10^7 dpm/mmol) according to the procedure of Lundström and Agurell.[6] Kuhn–Roth oxidation of XXX gave acetic acid collected as sodium acetate (8.80×10^7 dpm/mmol) which on Schmidt degradation afforded carbon dioxide possessing an activity of 8.79×10^7 dpm/mmol.

Degradation of the Schiff's Base XXVIII Derived from [9-^{14}*C*]-Peyoruvic Acid (XXVI). The radioactive Schiff's base (2.3 mg, 1.06×10^6 dpm/mmol) was mixed with 25 mg of cold XXVIII and reduced with sodium borohydride to yield anhalonidine (II), specific activity 1.058×10^6 dpm/mmol. Kuhn–Roth oxidation of II afforded acetic acid collected as sodium acetate (1.051×10^6 dpm/mmol). Schmidt degradation of acetic acid liberated carbon dioxide (nonradioactive) and methylamine, which on oxidation with potassium permanganate,[20] yielded carbon dioxide having an activity of 1.05×10^6 dpm/mmol.

Acknowledgments. The authors appreciate the assistance of Mr. Edward A. Sokoloski, National Heart and Lung Institute, in obtaining the 100-MHz nmr spectra. They also thank Dr. A. Brossi of Hoffman-La Roche, Inc., Nutley, N. J., for the samples of DL-anhalonidine and anhalamine hydrochlorides.[41]

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(40) See Scheme IV, footnote *d*.

(41) *Cf.* A. Brossi, F. Schenker, and W. Leimgruber, *Helv. Chim. Acta*, 47, 2089 (1964), for the synthesis of these alkaloids.

Methylchlorocarbene[1]

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Abstract: Methylchlorocarbene, CH_3CCl, was generated by photolysis of methylchlorodiazirine and added to tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, and *trans*-butene to give the anticipated cyclopropanes. Vinyl chloride was also formed by rearrangement of CH_3CCl. The relative reactivities (25–30°) of the above olefins toward CH_3CCl were 3.87, 2.44, 1.00, 0.74, and 0.52, respectively. In additions to trimethylethylene and *cis*-butene, CH_3CCl added so as to give mainly that cyclopropane isomer in which Cl was syn to the larger number of methyl groups. Syn:anti ratios were 1.45:1 and 2.84:1, respectively. Additions of CH_3CCl to *cis*-butene and *trans*-butene were stereospecific. Discussion of the data correlates the reactivity and stereoselectivity of several carbenes of structure XCCl.

Although there have been many quantitative studies of selectivity in carbene–olefin addition reactions, the carbenic substituents have been largely restricted to hydrogen, halogen, aryl, and carboalkoxy.[3] Those few cases in which the substituents have been "alkyl" have generally been concerned with highly unsaturated species,[4] in which intramolecular rearrangements of the carbene in solution either cannot occur, or are of rate comparable to intermolecular reaction of the carbene with an olefin.

By way of contrast, the facile and manifold rearrangements of simple alkylcarbenes[5] have precluded study of their addition to olefins, thus all but preventing assessment of the influence of simple alkyl substituents on carbene selectivity.

Methylcarbene has been successfully added to propene, but not to higher alkenes.[6] Phenylmethylcarbene, in which resonance interaction of the carbenic p orbital[7] and the phenyl group presumably slows the intramolecular 1,2-hydride shift, does add to alkenes at rates competitive with its rearrangement to styrene.[8]

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(1) Stereoselectivity of Carbene Intermediates. VII.[2]

(2) Part VI: R. A. Moss, J. R. Whittle, and P. Freidenreich, *J. Org. Chem.*, **34**, 2220 (1969).

(3) R. A. Moss, in preparation.

(4) (a) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969); (b) H. D. Hartzler, *J. Org. Chem.*, **29**, 1311 (1964), and references therein; (c) R. A. Moss, *ibid.*, 31, 3296 (1966); (d) M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969); (e) W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969), and references therein; (f) W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *ibid.*, **90**, 1849 (1968), and references therein; (g) P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966); **87**, 2493 (1965); (h) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963).

(5) For a brief, recent review see: R. A. Moss, *Chem. Eng. News*, **47**, 60 (June 16, 1969); 50 (June 30, 1969). We here omit discussion of alkylcarbenoids.

(6) (a) H. M. Frey, *J. Chem. Soc.*, 2293 (1962); *Chem. Ind. (London)*, 218 (1962). (b) See, however, H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1700 (1965).

(7) We assume sp^2 hybridization for a singlet carbene.

(8) (a) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, 31, 2759 (1966); (b)

Its selectivity toward alkenes, however, has not yet been studied. Moreover, such a study may suffer complications due to simultaneous additions of the singlet and triplet (ground state) carbene.[8c]

Methylchlorocarbene is a good choice for a study of the effect of a methyl substituent on carbenic selectivity. The ground state is likely to be singlet;[9] interaction of the carbenic center with the chlorine should slow rearrangement to vinyl chloride such that addition to olefins would be observable, and the carbene is readily available from methylchlorodiazirine.[10] Moreover, the stereoselectivity of methylchlorocarbene would be of interest with regard to the behavior of related carbenes.[11]

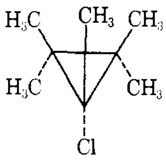
Methylchlorocarbene has been implicated as an intermediate in the thermolysis of methylchlorodiazirine.[10] The gas-phase decomposition has been studied by kinetics, and a stabilizing effect of the Cl on CH_3CCl of about 2 kcal/mol, relative to $(CH_3)_2C$, has been suggested.[12] Intermediacy of CH_3CCl (or, more likely, a related carbenoid) has been cited by Kirmse and Bülow, who treated 1,1-dichloroethane with alkyllithium.[13] Under the reaction conditions, the putative methylchlorocarbene reacted exclusively with additional alkyllithium, affording derived dialkylcarbenoids. CH_3CCl has not yet been trapped by alkenes. Some related species have also been reported.[14–17]

We have now studied the addition of CH_3CCl, as generated by the photolysis of methylchlorodiazirine, to various simple alkenes. We report here on the stereospecificity, stereoselectivity, and interalkene discrimination of the presumed carbene intermediate.

Results

Synthesis and Identification of 1-Chloro-1-methylcyclopropanes. Methylchlorodiazirine was photolyzed ($\lambda > 300$ mμ) in tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, and *trans*-butene. 1-Chloro-1-methylcyclopropanes I–V, respectively, were isolated by preparative gas chromatography (gc) of the photolysates. The photolyses in trimethylethylene and *cis*-butene led to the expected isomer pairs IIa,IIb and IVa, IVb. Vinyl chloride, in comparable yields, was also observed.

Structures were assigned on the basis of spectral data. Although the compounds exhibited good gc behavior, they were very volatile and not easily manipulated. Samples which were gc pure repeatedly gave poor elemental analyses (see Experimental Section). Adducts II–V showed ^{35}Cl and ^{37}Cl containing parent ions in their 70-V mass spectra. Cyclopropane I did not show a parent ion, but had a strong $(M - Cl)^+$ ion. This ion was the base peak in the spectra of adducts II–V.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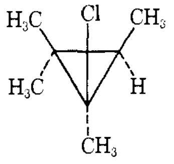
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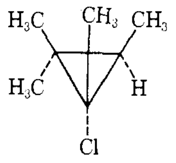
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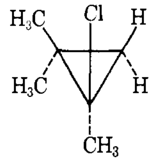
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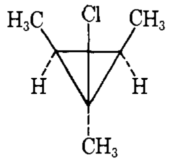
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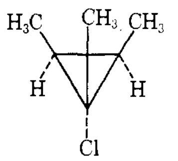
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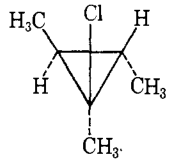
V

Crucial information was obtained from the nmr spectra. Vinyl protons were absent and all adducts showed an unsplit three-proton signal in a region consonant with the part structure CH_3–C–Cl. Relevant data are collected in Table I.

Table I. Nmr Data for 1-Chloro-1-methylcyclopropanes[a]

Compd	CH_3–C–Cl[b]	Other CH_3 groups
I	1.55	1.17 s, 1.03 s
IIa	1.63	1.10 "d" ($J = 6$), 1.08 s[c]
IIb	1.47	1.31 s, 0.98 s[d]
III	1.65	1.34 s, 1.16 s[e]
IVa	1.57	1.00 "d"[f]
IVb	1.38	0.88[g]
V	1.56	1.23 "d", 1.10 "d"[h]

[a] In CCl_4 solution, Varian A-60 spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane; s = singlet, d = doublet. Signal integrals were acceptable. [b] All signals were singlets. [c] The CH_3–C–H system is AB_3 with $J \sim 7$ cps and $J/\Delta\nu \sim 0.21$. The ring proton shows the expected six lines (F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 102, 279) with line five at δ 0.53. [d] The ring proton and the methyl protons anti to Cl are apparently degenerate. The integral ratio of the three signals is 3:3:7. [e] The ring protons are an AB system, $J = 6$ cps, δ 0.78 and 0.53. [f] The ring protons are a multiplet δ 1.0–0.65. [g] Nmr determined on IVa–IVb mixture. [h] B portions of AB_3 systems. The ring protons appear to be centered at δ 0.83 and 0.42.

Structures were assigned to each isomer of the pairs IIa,IIb and IVa,IVb by means of nmr and thermal lability experiments. With regard to the nmr spectra, the methyl group gem to Cl should be shielded by placing *syn*-methyl groups at C_2 and/or C_3, while it should be deshielded by placing *anti*-methyl groups at those positions.[18] This allows differentiation of structure in IIa,IIb[19a] and IVa,IVb.[19c]

H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966); (c) I. Moritani, Y. Yamamoto, and S-I. Murahashi, *ibid.*, 5697 (1968).

(9) Phenylchlorocarbene has been found to have a singlet ground state. Private communication from Professor E. Wasserman, Rutgers University.

(10) W. H. Graham, *J. Amer. Chem. Soc.*, **87**, 4396 (1965). We thank Dr. Graham for detailed discussion of the synthesis of this compound.

(11) See ref 2 and work cited therein.

(12) M. R. Bridge, H. M. Frey, and M. T. H. Liu, *J. Chem. Soc. A*, 91 (1969).

(13) W. Kirmse and B-G. v. Bülow, *Chem. Ber.*, **96**, 3316, 3323 (1962).

(14) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, 87, 5807 (1965).

(15) R. J. Bussey and R. C. Neuman, Jr., *J. Org. Chem.*, **34**, 1323 (1969).

(16) D. Seyferth, D. C. Mueller, and R. L. Lambert, Jr., *J. Amer. Chem. Soc.*, 91, 1562 (1969).

(17) D. C. Mueller and D. Seyferth, *ibid.*, 91, 1754 (1969).

(18) The qualitative argument is based on the effect of the anisotropy of the C–C bonds between the ring and added methyl carbons. See, for example, L. M. Jackman, "Applications of Nuclear Magnetic

Substantiation of these assignments could be obtained from chemical data. Thus, heating the IIa,IIb mixture at 160° for 2.7 hr (CCl_4 solvent, sealed tube, CH_2Cl_2 standard) resulted in the destruction of IIb but not of IIa. A parallel observation was made on the IVa,IVb isomer mixture. After 12 hr at 184–194°, other conditions as above, IVb was extensively destroyed, relative to IVa. These results are understandable, if the nmr assignments are correct. The energetically preferred course for the thermolytic opening of the chlorocyclopropanes should be a concerted, disrotatory process, in which substituents *cis* to the chloride leaving group must rotate *toward* each other. Such motions will relieve the methyl–methyl nonbonded interactions present in the IIb and IVb ground-state molecules, but the same motions would create serious nonbonded interactions in the transition states derived from IIa and IVa.[20] Under this analysis, the observed differences in thermolysis rates within the IIa,IIb and IVa,IVb isomer pairs lead to structural assignments in harmony with those made on the basis of nmr spectra.

Stereospecificity. Gc permitted separation of the *trans*-butene adduct, V, from the isomeric *cis*-butene adducts, IVa and IVb. It was thus shown that addition of CH_3CCl to *cis*-butene gave only cyclopropanes IVa and IVb; less than 1% of V could have been present, relative to the IV isomers. Addition of CH_3CCl to *trans*-butene afforded a maximum of 1% IV, relative to V. Since the *trans*-butene used contained 1% *cis*-butene, this reaction, too, can be regarded as >99% stereospecific.[21] The high cis addition stereospecificity displayed in reactions of CH_3CCl with *cis*- and *trans*-butene suggests that the carbene is reacting as a singlet.[22]

Stereoselectivity. The stereoselectivity of CH_3CCl additions to trimethylethylene and *cis*-butene was determined by gc analysis of crude product mixtures. The isomer ratios obtained were independent of photolysis times. From addition of CH_3CCl to trimethylethylene, IIa/IIb was determined as 1.45 ± 0.02 (three experiments). From addition of CH_3CCl to *cis*-butene, IVa/IVb was determined as 2.84 ± 0.08 (four experiments). Thus, in both cases, CH_3CCl adds to the olefins so as to yield an excess of that cyclopropane in which Cl is syn to the larger number of methyl groups.

Relative Reactivity Experiments. Competitive additions of CH_3CCl in binary olefin mixtures were carried out in the usual way. Methylchlorodiazirine was photolyzed for 3–5 hr in olefinic solutions (sealed tube, 25–30°). Each olefin was present in at least tenfold excess over the diazirine. Variation of photolysis time or temperature within the noted ranges made little difference in observed relative reactivities. Products were shown to be stable to gc conditions and were so quantitatively analyzed (calibrated thermal conductivity detector). Relative reactivities of the olefins are collected in Table II.

Table II. Reactivity of Olefin$_i$ (Relative to Isobutene) toward CH_3CCl, 25–30°

Case	Olefin$_i$	$k_i/k_{isobutene}$	% av dev$_n$[a]
1	Tetramethylethylene	3.87	12.$_4$
2	Trimethylethylene	2.44[b]	2.4$_2$
3	Isobutene	1.00	
4	*cis*-Butene	0.741[b]	2.2$_2$
5	*trans*-Butene	0.518	1.5$_2$

[a] Average deviation (%) of *n* experiments. [b] Composite of both isomeric cyclopropane products.

Cross-check experiments were also carried out. From cases 1 and 2, $k_{tetramethylethylene}/k_{trimethylethylene}$ is calculated to be 1.58. A direct competition experiment of these olefins for CH_3CCl gave 1.60. From cases 4 and 5, $k_{cis\text{-butene}}/k_{trans\text{-butene}}$ is calculated to be 1.43. A direct competition experiment of these olefins for CH_3CCl gave 1.44.

Discussion

Stereoselectivity. The stereoselectivities of some chlorocarbenes, generated by methods likely to give free carbenes, are compared in Table III.

Table III. Stereoselectivity of XCCl, *syn*-Cl:*syn*-X[a]

Olefin	X			
	H[b]	CH_3[c]	C_6H_5[d]	F[e]
Trimethylethylene	1.0	1.45	1.28	2.20
cis-Butene	1.0	2.84	1.97	2.40

[a] *syn*-Cl:*syn*-X refers to the kinetically controlled ratio of the product cyclopropane isomers in which Cl is syn to the larger number of methyl groups or X is syn to the larger number of methyl groups, respectively. [b] $ClCHN_2$ thermolysis at −30°, ref 23. [c] This work, 25–30°. [d] Photolysis of phenylchlorodiazirine, 25°, ref 2. [e] $(FCl_2C)_2C{=}O + K^{+-}O\text{-}tert\text{-}C_4H_9$, 25°, ref 2 and R. A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967); *Tetrahedron*, **23**, 2549 (1967).

Chlorocarbene shows no stereoselectivity. This is in keeping with its near lack of discrimination between different olefins.[23] Formulation of the transition state for its addition reaction as "loose" or "reactant-like" can rationalize this behavior, since the nonbonded

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Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1959, pp 112–117.

(19) (a) Note also (Table I) that IIa shows a high-field cyclopropyl proton, shielded by two *syn*-methyl groups, relative to the analogous lower field proton of IIb, which is syn to one methyl group and one chloro group. (b) For a discussion and references on alkyl group shielding of *syn*-cyclopropyl protons see: D. T. Longone and A. H. Miller, *Chem. Commun.*, 447 (1967). What little is known about the effect of a *syn*-chloro group on a cyclopropyl proton resonance suggests that deshielding should be observed. This would reinforce the differential shielding of the IIa and IIb cyclopropyl protons caused by the methyl groups. See: L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 228 ff. See also ref 8a. (c) Although it seems possible that the all-*cis*-trimethylcyclopropane arrangement in IVb and IIb could lead to Van der Waals deshielding of the methyl resonances further complicating the situation, the methyl resonances of *cis*-1,2,3-trimethylcyclopropane itself are at δ 0.85,[19d] a reasonable value since the methyl of methylcyclopropane is at *ca.* δ 1.0[19e] and in good agreement with the CH_3–C–CH signals of IVb (δ 0.88, see Table I). The latter comparison assumes that the *anti*-chloro group in IVb would have but a small effect on the CH_3–C–H signals, a reaonable idea.[19f] (d) P. Waitkus, E. B. Sanders, L. I. Peterson, and G. W. Griffen, *J. Amer. Chem. Soc.*, **89**, 6318 (1967). (e) H. Weitkamp, U. Hasserodt, and F. Korte, *Chem. Ber.*, **95**, 2280 (1962). (f) See G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **82**, 5723 (1960), Figure 1, spectrum e.

(20) C. H. DePuy, *Accounts Chem. Res.*, 1, 33 (1968); R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). For a recent closely related application, see M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969).

(21) *cis*-Butene reacts with CH_3CCl somewhat more rapidly than does *trans*-butene; see below.

(22) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956). Discussions: P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, Chapter 12; G. L. Closs, *Top. Stereochem.*, 193 (1968).

(23) G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4270 (1965).

interactions which determine the stereoselectivity will then be minimal.[23,24] In contrast, methylcarbene (from diazoethane) adds to propene to form more *cis*- than *trans*-1,2-dimethylcyclopropane (1.4/1).[6a] It becomes a matter of some interest, then, to learn what stereoselectivity will be displayed by CH_3CCl, which should be a more discriminating species than either of the monosubstituted carbenes CH_3CH or $ClCH$.

With FCCl, syn Cl addition exceeds syn F addition (Table III) even though *a priori* steric considerations ($Cl > F$) might have pointed to the opposite outcome. Dominance of electrostatic attraction of the more polarizable Cl for the larger number of olefinic methyl groups in the two possible transition states has been held responsible.[25] With CH_3CCl, both steric considerations ($CH_3 > Cl$)[26] and polarizability considerations ($Cl > CH_3$)[27] reinforce. Syn Cl addition is predicted and observed. Syn Cl addition is also observed for C_6H_5CCl. The major factor here is probably the large size differential between phenyl and chloro groups.[2,24,28] Note, however, that syn Cl addition is more pronounced for CH_3CCl than for C_6H_5CCl. Since phenyl is more sterically demanding than methyl, one might have expected the opposite. However, the π electrons make phenyl more polarizable than methyl, presumably offsetting the steric differential. Halogen polarizability is also involved in determining the phenylhalocarbene stereoselectivities, since C_6H_5CF, which carries the least polarizable halogen, shows anti F stereoselectivity in its addition to trimethylethylene.[28]

Discrimination. In Table IV we have collected relative reactivity data for various olefins with four carbenes of structure XCCl. Each of these species is likely to react as a free, singlet carbene.[29]

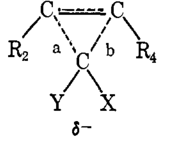
Table IV. Relative Reactivities of Olefins toward XCCl

	X			
Olefin	CH_3[a]	C_6H_5[b]	Cl[c]	F[d]
Tetramethylethylene	3.87	5.1	7.40	31
Trimethylethylene	2.44[e]	3.2[e]	3.05	6.5[e]
Isobutene	1.00	1.00	1.00	1.00
cis-Butene	0.74[e]	0.37[e]	0.23	0.14[e]
trans-Butene	0.52	0.20	0.15	0.097
"Spread" [f]	7.45	25.5	49.3	320
m[g]	0.50	0.83	1.00	1.48

[a] This work, 25–30°. [b] Reference 2, 25°. [c] First two values, R. A. Moss and A. Mamantov, unpublished work. Other values, ref 25, −10°. [d] Reference 25, −10°. [e] Composite of both modes of addition to this olefin. [f] Ratio of largest to smallest relative reactivity. [g] Least-squares slopes of log ($k_i/k_{isobutene}$) for XCCl at t° *vs.* log ($k_i/k_{isobutene}$) for CCl_2 at −10°.

That carbenes are generally electrophiles in their addition reactions with olefins has been a principal tenet of carbene chemistry for more than a decade.[5,30,31]

Qualitative ideas have usually been expressed in terms of transition states such as VI, in which the relative strengths of bonds a and b are expected to be sensitive to steric and electronic alterations of R_i and X and Y.



VI

Recently, important new investigations have appeared. Differential activation energies for additions of CF_2 to alkenes have been correlated with calculated differential π-electron energies of the corresponding transition states, VI.[32] Linear free-energy graphs were presented correlating olefin relative reactivities toward CF_2 addition with those of FCCl and CCl_2 additions.[32] The slopes of these correlations were: CF_2 *vs.* FCCl, $m = 1.12$ (−10°) and CF_2 *vs.* CCl_2, $m = 1.87$ (−15°). The carbene selectivity ordering was thus $CF_2 > FCCl > CCl_2$.

Other quantitative studies have analyzed additions of CCl_2 to simple alkenes ($\rho^* \sim -4.3$, $\delta \sim 1.0$),[33-35] to substituted α-methylstyrenes ($\rho = -0.38$),[36] and to substituted styrenes ($\rho = -0.62$).[37] Skell and Cholod[33] also correlated relative olefin reactivities toward CCl_2 addition with analogous data for six other carbenes. We have previously discussed one such relationship for FCCl and CCl_2 and reviewed several earlier attempted correlations.[24] More recently we pointed out that carbene selectivity in olefin addition does not seem to be a simple additive function of substituents.[28] We have now observed that there may be at least a limited linearity of structure-selectivity response in a series of disubstituted carbenes, when one substituent is kept constant, while the second is varied (see below).

CH_3CCl is seen to be a moderately selective carbene. Thus over the olefin series of Table IV, HCCl shows a "spread" of 1.21 (−30°)[23] and HCF, which should be more discriminating, shows a spread of only 2.10 (22°).[38] The spread for CH_3CCl is 7.45. It appears that the methyl group does contribute to enhanced discriminating ability, relative to HCX. Presumably, this reflects a more stabilized carbene in the CH_3CCl case, VII, which engenders a more charge-separated, more product-like transition state, VI.[39] In its olefin discriminating ability, CH_3CCl seems somewhat less selective than

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(24) For a review of "Stereoselectivity in the Addition of Carbenes to Olefins," see R. A. Moss in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1970, p 35 ff.

(25) See Moss and Gerstl, Table III, footnote *e*.

(26) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, pp 212–215.

(27) Reference 26, pp 196–199.

(28) R. A. Moss and J. R. Przybyla, *Tetrahedron*, **25**, 647 (1969).

(29) The multiplicity follows from observed stereospecificity. The "freeness" of Cl_2C and FCCl follows from P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 6035 (1969). See also the brief discussions in ref 5 and 25.

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

(31) W. v. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(32) R. A. Mitsch and A. S. Rodgers, *Int. J. Chem. Kinet.*, **1**, 439 (1969).

(33) P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 7131 (1969).

(34) See G. Mouvier and J. E. DuBois, *Bull. Soc. Chim. Fr.*, 1441 (1968), for the general method.

(35) See R. A. Moss and A. Mamantov, *Tetrahedron Lett.*, 3425 (1968), for an independent determination of δ.

(36) I. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

(37) D. Seyferth, J. Y-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, **90**, 6182 (1968).

(38) Y-N. Tang and F. S. Rowland, *ibid.*, **89**, 6420 (1967).

(39) It has been pointed out[33] that there is an *inverse* relation between selectivity and electrophilicity. A nonstabilized singlet carbene, *e.g.*, CH_2, has a free vacant p orbital and is highly electrophilic and nearly indiscriminant. In dihalocarbenes resonance interactions decrease the "freeness" of the p orbital, *decrease* the electrophilicity, and, therefore, *provoke* greater π-electron changes upon addition to olefins *via* VI, and consequently evoke a greater rate spread over a series of olefins.

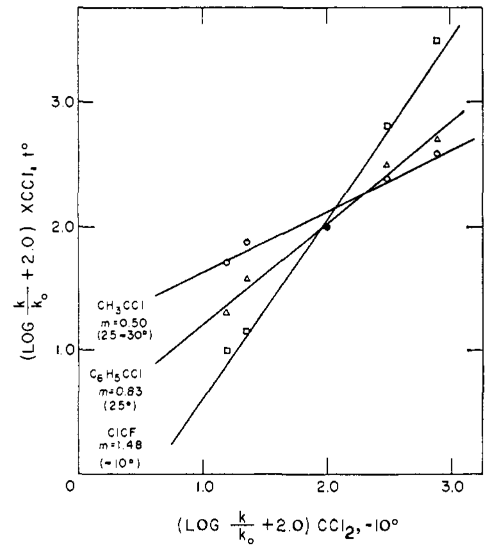


Figure 1. Log (k/k_0) for XCCl at t° vs. log (k/k_0) for CCl_2 at −10°. Relative rates were all multiplied by 100: ○ = CH_3CCl; △ = C_6H_5CCl; □ = ClCF; ● = log $(k_{isobutene}/k_{isobutene}) = 0.00$ for all carbenes. The correlation coefficients are 0.98, 0.99, and 0.99, respectively. From left to right, along each line, the olefins are *trans*-butene, *cis*-butene, isobutene, trimethylethylene, and tetramethylethylene. See Table IV and text.

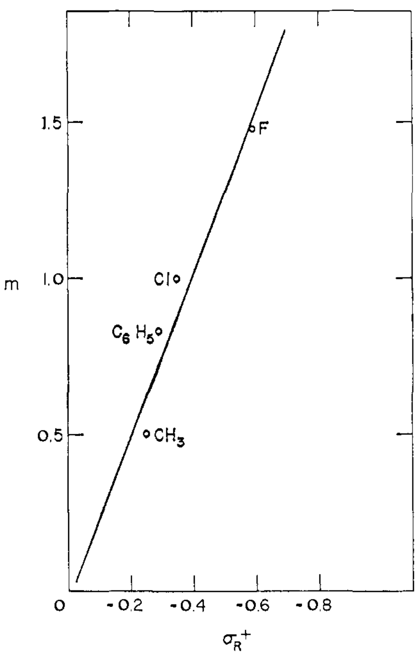
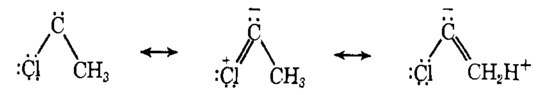


Figure 2. Slopes (m) of log (k/k_0) for XCCl vs. log (k/k_0) for CCl_2 (see Figure 1) vs. σ_R^+. The correlation coefficient is 0.96.

dimethylvinylidene carbene.[4b] Comparison with the other carbenes in Table IV shows that phenyl does contribute more than methyl toward development of discrimination, presumably because of greater resonance



VII

stabilization of the singlet carbene. On the basis of either relative reactivity spreads or slopes of log $(k/k_0)_{XCCl}$ vs. log $(k/k_0)_{CCl_2}$ graphs (see Figure 1), the selectivity order (inverse of electrophilicity order[39]) is FCCl > CCl_2 > C_6H_5CCl > CH_3CCl.[40]

The existence of the relation $(\log k_I/\log k_{II})_A = m(\log k_I/\log k_{II})_B$ for relative reactivities of oelfins I and II toward carbenes A and B can be shown to depend explicitly only on transition-state terms and olefin ground-state energies. Carbene ground-state energy differences are implicit in the m term or slope. An increase in carbene ground-state stability should be reflected in a greater discrimination between olefins.[31,33,39] Note, then, that the regular variation in spreads and m values of the carbenes of Table IV is in keeping with qualitative ideas on the abilities of CH_3, C_6H_5, Cl, and F, in that order, to increasingly donate electron density to an adjacent vacant carbon 2p orbital. Moreover, it is perhaps very significant that a fair linearity exists between the m values and σ_R^+ for the four substituents, as shown in Figure 2.[41] Figures 1 and 2 have been presented as illustrative of the direction in which our results are leading us. We are refining these relations by redetermining relative rates for CCl_2 and FCCl at 25°. Even at present, however, the apparent relation between m and σ_R^+ not only seems to manifest what has, until now, been only a qualitative idea, but, more importantly, may make possible several *predictions* of carbene selectivities. We intend to be guided by this relationship in a study of carbenes which should be even more selective than FCCl[24] and CF_2.[32] One must note, however, that the responses of CF_2 and CCl_2 to changing olefin structure seem to be guided, especially in the latter case, largely by entropy of activation changes.[32,33] An interpretation has been offered.[33] Meanwhile, we note that real insight into carbene selectivity is still developing and that the present results are beginnings.

Experimental Section

Methylchlorodiazirine.[10] A reaction train was constructed which consisted of a 1000-ml, three-necked flask, fitted with a 250-ml dropping funnel, magnetic stirring bar, stopper, and an adapter leading to the first of four traps connected in a series and attached, finally, to a vacuum pump. The first trap was filled with KOH pellets. The second trap contained a small amount of anhydrous $CaCl_2$ and was cooled with liquid nitrogen. The third trap contained a preweighed sample of the substrate olefin intended for the carbene addition, or, in the case of a projected competition reaction, it contained a weighed binary mixture of olefins. It was cooled in liquid nitrogen. The fourth trap was empty, cooled with liquid nitrogen, and connected to the vacuum pump. In a typical experiment, the reaction flask was charged with 1.98 g (21 mmol) of acetamidine hydrochloride (Eastman), 8.3 g (196 mmol) of LiCl, and 125 ml of dimethyl sulfoxide. The dropping funnel was charged with a solution of 50 g (860 mmol) of NaCl in 250 ml of commercial Clorox. The system was evacuated to about 1 mm and the Clorox solution was added to the reaction flask, with stirring, over a period of 6 min. The system was maintained at low pressure for another 4 min. The reaction flask and the vacuum pump were now sealed off from the train of traps, and the diazirine which had collected over $CaCl_2$ in trap 2[42] was allowed to warm slowly to room temperature and thus to distill into the third trap, which contained the olefin(s). After the distillation, the third trap was sealed

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[40] Although CH_3CCl and C_6H_5CCl were studied at *ca.* 25° and CCl_2 at −10°, the slopes of the log–log graphs are not very sensitive to the temperature effect. Using preliminary data for CCl_2 relative rates determined at 25°, least-squares m values for the CH_3CCl and C_6H_5CCl data vs. the 25° CCl_2 data showed no significant change to the second decimal place, as compared to the m values of Table IV.

[41] For σ_R^+ values see: S. Ehrenson, *Progr. Phys. Org. Chem.*, 2, 232 (1964).

[42] An analysis of the crude product methylchlorodiazirine indicated that the impurities present were $CHCl_3$, CH_2Cl_2, and CH_3Cl. Private communication from Dr. W. H. Graham.

by closing its stopcocks, and allowed to warm to 25°. The contents were thoroughly mixed.

Synthesis of Cyclopropanes I–V. In a typical procedure, the third trap contained 10–15 ml of isobutene (liquid). A solution of the diazirine, prepared as above (21 mmol, maximum) in the isobutene was irradiated for 2–5 hr with a G.E. Sunlamp (Pyrex filter). Temperature was maintained at 25–30° with a water bath. After photolysis, isobutene was allowed to evaporate and 130 mg of product was obtained (estimated yield of III, 5–10%). Crude product was chromatographed on a 0.25 in. × 10 ft 10% SE-30 on 45–60 GCR column (Aerograph, A-90-P3 instrument) at 49°. At a He flow rate of 60 ml/min the product, III, had a retention time of 13 min.[43]

The infrared spectrum of III [CCl_4 + $(CH_3)_4Si$] showed bands at 3.43 (s), 6.94 (s), 7.25 (s), 8.23 (s), 8.79 (s), 9.23 (s), 9.71 (m), and 9.97 (m) μ.[44]

Anal. Calcd for 1-chloro-1,2,2-trimethylcyclopropane, $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89. Found: C, 61.36; H, 9.69; Cl, 28.90.[45]

The other new cyclopropanes were synthesized exactly as described for III, from olefins of >99% purity.

1-Chloro-1,2,2,3,3-pentamethylcyclopropane (I). We obtained 230 mg of crude product, from which I was isolated by gc; retention time, 51 min.[43]

The infrared spectrum [CCl_4 + $(CH_3)_4Si$] showed bands at 3.35 (s), 3.43 (s), 6.86 (s), 7.25 (s), and 9.35 (s) μ.

Anal. Calcd for $C_8H_{15}Cl$: C, 65.51; H, 10.31; Cl, 24.18. Found: C, 65.14; H, 10.43; Cl, 23.77.

1-Chloro-1,2,2,3-tetramethylcyclopropanes (IIa, IIb). We obtained 330 mg of crude product. Retention times by gc[43] were 24 and 27 min for IIa and IIb, respectively.

The infrared spectrum (neat) showed absorptions at 3.41 (s), 6.88 (s), 7.24 (s), 8.83 (s), 9.29 (s), and 11.83 (s) μ (mixture of the isomers).

Anal. Calcd for $C_7H_{13}Cl$ (mixture of isomers): C, 63.39; H, 9.88; Cl, 26.73. Found: C, 63.27; H, 9.72; Cl, 25.78.

1-Chloro-1-methyl-2,3-*cis*-dimethylcyclopropanes (IVa, IVb). We obtained 120 mg of crude product. Retention times by gc[43] were 17.5 and 20.5 min for IVa and IVb, respectively.

The infrared spectrum of the isomer mixture [CCl_4 + $(CH_3)_4Si$] showed bands at 3.43 (s), 6.93 (s), 7.23 (s), 8.49 (s), 9.03 (s), 9.36 (s), and 9.80 (s) μ.

Anal. Calcd for $C_6H_{11}Cl$ (mixture of isomers): C, 60.76; H, 9.35; Cl, 29.89. Found: C, 61.16; H, 9.27; Cl, 30.15.

1-Chloro-1-methyl-2,3-*trans*-dimethylcyclopropane (V). We obtained 210 mg of crude material. Retention time by gc[43] was 15.5 min.

The infrared spectrum [CCl_4 + $(CH_3)_4Si$] showed bands at 3.42 (s), 6.89 (s), 7.23 (s), 8.52 (s), 8.92 (m), 9.42 (s), and 10.12 (s) μ.

Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 60.15; H, 9.09.[45]

Relative Reactivity Experiments. These experiments were carried out exactly as described for the syntheses, except that a known mixture of olefins was present in the third trap of the reaction train. Acetamidine hydrochloride (24 mmol) was used. After photolysis, the low-boiling olefinic solutions were cooled to −70° and, while cold, transferred to a round-bottomed flask which contained a stirring bar and an exit carrying an ice condenser capped with a drying tube. The olefinic solution was stirred and allowed to warm to room temperature, and thus to evaporate through the condenser. Generally 1 ml of pentane was added to facilitate analysis of the residue by gc. Relative reactivities were calculated from the appropriate gc peak integrals (corrected for relative thermal conductivity detector response) by means of the equation: $k_A/k_B = (P_A/P_B)\cdot(O_B/O_A)$.[31]

Experiments pertaining to the stereospecificity and stereoselectivity of the CH_3CCl additions are described above.

Other Reaction Products. When the methylchlorodiazirine generated from 25 mmol of acetamidine hydrochloride was photolyzed in 10 ml of trimethylethylene (4 hr, 14°) vinyl chloride was detected in the photolysate by gc on the 10 ft SE-30 column at ~5°. Other conditions were: injector, 154°; detector, 169°; He head pressure, 5 psig. After elution of vinyl chloride, column temperature was raised to 51° (He 12 psig) and adducts IIa and IIb eluted. The ratio of peak areas (vinyl chloride):II was 0.63 and 0.46 for two experiments. This experiment was repeated two more times using decreasing quantities of the diazirine precursor so as to ensure that photolysis had been complete and that residual methylchlorodiazirine was not yielding vinyl chloride by pyrolysis during the gc analysis. Six-hour photolyses on reaction scales 0.25 and 0.167 times as large as above gave (vinyl chloride):II ratios of 0.54 and 0.57, respectively. The average ratio for all experiments was 0.55 ± 0.05. Difficulty was encountered in attempts to calibrate the detector with pure mixtures of products, largely because vinyl chloride is so volatile (bp −14°). The calibration coefficient necessary to convert the gc peak ratio to the mole ratio was determined to be 0.63 ± 0.17 (five experiments). The very poor reproducibility here makes the final product ratio, (vinyl chloride):II, 0.35, quite uncertain. It can be qualitatively concluded, however, that the addition and rearrangement products are formed in comparable yields under our conditions.

Although a careful search for insertion products of CH_3CCl was not conducted, no other products having retention times similar to the cyclopropanes were observed in the olefinic photolyses. It seems likely then that addition is much more rapid than insertion when CH_3CCl is generated in olefinic solution.

Acknowledgments. We thank the National Institutes of Health (GM-13585) and the National Science Foundation (GP-12645) for financial support.

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[43] All gc work was carried out with this column and stated retention times refer to these conditions with injector and detector temperatures of 174–179° and 195–234°, respectively.

[44] Nmr spectra and mass spectral data are described above for all new cyclopropanes. $(CH_3)_4Si$ ir bands are not included.

[45] Best of several analyses. Analyses were by Micro-Tech Laboratories, Skokie, Ill., and by G. Robertson, Florham Park, N. J.