fluoro-2-(N-fluorimino)propane (X). Infrared maxima (neat) were found at 3.33, 3.37, and 3.44 (CH), and 6.05 μ (C=N).

Anal. Calcd for $C_3H_4F_4N_2$: C, 25.01; H, 2.80; F, 52.75; N, 19.45; mol wt, 144. Found: C, 26.18; H, 2.65; F, 52.74; N, 19.37; mol wt, 144 (mass spectrum).

The third and minor component (30-min retention time) was the *anti*-**1-difluoramino-3-fluoro-2-(N-fluorimino)propane** (X) which is characterized below.

B. **In the Absence of Sodium Fluoride.**—The reaction of N_2F_4 with allene was repeated as described above, with the exception that the sodium fluoride was omitted. There was obtained a dark reaction product from which only 14 g of volatile product was obtained. A gas chromatographic analysis[27] on a 6-ft column at 50° again gave three peaks but this time in a ratio of about 1:10:13, corresponding to *syn*-XI, *syn*-X, and *anti*-X (16-, 22-, and 30-min retention times, respectively). The 30-min retention-time peak was separated by preparative gas chromatography, bp 110°, and identified as *anti*-**1-difluoramino-3-fluoro-2-(N-fluorimino)propane** (X). Infrared maxima (neat) were found at 3.29 (CH), 3.37 (CH), and 6.02 μ (C=N).

Anal. Calcd for $C_3H_4F_4N_2$: F, 52.75; N, 19.45; mol wt, 144. Found: F, 51.45; N, 19.18; mol wt, 144 (mass spectrum).

syn-**3-Fluoro-2-(N-fluorimino)propionitrile** (XI).—A well-stirred mixture of 5.0 g of *syn*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane, 10 ml of *o*-dichlorobenzene, and 5.0 g of powdered sodium fluoride was heated at 100° for 18 hr. The volatiles were distilled into a −78° trap, *in vacuo*, and this liquid was redistilled to give 3.0 g (82%) of *syn*-3-fluoro-2-(N-fluorimino)propionitrile as a colorless liquid, bp 98°, n^{25}D 1.3730, homogeneous to gas chromatography and showing infrared, nmr, and mass spectra identical with those of the sample prepared above.

anti-**3-Fluoro-2-(N-fluorimino)propionitrile** (XI).—A well-stirred mixture of 3.2 g of *anti*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane, 10 ml of *o*-dichlorobenzene, and 5.0 g of powdered sodium fluoride was heated at 150° for 18 hr. The product was distilled into a −78° trap, *in vacuo*, and this liquid was redistilled to give 2.2 g (90%) of *anti*-3-fluoro-2-(N-fluorimino)propionitrile as a colorlesss liquid, bp 97–98°, n^{25}D 1.3810, homogeneous to gas chromatographic analysis[27] (retention time 23.5 min). The infrared spectrum (neat) showed peaks at 3.37 (CH_2), 4.44 (C≡N), 6.18 (C=N), 9.3 (NF), and 10.85 μ (NF).

Anal. Calcd for $C_3H_2F_2N_2$: C, 34.62; H, 1.94; F, 36.52; N, 26.92; mol wt, 104. Found: C, 35.27; H, 1.74; F, 36.48; N, 26.03; mol wt, 104 (mass spectrum).

Registry No.—*cis*-Ia, 13052-49-8; *trans*-Ia, 13052-50-1; *cis*-Ib, 13100-47-5; *trans*-Ib, 13015-97-9; *cis*-Ig, 13015-98-0; *trans*-Ig, 13015-99-1; IIa, 13016-00-7; IIc, 13016-01-8; IId, 13000-66-3; IIe, 10036-38-1; IIIf, 13016-03-0; IIIf anilide, 13016-04-1; IIIg, 13000-67-4; IVa, 13016-05-2; VI, 13016-06-3; VII, 13016-07-4; *syn*-X, 13016-08-5; *anti*-X, 13016-09-6; *syn*-XI, 13016-10-9; *anti*-XI, 13016-11-0; tetrafluorohydrazine, 3744-07-8; allene, 463-49-0; 2,3-bis(N-fluorimino)-1,1,1,4,4,4-hexafluorobutane, 13016-12-1; *syn*-$CF_3C(=NF)CHF_2$, 13016-13-2; *anti*-$CF_3C(=NF)CHF_2$, 13016-14-3; perfluoro-2-heptyne, 13016-15-4.

Acknowledgment.—The authors are indebted to the late Mr. Miller Nelson for assistance in carrying out the N_2F_4 reactions, to members of the Physical and Analytical Division for gas chromatography, infrared, mass spectral, and nmr analyses, and to Dr. E. M. Atadan of the Explosives Department for generous supplies of N_2F_4.

Chlorofluorocarbene and Dichlorocarbene. Comparative Reactivities in Addition to Olefins[1,2]

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Received January 17, 1967

Relative rates of addition of chlorofluorocarbene to tetramethylethylene (31.0), trimethylethylene (6.5), isobutene (1.00), *cis*-butene (0.14), *trans*-butene (0.097), and 1-butene (0.0087) have been determined at −10°. The carbene was generated from *sym*-tetrachlorodifluoroacetone and potassium *t*-butoxide. An analogous set of data was obtained for dichlorocarbene (from chloroform and butoxide). The newly determined rates, relative to isobutene, were *cis*-butene (0.23), *trans*-butene (0.15), and 1-butene (0.011). A discussion of the factors influencing these rates is included. The importance of steric factors both in over-all addition rates and in chlorofluorocarbene stereoselectivity is stressed. Apparent reactions of chlorofluorocarbene aud potassium *t*-butoxide were observed.

Several investigators have tried to assess quantitatively electronic interactions between carbenic centers and various substituents. Perhaps the most basic attempt was that of Hine and Ehrenson, who, from extensive studies of haloform hydrolysis, derived parameters which reflected "the relative abilities of the four halogens to supply electrons to the deficient carbon atom." [3] Others attempted to study substituent carbene interactions by examining how carbene "electrophilicity" [4a,b] altered with substituent variation.[4c] Though many studies have been carried out to demonstrate the electrophilic character of carbene reactions,[5] these attempts to formally correlate electrophilicity and substituent variation have been fewer in number, and modest in success. Thus, Doering and Henderson compared the selectivity of dichlorocarbene over a set of olefinic substrates with the selectivity of dibromocarbene over the same set.[4c] Closs and Schwartz attempted a similar comparison of dichlorocarbene and chlorocarbene.[6] Closs and Moss studied the relative selectivities of substituted phenylcarbenes, over a constant set of olefins, as a function of substituent.[7]

For reasons appearing below, none of these attempts were particularly successful. We were therefore encouraged by our observation that, over a limited set of olefins, logarithms of relative addition rates of chlorofluorocarbene (CFC) and dichlorocarbene (DCC) ap-

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(1) Part IV in the series, "Stereoselectivity of Carbene Intermediates."

(2) Part III: R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

(3) J. Hine and S. J. Ehrenson, *J. Am. Chem. Soc.*, **80**, 824 (1958), and references therein.

(4) (a) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) W. v. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(5) See (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964.

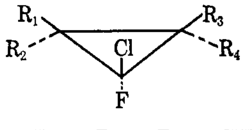
(6) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960).

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

peared to be related linearly.[8] In order to probe the possible correlation more carefully, we have extended our initial studies with CFC[2] to the monoalkylethylene, 1-butene. During this work, it became apparent that potassium *t*-butoxide, the generative base, is significantly converted to isobutylene by CFC. We also determined relative rate data for DCC. The results follow.

Results

Synthesis of Cyclopropanes.—Compounds I–V were available from previous studies.[2] Preparation of VI was similarly attempted, *i.e.*, by addition of *sym*-tetrachlorodifluoroacetone to a slurry of potassium *t*-butoxide in 1-butene, at −10°.[2,9] The principal low-boiling product isolated from this reaction by gas chromatography (gc) *was not* the expected mixture of VIa and VIb, but III, a cyclopropane previously obtained by reaction of CFC and isobutene.[2] The desired adducts VIa and VIb were also present in a yield of about 2% (based on haloacetone). The ratio III/VI was about 1.2.



I, $R_1 = R_2 = R_3 = R_4 = CH_3$
IIa, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
b, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$
III, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
IVa, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
b, $R_1 = R_3 = H$; $R_2 = R_4 = CH_3$
V, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
VIa, $R_1 = C_2H_5$; $R_2 = R_3 = R_4 = H$
b, $R_1 = R_3 = R_4 = H$; $R_2 = C_2H_5$

Compounds VIa and VIb were isolated as a mixture by preparative gc. In the infrared, the mixture displayed the expected intense CF absorption in the 8.5–9.5-μ region.[2,9] Proton nmr revealed the absence of vinylic hydrogen atoms. A multiplet appeared (8.2–9.3 τ) similar to that observed for the dichloro analog of VI, but more complex because of the additional splitting due to fluorine. The F^{19} nmr was most important. The anticipated two signals were observed: a low-field triplet of doublets, centered at 7387 (upfield from internal trichlorofluoromethane) with major coupling 17, minor coupling 6, and base width 64 cps; a high-field crude doublet, centered at 8658, with major coupling of 17, and base width of 49 cps. In both signals, all peaks exhibited the fine structure associated with fluorine–methyl coupling.

All the data are in keeping with formulation of the material as a mixture of VIa and VIb. Moreover, the low-field F^{19} nmr signal must be assigned to VIa, the high-field signal being assigned to VIb. A 17-cps coupling is expected for the *cis,vic*-HF structure, but the nature of the 7387-cps signal suggests its origin in a compound with two such protons, as well as one *trans,vic* proton ($J = 6$ cps). The doublet nature of the 8658-cps signal suggests its origin in a compound possessing only one *cis, vic* proton.[10] Strong confirming evidence for these assignments is available. We have demonstrated the extraordinary sensitivity of F^{19} chemical shifts to ring alkylation in cyclopropyl fluorides.[2] Relative to a cyclopropyl proton, *trans* alkyl groups deshield, while *cis* alkyl groups shield cyclopropyl fluorine. The observed differential chemical shift of 1271 cps independently forces assignments identical with those based on splitting data.

From the integral intensities of the two F^{19} signals, the VIa/VIb ratio was found to be $1.53 \pm 0.02_2$,[11] indicating preferential *syn*-chloro addition of CFC to 1-butene. This is in keeping with earlier observations for trimethylethylene and *cis*-butene, in which CFC added to produce an excess of that isomer in which chlorine was *syn* to the larger number of alkyl groups.[2]

Having isolated and identified the desired products VI, we studied the origin of III in the product mixture, tentatively concluding that it arose *via* deoxidation of the generative base, *t*-butoxide. The isobutene so produced was selectively attacked by more CFC, yielding III. Given that isobutene is 115 times as reactive as 1-butene toward CFC, it is clear that even relatively small amounts of adventitious isobutene in 1-butene would result in observable III at low over-all cyclopropane yields. Supporting evidence follows. (1) The reaction of potassium *t*-butoxide in *pentane* with the haloacetone also yields III (but none of the other cyclopropanes). (2) *Inverse addition* of small portions of butoxide to haloacetone in 1-butene significantly lowers the III/VI distribution to 0.2, while raising the over-all yield of VI to 11%. (Compare 1.2 and 2% for direct addition, above.) (3) Gc data suggests that III is also formed when more reactive olefins are employed as substrates in direct addition syntheses, but that the relative yield of III decreases with increasing substrate reactivity.

The three observations are consistent with a competition between addition of CFC to a substrate olefin or to isobutene formed by deoxidation of *t*-butoxide.[12]

Synthesis of necessary DCC adducts was straightforward and accomplished by addition (−10°) of chloroform to a slurry of potassium *t*-butoxide in the requisite olefin.[4c] The dichloro analogs of III, IV, V, and VI were thus prepared, isolated by gc, and identified by elemental and spectral analyses. The greater reactivity of DCC relative to CFC (see below) suggested that butoxide deoxidation should intrude less importantly in DCC addition to olefins. Though addition of chloroform to a butoxide–pentane slurry (−10°) yielded dichloro III, *direct* addition of chloroform to a 1-butene–butoxide slurry yielded mainly dichloro VI. The dichloro III/dichloro VI ratio was 0.18. (Compare 1.2 for CFC, above.) Dichloro III contributed less than 2% of dichloro IV and V in their direct addition syntheses from *cis*- and *trans*-butene.

Relative Addition Rates.—Typical olefin–carbene competition experiments[4b] were carried out for CFC and DCC. Most of the CFC data were already available,[2]

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[8] Reference 2, footnote 28.

[9] J. P. Oliver, U. V. Rao, and M. T. Emerson, *Tetrahedron Letters*, 3419 (1964), and references therein.

[10] Discussions of the dependence of $J_{\mathrm{H-F}\ vic}$ on dihedral angle appear in K. L. Williamson, Y. F. Li, F. H. Hall, and S. Swager, *J. Am. Chem. Soc.*, **88**, 5678 (1966); R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966); J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2791 (1966); R. F. Merritt and T. E. Stevens, *ibid.*, **88**, 1822 (1966). See also ref 2.

[11] Determined on gc eluents. Rechromatographed material gave unaltered nmr integrals.

[12] Discussions of the deoxidation reaction appear in J. Hine, E. L. Pollitzer, and H. Wagner, *J. Am. Chem. Soc.*, **75**, 5607 (1953); P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); **82**, 2971 (1960).

but were rechecked in the interest of accuracy. These competition experiments were somewhat complicated by the deoxidation side reaction. Initial determinations of the rate ratio trimethylethylene–isobutene gave a value of 5.43, which was too small. Thus, determination of this ratio by *inverse* addition of butoxide to haloacetone dissolved in mixed olefin gave 6.48. Presumably in the direct addition competition, adventitious isobutene, produced *via* butoxide deoxidation, contributes to the yield of III.[13] We also observed that trimethylethylene–isobutene rate ratios obtained from direct addition *triple* competitions, in which tetramethylethylene was present, were also in the 6.4–6.6 range. CFC competition data, determined by gc (calibrated thermal conductivity detector) on crude product mixtures, appear in Table I. Reproducibility within each case, and cross checks relating cases 1, 3, and 6, and cases 2, 4, and 5 are all satisfactory. Competition data newly determined for DCC appear in Table II. Table III is constructed, relating all data for each carbene to an isobutene standard.

TABLE I

COMPETITION OF VARIOUS OLEFIN PAIRS FOR CFC AT −10°

Case	Olefin 1	Olefin 2	k_1/k_2	Av dev_n[a]
1	*cis*-Butene	*trans*-Butene	1.37	0.03_2
2	Trimethylethylene	Isobutene	5.43[b]	0.11_3
			6.50[c]	0.05_3
3	Trimethylethylene	*cis*-Butene	47.7	0.07_2
4	Tetramethylethylene	Trimethylethylene	4.36	0.32_6
5	Tetramethylethylene	Isobutene	31.2	0.90_4
6	Trimethylethylene	*trans*-Butene	67.0	1.5_2
7	*cis*-Butene	1-Butene	15.6	0.45_2

[a] Average deviation of *n* experiments. [b] Direct addition. [c] Inverse addition and triple competition results. This value is considered the more accurate one and is used henceforth.

TABLE II

COMPETITION OF VARIOUS OLEFIN PAIRS FOR DCC AT −10°

Case	Olefin 1	Olefin 2	k_1/k_2	Av dev_n
1	*cis*-Butene	Isobutene	0.23	0.004_2
2	*trans*-Butene	Isobutene	0.15	0.000_2
3	1-Butene	*cis*-Butene	0.047	0.002_2

TABLE III

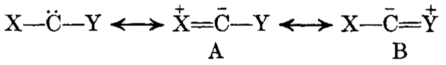
RATES OF CFC AND DCC ADDITION TO SELECTED ALKENES (RELATIVE TO ISOBUTENE) AT −10°

Olefin	CFC	DCC
Tetramethylethylene	31	6.5[a]
Trimethylethylene	6.5	2.8[a]
Iso-Butene	1.00	1.00
cis-Butene	0.14	0.23
trans-Butene	0.097	0.15
1-Butene	0.0087	0.011

[a] From reference 4c.

Discussion

Produced under comparable conditions, CFC appears more selective, in an electrophilic sense, than DCC. Over the set of alkenes employed, in which every simple substitution pattern is represented, the maximum rate ratio, tetramethylethylene/1-butene, is 3560 for CFC, but only 590 for DCC. Both carbenes may be pictured as adding *via* a transition state (TS) in which, relative to ground state, significant positive charge resides on olefinic carbon(s).[14,15] The greater selectivity of CFC presumably reflects a greater internal (ground state) stabilization, which leads to addition TS's with greater relative positive charge on olefinic carbon. Differences between olefins in their ability to tolerate such charge are thus more apparent during CFC addition. Hine has pointed out[3,5b] that, for singlet dihalocarbenes,[16] contributions from canonical forms A and B and hence stabilization of the carbene should increase in the order



$$\mathrm{X{-}\ddot{C}{-}Y} \longleftrightarrow \underset{\text{A}}{\mathrm{\overset{+}{X}{=}\overset{-}{C}{-}Y}} \longleftrightarrow \underset{\text{B}}{\mathrm{X{-}\overset{-}{C}{=}\overset{+}{Y}}}$$

I < Br < Cl < F. As we have observed,[2] the data are consistent with expectations based on this prediction.[17]

If logarithms of the CFC data are plotted against those of the DCC data (Table III), it can be learned if a proportionality of $\Delta\Delta F^{\neq}$ exists for the two sets of addition reactions. Similar correlations have previously been attempted by Doering (DCC *vs.* dibromo carbene),[4c] and by Closs (DCC *vs.* chlorocarbene).[6] Doering observed, "...scatter about a hypothetical line is so large that no slope can be determined.... relatively dibromocarbene reacts slower than dichlorocarbene, the greater the degree of [olefin] substitution. This falling off may indicate the operation of a steric factor." [4c] The correlation reported by Closs[6] is subject to revision because the stereoselectivities of the chlorocarbenoid were later found to have been reversed,[19] and because the chlorocarbenoid was prepared *via* lithium dichloromethide, and probably should not be compared with DCC from chloroform and potassium *t*-butoxide.[14,15,20]

We were encouraged by observation of linearity in a log–log relative-rate plot of our data for the more heavily substituted olefins, and also by our ability to generate both CFC and DCC under comparable conditions of temperature and generative base. The suggested log–log plot appears in Figure 1.

Only a qualitative linear correlation is obtained. In particular, good correlation exists over the three most reactive olefins or over the three least reactive olefins; a passable correlation exists over the whole set only if the 1-butene point is excepted.

Upon closer examination of the figure and of the data in Table III, it appears that the *selectivity of CFC rela-*

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[13] Other competition values, *e.g.*, tetramethylethylene–isobutene, were much less sensative to the inverse direct variation.

[14] Some evidence exists suggesting that carbenic species produced *via* trihalomethide–potassium ion pairs closely approximate actual divalent carbon species.

[15] See the brief discussion in R. A. Moss and R. Gerstl, *Tetrahedron*, **22**, 2637 (1966).

[16] CFC and DCC are believed to react as singlets under our conditions. Both are stereospecific in their additions to *cis*- and *trans*-butene, within the limits of analysis (1–2%).

[17] Physical data, revealing substantial double-bonded-halogen character, exist for CF_2. See, for example, J. P. Simons, *J. Chem. Soc.*, 5406 (1965). Available data indicate that, as expected, CF_2 is more discriminating than CFC in olefin addition; see R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965). Also see ref 18.

[18] R. A. Mitsch (private communication) and A. S. Rodgers inform us that a good correlation for DCC and CF_2 exists over five olefins of the present set. However, 1-butene was not investigated. Furthermore, *trans*-butene is more reactive than *cis*-butene toward CF_2, whereas the opposite is true for DCC. This may be related to the fact that the CF_2 was produced *via* photolysis of difluorodiazerene, but the DCC was produced as reported here.

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

[20] See the discussion in G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965). For other viewpoints, see D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965); G. Kobrich and H. R. Merkle, *Chem. Ber.*, **99**, 1782 (1966), and references therein.

tive to DCC falls off as less reactive olefins are employed as substrates. The ratio *trans*-butene/1-butene is 13.6 for DCC, but only 11.1 for CFC; for *cis*-butene/1-butene and *cis*-butene/*trans*-butene the respective rate ratios are 21.3 *vs.* 15.6 and 1.5 *vs.* 1.4. With reference to Figure 1, the slope of the line determined by the three most reactive olefins is 1.8, while the slope of a line defined by the three least reactive olefins is about 0.9. Thus there is a *selectivity reversal*, DCC becoming more discriminating than CFC with the less reactive olefins. Either CFC is more reactive toward the poorer olefins than expected on the basis of its behavior toward the more reactive olefins, or, on the same basis, DCC is less reactive toward the poorer olefins. We believe the latter interpretation to be the better.

The attempted correlation covers a large rate span. Application of the Hammond postulate suggests that the addition TS will be considerably tighter for 1-butene than, *e.g.*, isobutene. Differential steric requirements of CFC and DCC are expected to become more important as substrate reactivity decreases.[21,22] As DCC ought to be more sensitive to steric hindrance in a tight TS, its addition rate would be expected to decrease more sharply than that of CFC.

The contention that steric hindrance is large in additions of very selective carbenes to 1-butene receives some support from a consideration of CFC stereoselectivity. When apparent at all, carbene stereoselectivity is expressed in the substrate order *cis*-butene > 1-butene > trimethylethylene,[7,24,25] but for additions to these olefins of CFC, a carbene far more selective than any for which stereoselectivity data are yet available, *syn*-Cl/*anti*-Cl is 3.1, 1.5, 2.4. In addition to 1-butene, the *syn*-Cl mode is *less favorable* than expected. (*syn*-Cl refers to addition with Cl *syn* to the larger number of olefinic alkyl groups.) This appears to be a reflection of adverse steric effects.[26]

Finally, note that combining stereoselectivity and relative rate data for CFC and then plotting separate rates for *syn*-Cl and *anti*-Cl additions to the properly nonsymmetric olefins do not lead to better correlations (*cf.* square points, Figure 1). Indeed, over the set of data, excluding 1-butene, the best correlation is made *disregarding* CFC stereoselectivity.[18]

Experimental Section[27]

Reagents.—*sym*-Tetrachlorodifluoroacetone was purchased from Allied Chemical Corp. It, potassium *t*-butoxide (MSA), and chloroform (Matheson Coleman and Bell) were used without further purification. Olefins were rated 99% or better: tetramethylethylene (Phillips), trimethylethylene (Aldrich), *trans*-butene, *cis*-butene, isobutene, and 1-butene (Matheson). The first two were redistilled prior to use. *trans*-Butene was dried ($CaCl_2$).

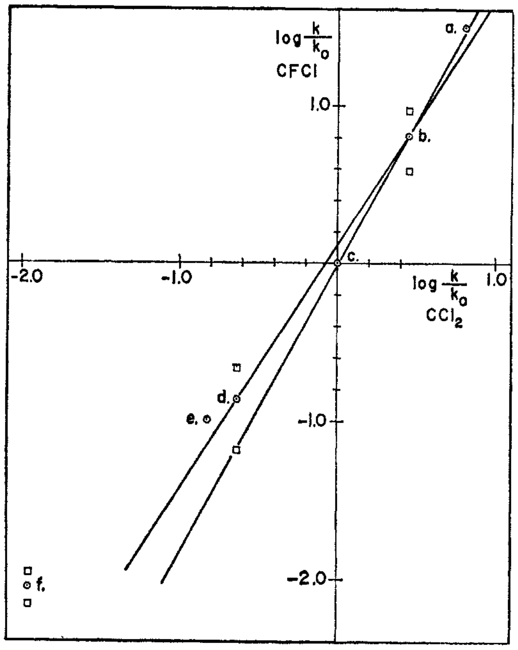

Figure 1.—Log rate of chlorofluorocarbene addition to olefin i, relative to isobutene (ordinate), *vs.* log rate of dichlorocarbene addition to olefin i, relative to isobutene (abscissa). Olefins are a, tetramethylethylene; b, trimethylethylene; c, isobutene; d, *cis*-butene; e, *trans*-butene; f, 1-butene. Two correlations are shown, one determined only by a, b, and c; the other determined by all points except f. The square points above and below b, d, and f represent relative rates of chlorofluorocarbene addition in the *syn*-Cl and *anti*-Cl modes (corrected by a statistical factor of 2).

Syntheses of Cyclopropanes.[28]—**1-Chloro-1-fluoro-2-ethylcyclopropane (VIa and b).**—A three-neck, 100-ml flask was equipped with a low-temperature thermometer, Dry Ice condenser, magnetic stirring bar, and an adapter connected by Gooch tubing to a reservior containing 12 g (0.11 mole) of potassium *t*-butoxide. In the flask were placed 25 g (0.45 mole) 1-butene and 14 g (0.12 equiv) of tetrachlorodifluoroacetone. These reagents were stirred magnetically and maintained at −10°. The butoxide was added slowly and in very small amounts over a 2-hr period. After 1 additional hr of stirring at −10°, the mixture was diluted with water and washed several times with additional water. The organic phase was separated and dried over $MgSO_4$. After filtration, the product was distilled at 60 torr, collecting all distillate boiling below 41° in a Dry Ice cooled receiver. There was obtained 2.7 g of clear liquid, shown by vpc to be 56% VI. Yield based on haloacetone was 10–11%. Pure VI was obtained by preparative gc on a 20-ft × $^3/_8$ in. 20% SF-96 column (65°). Proton and fluorine nmr spectra are described above; infrared showed 3.40, 6.95, 7.90, 8.05, 8.60, 8.70, 9.80, 10.65, 11.80 μ (neat).[29]

Anal. Calcd for C_5H_8ClF: C, 48.99; H, 6.58; Cl, 28.93. Found: C, 49.08; H, 6.61; Cl, 31.61.[30]

1,1-Dichloro-2,2-dimethylcyclopropane.[4c]—A 100-ml, three-neck flask fitted with an addition funnel, low-temperature thermometer, stirring bar, and gas inlet was dried and filled with nitrogen. After cooling, 18.9 g (0.34 mole) of isobutene was added, followed by 2.0 g (0.018 mole) of potassium *t*-butoxide. At −10°, 3 g (0.025 mole) of chloroform was added dropwise

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(21) In the "looser" TS's corresponding to the more reactive substrates, differential steric effects, noted by Doering for DCC and dibromocarbene,[4c] do not seem to hinder comparison of DCC and the smaller CFC. As expected, graphic comparison of DCC and phenylbromocarbene[14,15] gave results very similar to Doering's. As an essentially parallel argument, see also H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4997 (1961).

(22) $\Delta\Delta S^{\ddagger}$ terms will therefore make varying contributions to $\Delta\Delta F^{\ddagger}$ terms over the two sets of data. Failure to obtain a linear-free-energy relationship under such conditions is expected and essentially general.[23]

(23) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(24) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960); see ref 19.

(25) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

(26) Stereoselectivity seems to depend on a delicate balance of carbene-substituent polarizability and steric hindrance. Up to a point, increasing the tightness of a TS ought to enhance energy-lowering substrate–substituent electrostatic interactions for polarizable carbene substituents. Further tightening of the TS must make adverse steric factors dominant. An over-all decrease in addition rate often parallels increasing steric control of stereoselectivity; see R. A. Moss, *ibid.*, **30**, 3261 (1965).

(27) Boiling points are uncorrected. Infrared spectra were measured on Beckman IR-5A or Perkin-Elmer 137 instruments. Nmr spectra were determined as dilute CCl_4 solutions against internal TMS on Varian A-60 equipment (proton) or as dilute CCl_3F solutions on Varian A-56/60 equipment (F^{19}).

(28) See ref 2 for syntheses of compounds I–V. Direct addition synthesis of VI was carried out similarly.

(29) Representative peaks are reported.

(30) Best of two analyses. Chlorine seems generally to analyze high in chlorofluorocyclopropanes.[2]

with stirring, over 30 min. After an additional 30 min, the mixture was diluted with 5 ml of pentane and washed twice with 20-ml portions of water, and the organic phase was separated and dried over $CaCl_2$. The product was decanted, solvent was stripped, and the residue (1.5 g,) was submitted to gc on the previously described SF-96 column (82°). Other than chloroform the only high-boiling material was the desired cyclopropane; infrared showed 3.45, 6.87, 6.99, 7.28, 8.95, 9.07, 9.37, 9.62, 9.95, 10.34 μ (CCl_4); nmr[31] gave 1.37 (singlet, methyls), 1.21 (singlet, ring); integral ratio was 3:1. Other dichlorocyclopropanes were similarly prepared.

1,1-Dichloro-*cis*-2,3-dimethylcyclopropane.—Infrared gave 3.43, 6.87, 7.22, 8.14, 8.77, 10.23, 10.50 μ (CCl_4); nmr showed a multiplet, 1.80 to 1.23 disappearing beneath a larger absorption with sharp peaks at 1.18 and 1.07.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.34; H, 5.87; Cl, 50.82.

1,1-Dichloro-*trans*-2,3-dimethylcyclopropane.—Infrared gave 3.43, 6.91, 7.15, 8.24, 8.76, 9.23, 9.79, 10.40 μ (CCl_4); nmr showed peaks at 1.30 and 1.24 (major signal) superimposed on a multiplet extending from 1.42 to 0.87.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.40; H, 5.76; Cl, 50.95.

1,1-Dichloro-2-ethylcyclopropane.—Infrared showed 3.40, 6.87, 7.02, 7.26, 8.17, 8.57, 8.89, 9.15, 9.64, 9.95 μ (CCl_4); nmr gave a multiplet from 1.80 to 1.28, with maximum at 1.53, running into a crude triplet centered at 1.11, and superimposed on other absorptions which tail to 0.85.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.00. Found: C, 43.34; H, 5.85; Cl, 50.85.[32]

Reaction of Chloroform and Potassium *t*-Butoxide in Pentane.—In an experiment analogous to the syntheses described above, 2.0 g of potassium *t*-butoxide was treated with 3.0 g of chloroform in 20 ml of pentane, at −10°. After work-up and stripping of solvents, there remained 180 mg of yellow oil, possessing nmr absorptions identical with those of 1,1-dichloro-2,2-dimethylcyclopropane. It was not determined whether tetrachloroethene was also present in this oil. A similar experiment with tetrachlorodifluoroacetone afforded a product mixture in which the major low-boiling component was identified as III, by comparison of gc retention time and infrared spectrum with those of an authentic sample.

Competition Experiments.—All competition experiments (except for inverse addition runs) were performed under identical conditions. Apparatus was similar to that used in synthetic runs. Temperature was maintained at *ca.* −10°. An excess of carbene precursor over *t*-butoxide was used; a tenfold excess of each olefin was minimal. Reaction products were not distilled, but immediately analyzed by gc. For the CFC adducts, we used an F & M Model 500 instrument, fitted with an 8 ft × 0.25 in. DC-550 silicone oil column, with He flow of 180 ml/min, a column temperature of 65°, and an injection temperature of 140°.

Analysis of the DCC competitions was carried out on the SF-96 column, with a He flow 300 ml/min, a column temperature of 80°, and an injection temperature of 193°. An Aerograph A-90-P instrument was used. Detectors were calibrated with pure adducts in all cases.

From the product ratios determined by gc, relative rates were calculated from the standard expression $k_1/k_2 = (P_1/P_2)(O_2/O_1)$, where the P_i quotient represents the cyclopropane product ratio and the O_i quotient represents the mole ratio of starting olefins. Results appear in Tables I and II.

Registry No.—VIa, 13144-06-4; VIb, 13144-07-5; fluorochlorocarbene, 1691-88-9; dichlorocarbene, 1605-72-7; 1,1-dichloro-2,2-dimethylcyclopropane, 694-16-6; 1,1-dichloro-*cis*-2,3-dimethylcyclopropane, 1120-67-8; 1,1-dichloro-*trans*-2,3-dimethylcyclopropane, 1120-68-9; 1,1-dichloro-2-ethylcyclopropane, 13144-11-1.

Acknowledgments.—Support by the National Institutes of Health (GM-13585) and by the National Science Foundation (GP-4857) is gratefully acknowledged. We also wish to thank Mr. Ernest Anderson of The Bell Telephone Laboratories, Murray Hill, N. J., who determined the F^{19} nmr spectra.

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(31) Reported in parts per million (ppm) downfield from internal tetramethylsilane (TMS).

(32) As discussed above, this prepration also yielded some 1,1-dichloro-2,2-dimethylcyclopropane.

Some Chemistry of Compounds Related to [2.2]Metacyclophane[1,2]

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Received December 22, 1966

5,13-Dimethyl[2.2]metacyclophane has been prepared, some of its reactions have been studied, and the mechanisms of electrophilic substitution in [2.2]metacyclophanes are discussed. 4,5,9,10-Tetrahydropyrene derivatives substituted at the 1 and 2 positions have been synthesized, and the nmr spectra of various representatives of these structural types have been analyzed.

The chemistry of bridged aromatic compounds has been studied in considerable detail,[3] and has been richly rewarding. One of the first compounds of this general type to be prepared was [2.2]metacyclophane,[4] and the compound has been examined from time to time during the ensuing period.[5]

[2.2]Metacyclophane undergoes a few types of electrophilic aromatic substitution reactions, but such reactions do not lead to derivatives of the cyclophane, but rather to tetrahydropyrene derivatives (such as the formation of II as indicated in Scheme I). The formation of II from I might, *a priori*, proceed with the attack by the nitronium ion either preceding, following, or concurrent with the bridging of the two aromatic rings. Earlier[1] we presented arguments which indicated that it was most unlikely that the bridging of the aromatic rings followed the aromatic substitution, and which showed that the position of substitution and the rate of reaction were consistent with the attack by the nitronium ion on one ring, concurrent with the attack of the substituted ring on the other aromatic ring (path 2 in Scheme I).

Although tetrahydropyrene underwent substitution to give the same product (II) as that obtained from metacyclophane, the possibility that the reaction occurred by path 1 (in which the aromatic rings bridged to form tetrahydropyrene as a distinct intermediate) was not seriously entertained earlier, because the yield

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(1) For the previous paper in this series, see N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961).

(2) This research was supported by research grant GP-4290 from the National Science Foundation.

(3) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

(4) M. Pellegrin, *Rec. Trav. Chim.*, **18**, 457 (1899).

(5) Most of the pertinent literature is summarized in ref 1 and 3. Additional papers of interest include that by P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 6893 (1965), and others referred to below.