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Formation of Both CCl and CF in the Reaction of Atomic Carbon with Chlorofluorocarbons

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Although the reaction of atomic carbon with CCl_4 is reported to yield products of insertion into C–Cl bonds,[1] the reaction of carbon atoms with CF_4 generates CF with no sign of insertion products.[2] We now report that reaction of atomic carbon with chlorofluoromethanes results in the formation of the monovalent carbon intermediates CCl and CF (eq 1) in yields dictated by the

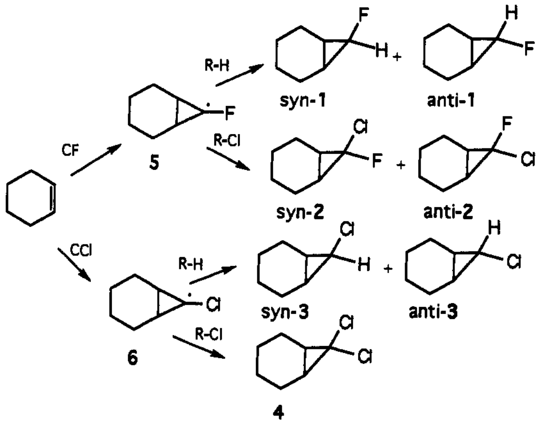
$$CF_{x-1}Cl_y + C\text{–}F \xleftarrow{C} CF_xCl_y \xrightarrow{C} C\text{–}Cl + CF_xCl_{y-1} \quad (1)$$

relative exothermicities of the abstraction reactions. These methylidyne intermediates are shown both to react with alkenes to give halocyclopropyl radicals and to abstract chlorine to give dihalocarbenes.

Reactions were carried out by cocondensing chlorofluoromethanes and cyclohexene with arc generated carbon at 77 K.[3] Products were washed from the reactor with methylene chloride and analyzed by GC, GCMS, and ^{19}F NMR. All products were identified by comparison of their spectra and retention times with those of authentic samples. Relative product yields were determined by GC integration.

In a previous study, we found that CF (from C + CF_4) reacts with alkenes to generate fluorocyclopropyl radicals which subsequently abstract hydrogen.[2] In the reaction of C with a chlorofluorocarbon, there is the possibility that both CCl and CF could form and that intermediates could abstract both H and Cl, with F abstraction by species other than C precluded on energetic grounds. Hence, reaction of C with a chlorofluorocarbon and cyclohexene could produce the seven products in Scheme 1. *syn*- and *anti*-**1** and -**2** arise by initial fluorine abstraction, while *syn*- and *anti*-**3** result from initial chlorine abstraction. The 7,7-dichloronorcarane (**4**) could arise by initial Cl abstraction to give CCl or by a concerted abstraction of two chlorines by carbon to produce dichlorocarbene. Table 1 lists product ratios and abstraction exothermicities in the reaction of C with F- and Cl-substituted methanes in the presence of cyclohexene.[4] The fact that *syn*- and *anti*-**3** are formed in the reaction of C with CCl_4 is strong evidence for the intermediacy of CCl in this system. If we assume that **1** and **2** are products of initial CF formation and that **3** and **4** result from initial CCl formation, we may estimate the ratios of CCl to CF products shown in Table 1 (corrected for statistical factors). Figure 1, which shows a plot of ln([CCl products]/[CF products]) as a function of the difference in abstraction enthalpies, demonstrates that the relative rates of the initial abstractions by carbon are governed by the enthalpies of the abstraction reaction. It should be noted that the ratios of CCl to CF products used to construct Figure 1 are those obtained by assuming that **4** results from initial abstraction of a single Cl. If **4** is not included as a product of initial Cl abstraction, one obtains a much poorer correlation between the products of abstraction and their enthalpies ($R = 0.72$ vs 0.98, Figure 1). We believe that this fact indicates that a major pathway to **4** involving concerted formation of CCl_2 is unlikely. In this connection, we also note that **4** is formed in the reaction of C + CF_3Cl (Table 1), in which concerted formation of CCl_2 is precluded. If concerted transfer of two chlorines to carbon were an important pathway, the reaction of C + CF_2Cl_2 would be expected to yield CF_2 products along with CCl_2 products. Such products are not observed in appreciable yield.[5]

Scheme 1



Although the above observations indicate that concerted formation of CCl_2 is unimportant in these reactions, they say nothing about subsequent abstractions by methylidyne intermediates to generate carbenes which then add to cyclohexene to give the observed halo- and dihalocyclopropanes. In particular, **1** and **3** could result from halocarbenes generated by the process in eq 2, while **2** and **4** could be products of dihalocarbenes produced as shown in eq 3. A consideration of the enthalpies of the hydrogen

$$C\text{–}X + R\text{–}H \rightarrow H\text{–}\ddot{C}\text{–}X + R^{\bullet} \quad (2)$$

$$C\text{–}X + R\text{–}Cl \rightarrow Cl\text{–}\ddot{C}\text{–}X + R^{\bullet} \quad (3)$$

abstractions from cyclohexene in eq 2 by CF ($\Delta H = 6.3$ kcal/mol) and CCl ($\Delta H = 13.6$ kcal/mol) indicates that both reactions are unfavorable[4,6] and would not be expected to play a major role in the formation of **1** and **3**. In fact, we have previously ruled out HCF as a precursor to **1** on the basis of the fact that syn:anti ratios change with hydrogen donor concentration.[2] Such a result is expected if the rate of an equilibrium between a syn and an anti 7-fluoronorcaran-7-yl radical, **5**, is comparable to the rate of H abstraction but inconsistent with formation of HCF which adds to cyclohexene. Since the rate of inversion of fluorocyclopropyl radicals has been shown to be slower than rates of intermolecular H abstraction,[7] this experiment works well to rule out the formation of **1** by HCF addition. However, the rate of inversion of chlorocyclopropyl radicals is faster than that of intermolecular H abstraction,[7] and this criterion cannot be used to evaluate the intermediacy of HCCl in the formation of **3**. In this case, we observe syn:anti ratios in **3** which are independent of H donor concentration and range from 1 to 0.9, depending on the chlorofluorocarbon substrate used. The syn:anti ratios which have been observed in HCCl additions appear to be dependent upon the method of carbene generation. In the present study, we have observed that reaction of HCCl, generated from CH_2Cl_2 and butyllithium at 195 K,[8] with cyclohexene gives *syn*- and *anti*-**3**

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[1] Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* **1965**, *87*, 5807.

[2] Rahman, M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 6296.

[3] The carbon atom reactor is modeled after that described in the following: Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

[4] Experimental heats of formation are from the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[5] GC analysis shows traces of a product with the same retention time as that of 7,7-difluoronorcarane in yields of less than 1% that of **4**.

[6] The heats of formation of the halocarbenes have recently been determined: Born, M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1994**, *116*, 7210.

[7] Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625 (report no. 108).

[8] Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723.

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Table 1. Relative Product Yields in the Reactions of Atomic Carbon with Chlorine- and Fluorine-Substituted Methanes and Cyclohexene[a]

	substrate				
product	CCl_4[b]	CF_3Cl	CF_2Cl_2	$CFCl_3$	$CF_4 + CCl_4$[c]
anti-**1**		0.41 ± 0.41	0.04 ± 0.02	0.03 ± 0.01	0.06 ± 0.04
syn-**1**		0.15 ± 0.15	0.02 ± 0.01	0.01 ± 0.00	0.02 ± 0.02
anti-**2**		0.1 ± 0.04	0.06 ± 0.01	0.09 ± 0.01	0.06 ± 0.01
syn-**2**		0.34 ± 0.03	0.21 ± 0.02	0.31 ± 0.04	0.19 ± 0.02
anti-**3**	1	1	1	1	1
syn-**3**	0.99 ± 0.04	1.0 ± 0.31	0.96 ± 0.02	0.09 ± 0.05	0.94 ± 0.09
4	3.25 ± 0.02	0.24 ± 0.11	1.74 ± 0.44	2.33 ± 0.70	5.36 ± 3.51
$[CCl_{prod}]/[CF_{prod}]$[d]		6.72	11.21	3.20	22.12
$\Delta H_{Cl\ abs}$ (kcal/mol)		–50.4	–60.9	–62.5	–66.8
$\Delta H_{F\ abs}$ (kcal/mol)		–39.3	–46.4	–60	–39.1

[a] Carbon was condensed with a 1:1 ratio of cyclohexene and chlorofluorocarbon. Relative yields are the average of four runs unless noted, otherwise. [b] Average of two runs. [c] Average of three runs. [d] Corrected for statistical factors.

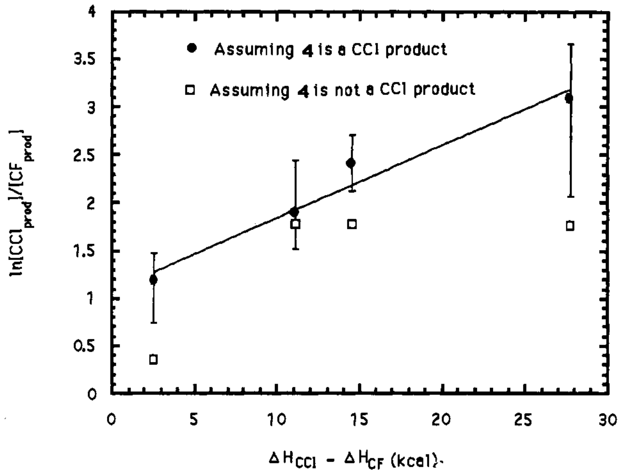

Figure 1. Plot of $\ln[CCl_{prod}/CF_{prod}]$ as a function of the enthalpy difference between abstraction of chlorine and abstraction of fluorine.

in a 2.1:1 ratio.[9] However, photolysis of chlorodiazomethane and cyclohexene at 243 K, a reaction more likely to involve a free carbene gives **3** with a syn:anti ratio of 1.[10] In contrast, H abstraction by the 7-chloronorcaran-7-yl radical, **6**, at 400 K gives **3** with syn:anti ratios of 4.[11,12] However, our reaction conditions and energetics are quite different from those which have been employed in previous studies of HCCl additions and abstractions by **6**. Thus, a comparison of our syn:anti ratios with those which have been observed is unlikely to provide conclusive evidence concerning the mechanism of formation of **3**. In view of the fact that formation of HCCl is thermodynamically unfavorable in this system, we feel that the major route to **3**, like that leading to **1**, involves addition of the methylidyne to the cyclohexene to give the corresponding cyclopropyl radical.

The question of Cl abstraction by CF and/or CCl (eq 3) is more problematic. With the exception of $CCl + CF_3Cl \rightarrow CCl_2 + CF_3$ ($\Delta H = 6.7$ kcal/mol), the enthalpies of dihalocarbene formation by chlorine abstraction are all favorable by 5–24 kcal/mol.[4] Hence, it is expected that Cl abstractions by the methylidynes will compete with double bond addition and both processes will lead to **2** and **4**. Although we cannot use syn:anti ratios to evaluate the intermediacy of CCl_2 in these reactions, we may compare the corresponding ratios observed in the addition of FCCl to cyclohexene to those observed in the carbon atom reactions. Table 1 shows that syn:anti ratios in **2** are remarkably independent of substrate and favor the product with a syn chlorine by factors of 3.2–3.6. In comparison, we observe that FCCl, generated from butyllithium and $CFCl_3$ at 243 K, adds to cyclohexene, giving **2** with a syn:anti ratio of 2.2:1. Others have reported a similar preference for syn addition of Cl in FCCl reactions.[9b,14] Although the syn:anti ratios in the carbon atom reactions are somewhat different from those we observe in the FCCl additions, both show a preference for the formation of the less stable syn isomer. The lower temperatures in the C atom reactions and Cl abstraction by **5** may be responsible for the differences.

These investigations demonstrate that reaction between C and chlorofluorocarbons is a ready source of both CCl and CF, whose ratios reflect the ease of the abstraction reaction. These monovalent carbon intermediates will react with alkenes to produce chloro- and fluorocyclopropanes and abstract chlorine to yield dihalocarbenes.

Acknowledgment. Support of this work through National Science Foundation Grant CHE-9013240 is gratefully acknowledged.

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(9) Similar preferences for *syn*-Cl products have been observed: (a) Closs, G. L.; Moss, R. A.; Coyle, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 4985. (b) Ando, T.; Yamanaka, H.; Terabe, S.; Horike, A.; Funasaka, W. *Tetrahedron Lett.* **1967**, 1123. (c) Fleming, I.; Thomas E. J. *Tetrahedron* **1972**, *28*, 5003.

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(11) (a) Ishihara, T.; Hayashi, K.; Ando, T. *J. Org. Chem.* **1975**, *40*, 3264. (b) Altman, L. J.; Baldwin, R. C. *Tetrahedron Lett.* **1971**, 2531.

(12) We have used AM1 calculations[13] to estimate K_{eq} for *anti*-**5** → *syn*-**5** = 3.62 and K_{eq} for *anti*-**6** → *syn*-**6** = 1.36 at 77 K.

(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(14) (a) Moss, R. A.; Gerstl, R. *J. Org. Chem.* **1967**, *32*, 2268. (b) Moss, R. A.; Gerstl, R. *Tetrahedron* **1967**, *23*, 2549. (c) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1990**, *55*, 589.