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STEREOSELECTIVITY OF CARBENE INTERMEDIATES—III
FLUOROCHLOROCARBENE[1]

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Abstract—Fluorochlorocarbene, produced *via* the action of potassium-t-butoxide on *sym*-tetrachlorodifluoroacetone, has been added to tetramethylethylene, trimethylethylene, *iso*-butene, *cis*-butene, and *trans*-butene. 1-chloro-1-fluorocyclopropanes were formed in fair yields. Rates of carbene addition to the olefins, relative to iso-butene, were 31, 6·5, 1·0, 0·14 and 0·097, respectively. Structures were assigned to the isomeric cyclopropanes (formed from trimethylethylene and *cis*-butene) by F^{19} NMR. In both cases, fluorochlorocarbene added so as to produce an excess of that isomer in which chlorine was *syn* to the largest number of Me groups. Isomer ratios were 2·35 (trimethylethylene) and 3·08 (*cis*-butene). Additions to *cis* and *trans*-butene were greater than 99% stereospecific.

FLUOROCHLOROCARBENE (FCC) is a known species. Kinetic studies of the basic decomposition of dichlorofluoromethane,[2] and of dichlorofluoroacetic acid,[3] suggest its existence. Interceptions of FCC have been reported in isopropoxide ion decomposition of dichlorofluoromethane;[4] and also in decomposition of the same haloform by potassium-t-butoxide in the presence of diazo compounds. (The latter process affords 1-chloro-1-fluoro olefins.)[5]

Addition of FCC to olefins has also been observed. Basic decomposition of dichlorofluoromethane[6] (or of methyl dichlorofluoroacetate[7]) in cyclohexene yields 7-chloro-7-fluoronorcarane. This compound can also be synthesized when FCC is generated *via* the action of potassium t-butoxide on *sym*-tetrachlorodifluoroacetone;[7,8] a method which appears to be both gentle and general for preparation of 1-chloro-1-fluorocyclopropanes. It has recently been extended to synthesis of 1-chloro-1-fluoro-2,2-dimethylcyclopropane (from isobutene).[9]

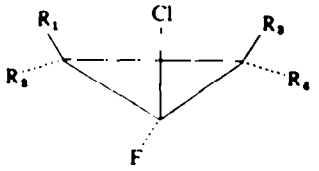
Our interest in carbene stereoselectivity[1,10] led us to examine more closely the addition of FCC to olefins. The apparent importance of both steric hindrance and substituent polarizability (in carbene stereoselectivity) make FCC a particularly inviting object of study; for here, the larger halogen is also the more polarizable; the directive effects will compete, and perhaps some idea of their relative importance will emerge.

[1] Paper II: R. A. Moss and R. Gerstl, *Tetrahedron* **22**, 2637 (1966).
[2] J. Hine and N. W. Burske, *J. Am. Chem. Soc.* **78**, 3337 (1956). See also: J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *Ibid.* **79**, 1406 (1957); J. Hine and S. J. Ehrenson, *Ibid.* **80**, 824 (1958).
[3] J. Hine and D. C. Duffey, *J. Am. Chem. Soc.* **81**, 1129 (1959).
[4] J. Hine, A. D. Ketley and K. Tanabe, *J. Am. Chem. Soc.* **82**, 1398 (1960).
[5] H. Reimlinger, *Chem. Ber.* **97**, 339 (1964), and Refs therein.
[6] W. E. Parham and R. R. Twelves, *J. Org. Chem.* **22**, 730 (1957).
[7] R. A. Moore and R. Levine, *J. Org. Chem.* **29**, 1883 (1964).
[8] B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963).
[9] J. P. Oliver, U. V. Rao and M. T. Emerson, *Tetrahedron Letters* No. 46, 3419 (1964).
[10] R. A. Moss, *J. Org. Chem.* **30**, 3261 (1965).

Long ago, Hine[2] pointed out that, among halogens, fluorine should be most efficient at resonance stabilization of a singlet carbene. A second intent of our study was the comparison of olefin-addition selectivities of dichlorocarbene and FCC, in order to demonstrate this effect.

RESULTS

FCC, generated *via* the action of potassium t-butoxide on *sym*-tetrachlorodifluoroacetone,[8] was added to tetramethylethylene, trimethylethylene, isobutene, *cis*-butene and *trans*-butene. Adducts I–V were isolated from crude product by distillation and/or preparative VPC. Structures were assigned to products by analogy to previous



I: $R_1 = R_2 = R_3 = R_4 = Me$
IIa: $R_1 = R_2 = R_3 = Me$, $R_4 = H$.
IIb: $R_1 = R_3 = R_4 = Me$, $R_2 = H$.
III: $R_1 = R_2 = Me$, $R_3 = R_4 = H$.
IVa: $R_1 = R_3 = Me$, $R_2 = R_4 = H$.
IVb: $R_1 = R_2 = H$, $R_3 = R_4 = Me$
V: $R_1 = R_4 = Me$, $R_2 = R_3 = H$

results,[8,9] by elemental analysis, and by spectroscopic techniques (IR, H NMR, and F^{19} NMR spectroscopy).

Thus, the newly prepared cyclopropanes gave satisfactory C, H, and Cl analyses. In the IR, all cyclopropanes displayed intense doublets in the 8·5–9·5 μ region characteristic of C—F bonds.[9,11] The spectrum of III contained all reported bands.[9]

NMR spectra. The proton NMR spectra, which are detailed in the Experimental, exhibited varying degrees of complexity. Of great significance was the total absence of vinylic hydrogen, supporting the cyclopropane structures. In all cases, methyl protons and ring protons were clearly observable. Two points require emphasis. Firstly, the products of FCC with *cis*-butene and trimethylethylene could not be separated into their isomeric components (IVa, IVb, and IIa, IIb). The observed spectra are composites, and hence more complex. Secondly, fluorine often couples with *all* protons in methylfluorocyclopropanes.[9] For example, in the spectrum of I, a large singlet is observed 68 c/s downfield from internal TMS, and a smaller singlet is observed at 66 c/s.[12] Since the singlets are not of equal intensity, they do not arise from two pairs of Me groups, with a differential chemical shift of 2 c/s. Rather, we suggest that one pair of Me groups absorbs at 68 c/s, while the second pair, absorbing at 67 c/s, couples to fluorine with $J = 2$ c/s. This coupling of fluorine to 6 equivalent protons should produce a septet in the F^{19} spectrum. Further small (ca. 0·5 c/s) coupling to the other Me protons leads instead to a broad, unresolved envelope for the F^{19} signal (see below). Other proton spectra are more complex, but all are qualitatively consistent with assigned structure.

[11] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* pp. 328 ff. Wiley New York (1958).
[12] A Varian A-60 instrument was used. All proton NMR's were measured as dilute solutions in CCl_4 containing 5% TMS.

The F^{19} spectra were of considerable value. Compounds I, III, and V possessed signals at the positions indicated in Table 1. The unresolved mixtures, IIa, IIb and IVa, IVb displayed two F^{19} signals. Structures corresponding to the components of these mixtures were assigned on the basis of signal character. Evidence has accumulated which suggests that the dependence of vicinal fluorine-proton coupling magnitude

TABLE 1. F^{19} NMR SIGNALS[a]

Adduct	δ[b]	Signal character	WHH[c]	WB[d]
IVb	9334 c/s	envelope	7 c/s	16 c/s
IIb	8745	envelope	8	18
I	8377	envelope	8	20
V	8265	multiplet	—	42
III	8038	multiplet	—	40
IIa	7834	multiplet	—	42
IVa	7164	triplet of multiplets, $J \simeq 18$	—	50

[a] Measured at 56·4 Mc. as solutions in CCl_4 with added CCl_3F or as solutions in CCl_3F. Resolution was ca. 1–2 c/s. [b] Chemical shift in c/s upfield from CCl_3F. For broad multiplets, the approximate center of gravity is given. [c] Width at half-height. [d] Width across base of signal.

on dihedral angle is essentially of the Karplus type.[13] Particularly instructive examples are several difluoroindanes and difluoroacenapthanes, in which *cis* vicinal H—F coupling is usually observed to be considerably stronger than *trans* vicinal H—F coupling.[13a] The F^{19} signals of Table 1 clearly separate into two groups; broadened singlets with half-height width of 7–8 c/s and base width of 20 c/s or less, and complex multiplets with base width of 40 c/s or more. We conclude that a signal of base width 40 c/s clearly indicates the presence of *cis* vicinal H—F coupling. Signals of base width 20 c/s indicate the absence of such coupling. (They are consistent with the presence of *trans* vicinal coupling.) The signals observed for the IIa, IIb and IVa, IVb mixtures can thus be assigned as in Table 1. Indeed, the major coupling is apparent in IVa, 18 c/s, and is of reasonable magnitude for the *cis* vicinal H—F coupling.[13a]

There appears to be an independent method of assigning configuration to the isomers. It is known that cyclopropyl protons are shielded by *cis* Me groups and deshielded by *trans* Me groups.[14] The observation that axial protons occur at higher field than equitorial protons in cyclohexane,[15] constitutes a more generally known example of the same phenomenon. These differential shieldings may be explained by reference to the anisotropic properties of the C—C single bond. It seems reasonable to expect that a similar shielding effect of *cis* Me groups and deshielding effect of *trans* Me groups should be exerted on the fluorine resonance of fluorocyclopropanes.

[13a] R. F. Merritt and F. A. Johnson, *J. Org. Chem.* **31**, 1859 (1966); [b] J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.* **88**, 2791 (1966); [c] R. F. Merritt and T. E. Stevens, *Ibid.* **88**, 1822 (1966); [d] L. D. Hall and J. F. Manville, *Chem. & Ind.* 991 (1965).

[14] For an example, see Ref 10.

[15] See L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* pp. 115 ff. Pergamon Press, New York (1959).

Support for this belief is obtained from studying models of 1-fluoro-2-methylcyclopropanes. Here, in terms of Jackman's discussion,[15] θ is ca. 67° for a *cis* Me group and ca. 30° for a *trans* Me group. (θ is the acute angle between the C—CH_3 bond and the line produced by connecting the midpoint of that bond with the fluorine nucleus. Values of θ greater than ca. 55° predict shielding by C–Me. Values of θ less than ca. 55° predict deshielding by C–Me.)

The magnitude of these differential shielding effects is expected to be far greater in F^{19} NMR than in H^1 NMR.[13b] Recently, Eliel has reported that axial fluorine in various cyclohexane derivatives invariably occurs at much higher field than equitorial fluorine.[16]

Examination of data in Table 1 clearly indicates that addition of a *cis* Me group and/or removal of a *trans* Me group lead to an upfield shift of the F^{19} signal. Conversely, we observe that addition of a *trans* Me group and/or removal of a *cis* Me group lead to a downfield shift of the F^{19} signal. As would be predicted, the chemical shifts of IVa and IVb are the extrema of the series.

These considerations fully support the configurational assignments reached previously. Moreover, they suggest a useful method for assigning configuration in related compounds. Clearly, however, care must be exercised. The great sensitivity of the F^{19} probe means that small variations in distances and bond angles will be greatly magnified in the chemical shifts. For example, III and V yield a differential shift of 200 c/s, even though both compounds have one *cis* and one *trans* Me group. While such sensitivity makes difficult quantitative understanding, it does not, we believe, impair structural differentiation of two isomers when both are in hand.

Stereospecificity. VPC enabled clean separation of IVa, IVb mixture from V. Pure adducts did not crack under these conditions. No IV was observed in the crude reaction product of FCC and *trans*-butene. The product from *cis*-butene and FCC contained at most 0·3% of V, relative to the IVa, IVb formed. The stereospecificity of the addition was greater than 99%.

Stereoselectivity. Although isomer pairs IIa, IIb and IVa, IVb were not separable by VPC, isomer ratios could be determined by integration of the F^{19} signals. For reaction of FCC and trimethylethylene, IIa/IIb, determined on crude product was $2{\cdot}35 \pm 0{\cdot}05_3$. In the crude product obtained from FCC and *cis*-butene, IVa and IVb were too dilute to permit accurate determination. The adducts were purified by preparative VPC. The F^{19} spectrum of the purified product gave IVa/IVb as $3{\cdot}08 \pm 0{\cdot}08_3$. Since the cyclopropanes were stable to VPC conditions, only a differential efficiency of collection from the VPC effluent could have invalidated this ratio. That such is not the case is suggested by the observation that IIa/IIb is very similar whether determined on crude or trapped product (2·28 *vs.* 2·35). With both olefins then, FCC added so as to produce an excess of that isomer in which chlorine is *syn* to the larger number of Me groups.

Relative rate experiments. Rechromatography of cyclopropanes resulted in no observable cracking. The thermal conductivity detector was calibrated for relative responses.[17] All adducts could be separated on a silicone oil column; and superimposition of VPC traces obtained from crude products of FCC and individual olefins

[16] E. L. Eliel and R. J. Martin, unpublished. We thank Professor Eliel for preprints of his MSS. Also, E. L. Eliel, *Symposium on Conformational Analysis, 152nd Meeting of the American Chemical Society.* New York, September 13 (1966).

demonstrated that by-products would not contribute to cyclopropanes in various mixed olefin runs. Competition experiments, i.e., experiments in which a mixture of two olefins, of known composition, was employed as carbene substrate, were then carried out. An excess of tetrachlorodifluoroacetone (relative to t-butoxide) and at least a ten-fold excess of each olefin were maintained. Temperature varied between $-15°$ and $-10°$. VPC analysis of crude product mixtures afforded the relative addition rates collected in Table 2.

TABLE 2. COMPETITION OF VARIOUS OLEFIN PAIRS FOR FCC

Case	Olefin 1/Olefin 2	k_1/k_2
1	*cis*-Butene/*trans*-butene	1·37
2	Trimethylethylene/isobutene	6·50
3	Trimethylethylene/*cis*-butene	47·7
4	Tetramethylethylene/trimethylethylene	4·36
5	Tetramethylethylene/isobutene	31·2
6	Trimethylethylene/*trans*-butene	67·0

The data can be cross-checked. Thus, from cases 2 and 5, a value of 4·80 was predicted for case 4; the deviation was ca. 10%. Similarly from cases 1 and 6, a value of 48·9 was predicted for case 3; the deviation was ca. 3%. These cross-checks suggest that errors in the data are well below 10%. Random duplicate runs showed good reproducibility, e.g., % a.d. for cases 1 and 3 were 2·2% and 1·5% respectively.

DISCUSSION

The similarity of generative procedures for dichlorocarbene,[18] dibromocarbene,[19] phenylchlorocarbene,[20] phenylbromocarbene[1] and FCC, probably validates comparison of their selectivities. Recent evidence suggesting "free" dichlorocarbene as intermediate in the basic decomposition of chloroform,[21,22] probably has similar implications for the related species enumerated above.

Previous discussions of carbene stereoselectivity have sought to explain why, in addition of monosubstituted carbenes and carbenoids to certain olefins, e.g. *cis*-butene, there is often observed a kinetic selectivity favoring formation of the most hindered product.[10,23–26] Generally, explanations have postulated a delicate balance of repulsive forces (steric) operating between carbene substituent and olefinic alkyl groups; and attractive forces (electrostatic) operating between the same groups. Attractive electrostatic forces are considered of import because, relative to ground state, the olefinic alkyl groups become somewhat positive during addition of the (electrophilic) carbene, and can thus more favorably interact with outer-orbital electrons carried

[17] Details of VPC experiments will be found in the Experimental section.
[18] W. v. E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.* **80**, 5274 (1958).
[19] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956).
[20] G. L. Closs and J. J. Coyle, *J. Org. Chem.* **31**, 2759 (1966).
[21] W. J. le Noble, *J. Am. Chem. Soc.* **87**, 2434 (1965).
[22] D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.* **86**, 2730 (1964).
[23] U. Schöllkopf, G. J. Lehmann, J. Paust and H. -D. Härtl, *Chem. Ber.* **97**, 1527 (1964), and Refs therein.
[24] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.* **86**, 4042 (1964).
[25] G. L. Closs, R. A. Moss and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).
[26] For drawings of the postulated transition states, consult Refs 10 and 24.

by the carbene substituent destined to become *syn* to them in the final product.[26] Polarizability of the carbene substituents' outer electrons is therefore expected to be of great importance in determining the stereoselectivity of addition.

Recently, two unsymmetrically disubstituted carbenes have been studied, phenylchlorocarbene[20] and phenylbromocarbene.[1] Comparison of addition reactions with *cis*-butene and trimethylethylene showed that both carbenes yielded an excess of that cyclopropane with halogen *syn* to the larger number of Me groups. The halogen-*syn* tendency was greater in the chloro case. A tentative interpretation was advanced: bromine is more polarizable than chlorine and should exhibit greater attractive electrostatic interactions with olefinic alkyl substituents; however this factor is offset by increased steric repulsion, bromine also being larger than chlorine.

A choice case for comparison of halocarbene stereoselectivities is FCC, in which a large differential polarizability of carbene substituents is available in a single carbene. The clear preference observed for *syn* chlorine addition can be interpreted

Table 3. Relative addition rates

Olefin	Cl—C̈—Cl[a]	Cl—C̈—F[b]
Tetramethylethylene	6·5	31
Trimethylethylene	2·8	6·5
Isobutene	1·0	1·0
cis-Butene	0·19[c]	0·14
trans-Butene	0·26[d]	0·097

[a] Calculated from data in reference 18. [b] Calculated from data in Table 1. [c] *cis*-Pentene. [d] *trans*-Pentene.

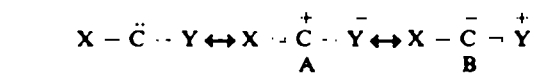
to mean that, in FCC, the greater polarizability of chlorine, relative to fluorine, outweighs the adverse size differential. The very selective nature of FCC additions (see below), with steady increase in rate of addition through tetrasubstituted olefins (as is observed with dichlorocarbene,[18] but not with dibromocarbene[19]) also attests to the relative unimportance of the steric factor in FCC additions. We note that the dominance of chlorine over fluorine in *syn* stereoselectivity parallels Schöllkopf's reports that phenoxycarbenoid addition to *cis* olefins generally results in a dominant *anti* stereoselectivity (for phenoxy), but that phenylthio and phenylselenocarbenoids exhibit *syn* stereoselectivity.[23,27] The trends observed for group VI substituted carbenic species thus parallel the trends observed for group VII carbenic species.

FCC is very discriminating in its addition reactions. In Table 3, relative addition rates of FCC are compared with those of dichlorocarbene.[18] Both species were generated under comparable conditions. Clearly, FCC is the more selective species. A factor of 320 separates its extreme rates. The comparable factor for dichlorocarbene is 34·2.[28] In accord with Doering,[18] we take the greater discriminating ability of FCC

[27] See U. Schöllkopf and J. Paust, *Chem. Ber.* **98**, 2221 (1965); U. Schöllkopf and H. Küppers, *Tetrahedron Letters* No. 2, 105 (1963); U. Schöllkopf and G. J. Lehmann, *Ibid.* No. 4, 165 (1962).

[28] A log–log plot of the data is linear with exception of the *cis*-butene point. It is possible that the reported value for dichlorocarbene is too low. In general, with *α*-elimination-produced carbenes, *cis* olefins react more rapidly than their *trans* isomers. Of course, part of the problem may be that butene points for FCC are being plotted against pentene points for dichlorocarbene. However the change from a methyl to an ethyl substituent in the substrate would not be expected to result in a large rate change.[19] We intend to investigate the cases in question.

to reflect a greater "internal stabilization." Hine pointed out some time ago[29] that, in singlet dihalocarbenes,[30] contributions from canonical forms A and B, and hence stabilization of the carbene, would increase in the order I < Br < Cl < F.



The present findings are consistent with these ideas. Clearly, difluorocarbene should be the most discriminating dihalocarbene. Though, apparently, quantitative data are scarce, it has been reported that difluorocarbene generated from difluorodiazirine, reacts 12·8 times faster with isobutene than with *cis*-butene.[31] The comparable datum for FCC is 7·1; and for dichlorocarbene, 5·3.[18]

EXPERIMENTAL[32]

Reagents. *Sym*-tetrachlorodifluoroacetone was purchased from Allied Chemical Corp. It and potassium t-butoxide (MSA) were used without further purification. Olefins were all rated 99% or better: tetramethylethylene (Phillips), trimethylethylene (Aldrich), *trans*-butene, *cis*-butene, and isobutene (Matheson). The first two were redistilled prior to use.

1-*Chloro*-1-*fluorocyclopropanes*

1-*Chloro*-1-*fluoro*-2,2,3,3-*tetramethylcyclopropane* (I). In a 3-neck, 100 ml flask, equipped with low temp thermometer, dropping funnel, Dry-Ice condenser (with N inlet) and magnetic stirring bar, there were placed 5·7 g (0·05 moles) potassium t-butoxide and 17 g (0·2 moles) tetramethylethylene. The stirred slurry was cooled to −10° and 6·9 g (0·06 equiv) tetrachlorodifluoroacetone were slowly added, temp being maintained at −5° to −10°. After addition, stirring was continued for 2 hr at −10°. The reaction mixture was diluted with water, then warmed to room temp. The organic layer was washed 5 times with 30 ml portions water, then dried over $MgSO_4$. Excess olefin was stripped. Product was distilled at 55–60°/60 torr, yield of I was 60%. [Distilled product was *ca.* 90% pure (VPC) and could be further purified by preparative VPC (condition B).] VPC: Retention times: condition A, 33 min; condition B, 16·5 min. IR: 3·33, 3·40, 8·81, 9·10, 9·66, 10·27, 10·98, 12·67 μ. NMR: The proton NMR is described above. (Found: C, 55·78; H, 7·96; Cl, 24·00. Calc. for $C_7H_{11}ClF$: C, 55·81; H, 8·05; Cl, 23·53%.)[33]

Adducts IIa, IIb. Prepared as described for I. Product was isolated by distillation, 60°/130 torr, in 60% yield. VPC: Retention times: condition A, 18 min; condition B, 10 min. IR: 3·39, 8·53, 8·84, 8·95, 9·10, 9·27, 10·04, 11·15 μ.[34] NMR: 2 lines at 74 and 72 c/s (downfield from internal TMS); a group of lines (3 and others unresolved) at 64, 62, 61 c/s. A broad, weak multiplet is spread under the base of both systems. The approximate integral of the higher field to lower field system is 2·0. Tentative assignments are: highfield system, *gem*-dimethyl groups; low field system, isolated Me groups; multiplet, ring protons. (Found: C, 52·86; H, 7·42; Cl, 26·18. Calc. for $C_6H_{10}ClF$: C, 52·75; H, 7·39; Cl, 25·95%.)

[29] See J. Hine, *Divalent Carbon* Chap 3 and Refs therein. The Ronald Press, New York (1964); particularly J. Hine and S. J. Ehrenson, *J. Am. Chem. Soc.* **80**, 824 (1958).

[30] In agreement with the implications of Hines's discussions,[29] and with the highly stereospecific and discriminant nature of FCC addition reactions, we believe that singlet FCC is being observed.

[31] R. A. Mitsch, *J. Am. Chem. Soc.* **87**, 758 (1965).

[32] Bps are uncorrected. IR spectra were measured as neat films on a Beckman IR-5A instrument. VPC was carried out on an F & M model 500 instrument fitted with an 8 ft, ¼ inch, DC-550 silicone oil column; He flow 180 ml/min, column temp 65°, inj. temp 140° (condition A); or, on an Aerograph model A-700 instrument fitted with a 20 ft, ⅜ inch, 20% SF-96 column, He flow 300 ml/min, column temp 95°, inj. temp 140° (condition B). For NMR conditions, see Ref 12 and Table 1.

[33] Microanalyses by Micro-Tech Laboratories, Skokie, Illinois.

[34] Here, as in all IR descriptions, a number of intense bands are arbitrarily selected. Numerous weaker bands and shoulders are not enumerated.

Adduct III. Prepared as described in Ref 9.

Adducts IVa, IVb. Prepared as described for I, except that pentane was added as a diluent at the end of the reaction period and before warming to room temp. Product was isolated by distillation, 66–70°, in 35% yield. VPC: Retention times: condition A, 13 min; condition B, 7·5 min. IR: 3·37, 3·40, 8·63, 8·96, 9·14, 9·35, 10·28, 11·58, 13·46 μ. NMR: A complex multiplet extending from 110 c/s upfield until it disappears beneath an intense system of overlapping absorptions with sharp maxima at 65 and 63 c/s. (Found: C, 49·12; H, 6·56; Cl, 29·09. Calc. for C_5H_6ClF: C, 48·99; H, 6·58; Cl, 28·93.)

Adduct V. Prepared as described for IV. Product was isolated by distillation at 66–67° in 30% yield. VPC: Retention times: condition A, 10 min; condition B, 6·5 min. IR: 3·37, 8·60, 8·84, 9·58, 10·10, 10·36, 11·03, 11·65, 12·76 μ. NMR: A system of overlapping bonds with a clear peak at 71 c/s. A (weaker) multiplet, beginning under this system and extending upfield to 43 c/s. (Found: C, 49·23; H, 6·75; Cl, 29·06. Calc. for C_5H_6ClF: C, 48·99; H, 6·58; Cl, 28·93%.)

Competition experiments

All competition experiments were run under identical conditions. Apparatus was identical to that employed in synthetic runs. Temp was maintained at $-12 \pm 2°$. An excess of haloacetone over t-butoxide was used; a ten-fold excess of each olefin was minimal. Reaction products were not distilled, but immediately analyzed by VPC, condition A. The thermal conductivity detector was calibrated with pure adduct mixtures in order to determine relative molar response. Relative to I, responses were: IIa, IIb, 0·90; III, 1·02; IV, 0·80; V, 0·82. The high value for III stood up to re-checking and cross-checking. From product ratios determined by VPC, relative rates were calculated from the standard expression $k_1/k_2 = P_1/P_2 \times O_2/O_1$, 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 Table 2.

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