Cyclization Procedure for the Dihaloalkanes. The dihaloalkanes were purchased from Aldrich and used as received. The typical experimental setup previously described was modified by using a three-neck 100-mL round-bottomed flask in place of the two-neck flask. Two of the necks were equipped with a septum and condenser as described before. To the third neck was attached a liquid addition funnel sealed at the top with a septum. Activated copper (16.5 mmol), made from lithium naphthalenide and CuI·P(*n*-Bu)$_3$ in THF, was prepared in the three-neck flask. An internal standard was added (typically 3 mmol), the temperature of the flask was adjusted, and stirring was initiated. For the 1,5-dihaloalkanes, nonane was used as the internal standard. In all other reactions decane was used. The dihaloalkane (4 mmol) was syringed into the addition funnel followed by THF (5–10 mL). The apparatus was shaken gently to mix the solutions thoroughly. The dihaloalkane solution was then added slowly (0.5 h) to the activated copper solution. For specific reaction temperatures and product yields see Table V. Aliquots (1 mL) were removed via syringe at timed intervals (1, 10, 30, 60, 120 min) and quenched with HCl (0.01 M, 0.2 mL). Most of the reactions were found to be complete within 10 min after all of the starting material was added. The organic layer from the quenched aliquot was analyzed by GC (columns II, III). Yields and identities of the cyclized product for 1,3-dibromobutane and 1,4-diiodobutane were established by the independent synthesis of methylcyclopropane by the method of Demjanow,[17] and cyclobutane by the method of Cason and Way.[18] The identities of all other cyclized compounds were established by comparing them to authentic commercial samples.

Formation of *trans*-Stilbene from *meso*-Stilbene Dibromide. *meso*-Stilbene dibromide was purchased from Aldrich. The reaction was carried out at room temperature as indicated for a typical cyclization procedure using nonane as the internal standard. The reaction was found to be complete in 10 min from the time all of the starting material was added. GC analysis (column I) showed an 83% yield of *trans*-stilbene with no detectable amount of *cis*-stilbene present.[19] In another experiment, *cis*-stilbene was treated with activated copper under the conditions stated above, and it was found that 80% of the *cis*-stilbene had isomerized to the trans compound in 1 min. At the end of 10 min the conversion was over 90%.

Acknowledgment. We gratefully acknowledge partial support of this work by the Research Foundation of SUNY administered by the Office of Sponsored Programs at the State University College at Buffalo through their Incentive Grant Program. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Special thanks go to professor Edward M. Schulman for providing the necessary ^{13}C NMR data, to professor Surgit Singh for providing the FT-IR data, and to professor Reuben D. Rieke for introducing G.W.E. to this field of research.

Registry No. CuI·PEt$_3$, 56667-47-1; CuI·PBu$_3$, 21591-31-1; lithium naphthalemide, 7308-67-0; lithium biphenylide, 34467-57-7; naphthalene, 91-20-3; biphenyl, 92-52-4; allyl chloride, 107-05-1; allyl bromide, 106-95-6; allyl iodide, 556-56-9; benzyl chloride, 100-44-7; benzyl bromide, 100-39-0; benzyl iodide, 620-05-3; 1,5-hexadiene, 592-42-7; 1,2-diphenylethane, 103-29-7; toluene, 108-88-3; *n*-heptyl iodide, 4282-40-0; *n*-heptyl bromide, 629-04-9; N-heptyl chloride, 629-06-1; tetradecane, 629-59-4; heptane, 142-82-5; 1-heptene, 592-76-7; 2-iodopropane, 75-30-9; 2-iodopentane, 637-97-8; 2-bromopropane, 75-26-3; 2-bromopentane, 107-81-3; 2,3-dimethylbutane, 79-29-8; pentane, 109-66-0; 1-pentene, 109-67-1; 2-pentene, 109-68-2; *t*-butyl iodide, 558-17-8; *t*-butyl bromide, 507-19-7; 2-bromo-2-methylbutane, 507-36-8; 1,3-dibromobutane, 107-80-2; 1,4-diiodobutane, 628-21-7; 1,5-diiodopentane, 628-77-3; 1,5-dibromopentane, 111-24-0; 1,6-diiodohexane, 629-09-4; 1,8-diiodooctane, 24772-63-2; methylcyclopropane, 594-11-6; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; 1-octene, 111-66-0; butane, 106-97-8; 1-butene, 106-98-9; hexane, 110-54-3; 1-hexene, 592-41-6; octane, 111-65-9; *trans*-stilbene, 103-30-0; *meso*-stilbene dibromide, 13440-24-9; *cis*-stilbene, 645-49-8; 2,2,3,3-tetramethylbutane, 594-82-1; 2-methylbutane, 78-78-4; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; 1,3-butadiene, 106-99-0; 1,4-pentadiene, 591-93-5; 1,7-octadiene, 3710-30-3.

(17) Demjanow, J. *Ber.* **1895**, *28*, 21.
(18) Cason, J.; Way, R. L. *J. Org. Chem.* **1949**, *14*, 31.
(19) The limit of detectability of *cis*-stilbene on our GC is ca. 2% under the conditions of reaction.

Chlorofluorocarbene from Reaction of Fluorotrichloromethane with Reduced Titanium. Synthesis of 1-Chloro-1-fluorocyclopropanes

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Received May 25, 1989

Generation of chlorofluorocarbene by reaction of $CFCl_3$ with reduced titanium at 0 °C, in the presence of various alkenes, produces 1-chloro-1-fluorocyclopropanes in good yield. Evidence from the syn/anti product ratios, including generation of chlorofluorocarbene from $CFBr_2Cl$, indicates that a free carbene and not a "carbenoid" species is involved. Solvent effects, effects of ratios of reagents, and the efficacy of other metals in this reaction were also examined. A cursory examination of $PhCCl_3$, CH_3CCl_3, and CF_2Br_2 in this reaction indicated that they are also useful carbene precursors, while $CHCl_3$, $CHFBr_2$, and $CHFI_2$ were all found to be ineffective.

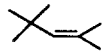
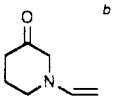
In a recent communication,[1] we reported a new method for generating chlorofluorocarbene from $CFCl_3$. In this paper, we report the full range of alkenes that we have studied and the experimental details of these reactions. Furthermore, we will present evidence supporting the conclusion that free chlorofluorocarbene is the likely reactive intermediate and that a "carbenoid" species is probably not involved.

Chlorofluorocarbene has been previously generated by the following methods: (a) thermolysis of $PhHgCFCl_2$ (an 89% yield of 7-chloro-7-fluorobicyclo[4.1.0]heptane from cyclohexene);[2] (b) base-induced decomposition of methyl dichlorofluoroacetate (60%);[3] (c) reactions of $CHFCl_2$ with

(1) Dolbier, W. R., Jr.; Burkholder, C. R. *Tetrahedron Lett.* **1988**, *29*, 6749.
(2) Seyferth, D.; Darragh, K. V. *J. Org. Chem.* **1970**, *35*, 1297.

0022-3263/90/1955-0589$02.50/0

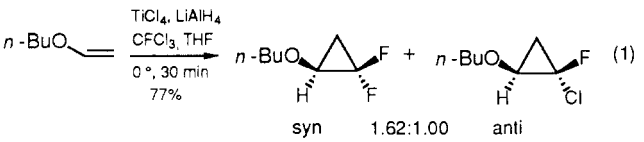
Table I. Yields of 1-Chloro-1-fluorocyclopropanes and Syn/Anti Ratios

alkene	NMR yield,[a] %	isolated yield,[a] %	syn/anti	isolated syn/anti
	92	83	5.65	6.11
	90	66		
	89	52	2.22	2.20
	88	78	1.51	1.29
	85	79	1.02	0.97
	85	72		
	77	57	1.62	1.66
	52	53	2.23	2.10
	43	42	1.31	1.33
 [b]	19	12	2.81	11.0
	12	13	1.37	1.32
	0			

[a] Determined by ^{19}F NMR of unrefined product mixtures. [b] Inverse addition.

methyllithium (21%),[4] with KO-t-Bu (24%),[5] or with ethylene oxide/tetraethylammonium bromide (45%),[6] and (d) base-induced decomposition of difluorotetrachloroacetone (36%).[7] Previous attempts to produce chlorofluorocarbene from $CFCl_3$ by reaction with alkyllithiums,[8] or with phosphines,[9] have been only partially successful. Low yields were obtained in both cases.

Our new method involves the use of reduced titanium, prepared according to the literature[10] from titanium tetrachloride and lithium aluminum hydride. The black, reduced titanium mixture is then cooled to 0 °C, the alkene added, and finally the $CFCl_3$ is added. After 30 min at 0 °C, the reaction is worked up, an internal standard added, and the yield determined from integration of the ^{19}F NMR spectrum. Isolated yields were obtained after fractional distillation at reduced pressure. Both *syn*- and *anti*-chlorofluorocyclopropanes are formed, as depicted in the example given in eq 1.



(1)

(3) Ando, T.; Hosaka, H.; Yamanaka, H.; Funasaka, W. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2013. Ando, T.; Ishihara, T.; Ohtani, E.; Sawada, H. *J. Org. Chem.* **1981**, *46*, 4446. Kano, H.; Kobayashi, K.; Isogai, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1926. Moore, R. A.; Levine, R. *J. Org. Chem.* **1964**, *29*, 1883.

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(5) Parham, W. E.; Twelves, R. R. *J. Org. Chem.* **1957**, *22*, 730.

(6) Weyerstahl, P.; Klamann, D.; Finger, C.; Nerdel, F.; Buddrus, J. *Chem. Ber.* **1967**, *100*, 1858.

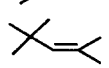
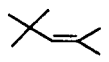
(7) Farah, B.; Horensky, S. *J. Org. Chem.* **1963**, *28*, 2494.

(8) Burton, D. J.; Hahnfeld, J. L. *J. Org. Chem.* **1977**, *42*, 828. Schlosser, M.; Spahic, B.; Chau, L. V. *Helv. Chim. Acta* **1975**, *58*, 2586.

(9) Burton, D. J.; Hahnfeld, J. L. *Fluorine Chemistry Reviews*; Tarrant, P., Ed.; Marcel Dekker, Inc.: New York and Basel, 1977; Vol. 8, Chapter 4, p 119.

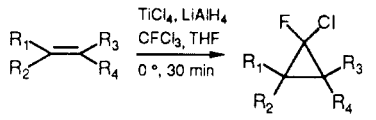
(10) Mukaiyama, T.; Shiono, M.; Watanabe, K.; Onaka, M. *Chem. Lett.* **1975**, 711.

Table II. Syn/Anti Ratios with $CFCl_3$ versus $CFBr_2Cl$

alkene	halomethane	syn/anti ratio
	$CFCl_3$	1.02
	$CFBr_2Cl$	1.02
	$CFCl_3$	5.65
	$CFBr_2Cl$	5.73

This new procedure has several advantages over previous methods for generating chlorofluorocarbene. The $CFCl_3$ is very inexpensive; it can be conveniently handled as a liquid (bp 23.7 °C) and stored in the refrigerator; reaction conditions are mild, no strong base is required, and the reaction occurs rapidly at 0 °C. Finally and perhaps most importantly, yields are good for most alkenes and no nonvolatile byproducts are produced, thus facilitating isolation of pure materials.

The yields and syn/anti ratios for reactions of chlorofluorocarbene with various alkenes (eq 2) are presented



(2)

in Table I. Both NMR and isolated yields are given. The isolated yields are generally slightly lower than the NMR yields. Also, in some cases the isolated chlorofluorocyclopropanes have a different syn/anti ratio than observed before isolation. For example, the anti isomer of *N*-(2-chloro-2-fluorocyclopropyl)pyrrolidinone appears to be unstable relative to the syn isomer, presumably because of the ability of the nitrogen to anchimerically assist in the loss of chloride in the anti isomer.

As can be seen from Table I, the yields of chlorofluorocyclopropanes decrease predictably, consistent with the decreasing nucleophilicity of the alkenes. Monoalkyl-substituted alkenes are, as expected, the least reactive and give very low yields, as has generally been observed in reactions with chlorofluorocarbene in the past.[4,11] However, as one might have expected, when the monosubstituted alkene bears an electron-donating substituent, such as in the case of *n*-butyl vinyl ether, reactivity is enhanced and a good yield is obtained.

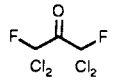
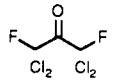
We conclude that reaction of $CFCl_3$ with reduced titanium produces free chlorofluorocarbene rather than a "carbenoid" species. This conclusion is based upon the observed values of the syn/anti product ratios and also upon the observed relative reactivity of the chlorofluorocarbene with two selected alkenes.

The syn/anti product ratios that we observe are very close to those reported in studies of a number of other unrelated methods of addition of chlorofluorocarbene to alkenes. For example, in three different base-induced reactions, chlorofluorocarbene was generated from tetrachlorodifluoroacetone in a reaction with 2-methyl-2-butene,[11] from $CFCl_2CO_2Et$ in a reaction with α-methylstyrene,[12] and from $CHFCl_2$ in a reaction with cyclohexene to give syn/anti product ratios of 2.35, 1.0, and 2.2, respectively. Such ratios compare with our respective observed values of 2.22, 1.02, and 2.23.

(11) Moss, R. A.; Gerstil, R. *J. Org. Chem.* **1967**, *32*, 2268. Moss, R. A.; Gerstl, R. *Tetrahedron* **1967**, *23*, 2549.

(12) Kostikov, R. R.; Molchanov, A. P.; Golovanova, G. V.; Zenkevich, I. G. *Zh. Org. Khim.* **1977**, *13*, 1846.

Table III. Relative Reactivity of 2,3-Dimethyl-2-butene and 2-Methyl-2-butene with Chlorofluorocarbene

entry	precursor	solvent	relative reactivity	syn/anti ratio for 2-methyl-2-butene
1		none	4.36[11]	2.4[11]
2		THF	4.95	2.29
3	$CFCl_3$	THF	3.53	2.13
4	$CFCl_3$	THF[a]	4.00	2.25

[a] Diluted 2-fold with THF.

In cases where *carbenoids* are believed to be involved, syn/anti ratios can vary quite dramatically. For example, free fluorocarbene was seen to give a syn/anti product ratio of 1.0 with cyclohexene,[13] while the copper and zinc carbenoids give values of 2.4[14] and 5.7,[15] respectively.

As a further test, reactions in which $CFBr_2Cl$ was substituted for $CFCl_3$ were carried out, using α-methylstyrene and 2,4,4-trimethyl-2-pentene as alkene substrates. It was reasoned that if *no* changes in the syn/anti product ratios were observed, then carbenoid intermediates could be effectively ruled out in these reactions. It would be expected that if carbenoids such as $ClTiCFCl_2$ and BrTiCFClBr were involved, the steric effects of the two reagents in the transition state for carbene addition would be different and that different syn/anti ratios would thus inevitably result.

As seen in Table II, with α-methylstyrene, $CFBr_2Cl$ gave a syn/anti ratio of 1.02, identical with the syn/anti ratio produced with $CFCl_3$. With the even more selective alkene, 2,4,4-trimethyl-2-pentene, the syn/anti ratio produced from the $CFBr_2Cl$ reaction was observed to be 5.73, which is very close to the value of 5.65 observed from $CFCl_3$. Thus, all of the evidence derived from the syn/anti product ratios strongly favors a free chlorofluorocarbene intermediate being involved.

Another recognized way to gain insight into the nature of the reactive intermediate is to measure the *relative reactivity* of different alkenes with chlorofluorocarbene. A carbenoid would be expected to have a different relative reactivity than does free chlorofluorocarbene. Furthermore, the relative reactivity of alkenes with chlorofluorocarbene from $CFCl_3/TiCl_4/LiAlH_4$ should be the same as the relative reactivity when this carbene is generated from a different source.

In this experiment, the relative reactivity of 2,3-dimethyl-2-butene versus 2-methyl-2-butene was measured because the reaction of these two alkenes with chlorofluorocarbene has been previously studied by Moss and Gerstl.[11]

Working in this study at −10 °C, as did Moss, we initially observed a relative reactivity of 3.53, which is clearly different from Moss' value of 4.36, where the chlorofluorocarbene had been generated by reaction of tetrachlorodifluoroacetone with base. Suspecting that the discrepancy in these values was due to our use of THF as solvent (Moss and Gerstl used no solvent), we diluted the reaction mixture with still more THF and obtained a quite different relative reactivity value of 4.00. (See Table III.) Moreover, with use of difluorotetrachloroacetone as the carbene precursor and carrying out the reaction in THF, a relative reactivity of 4.95 was observed. We conclude that the solvation of the chlorofluorocarbene intermediate affects its relative reactivity with alkenes. In our case, the presence of THF as solvent apparently enhances the selectivity of chlorofluorocarbene, probably through stabilization of the intermediate.

The precise nature of the reduced titanium mixture, prepared by the reduction of $TiCl_4$ with $LiAlH_4$, is not completely clear. From varying the amounts of $TiCl_4$ and $LiAlH_4$ (see Table IV), it is apparent that the stoichiometry of the reaction is one to one. Therefore, we propose eq 3

$$TiCl_4 + LiAlH_4 \xrightarrow{0\ ^\circ C,\ THF} Ti^0 + AlCl_3 + LiCl + 2H_2 \quad (3)$$

to be representative of this reduction step. The reduced titanium(0) may then react with $CFCl_3$, according to eq 4, to form $ClTiCFCl_2$ as a reactive intermediate. This

$$Ti^0 + CFCl_3 \xrightarrow{0\ ^\circ C,\ THF} [ClTiCFCl_2] \rightarrow :CFCl + TiCl_2 \quad (4)$$

titanium(II) species must be very unstable, disproportionating rapidly to titanium(II) chloride and chlorofluorocarbene. The chlorofluorocarbene would subsequently be trapped, in the presence of alkenes, to give the observed chlorofluorocyclopropanes.

The highly reactive nature of the reduced titanium is most likely due to its finely divided nature. It is well known that extremely finely divided metals exhibit a great increase in reactivity.[16] The reduced titanium mixture prepared in this way is far more reactive than commercial titanium metal powder (100 mesh), which was found not to react with $CFCl_3$ even after several days at room temperature.

Other reducing agents have in the past been used for the preparation of reduced titanium.[17] Magnesium turnings may be used, but we found that the reactions must then be carried out under argon instead of nitrogen. In addition, the mixture must be heated briefly at reflux to obtain complete reduction. We also observed that the yields of chlorofluorocyclopropanes were slightly lower when magnesium was used as the reducing agent.

The reduction of $TiCl_3$ with $LiAlH_4$ was also found to proceed smoothly to give an apparently identical reduced titanium mixture. It was found that the yields of chlorofluorocyclopropanes were virtually identical whether $TiCl_3$ or $TiCl_4$ was used as the source of the reduced titanium.

A reduced *zirconium* mixture was also prepared by reduction of $ZrCl_4$ with $LiAlH_4$ in order to compare its effectiveness in the reaction with that of titanium. The reduced zirconium mixture was allowed to react with $CFCl_3$ in the presence of α-methylstyrene at 0 °C for 30 min, but only a 2% yield of chlorofluorocyclopropane was obtained. Thus, zirconium would appear to be much less reactive than reduced titanium in this reaction.

Our initial, exploratory reactions of $CFCl_3$ and reduced titanium, using α-methylstyrene, were cararied out on approximately a 3-fold excess of alkene. Under these reaction conditions, the yield of chlorofluorocyclopropane was only 40%, based on the amount of $CFCl_3$ employed. Numerous variations in the amounts of $TiCl_4$ and $LiAlH_4$,

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(14) Kawabata, N.; Tanimoto, M.; Fujiwara, S. *Tetrahedron* **1979**, *35*, 1919.
(15) Nishimura, J.; Furukawa, J. *J. Chem. Soc. D* **1971**, 1375.
(16) Rieke, R. D. *Acc. Chem. Res.* **1977**, *10*, 301.
(17) Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248. Lai, Y. *Org. Prep. Proc. Int.* **1980**, *12*, 363.

Table IV. Yields of Chlorofluorocyclopropane from α-Methylstyrene as a Function of Mole Ratios of Reactants

run	alkene	$TiCl_4$	$LiAlH_4$	$CFCl_3$	temp, °C	time, h	yield,[a] %
1	2.7	1	1	1	0	1	40
2	2.7	1	1	1	0	3	37
3	2.7	1	1	1	40	0.08	47
4	2.7	1	1	1	−60	0.33	30
5	2.7	1.5	1.5	1	0	1	44
6	2.7	0.5	0.5	1	0	1	23
7	2.7	1.5	1	1	0	0.5	33
8	2.7	0.5	1	1	0	0.5	36
9	2.7	1	1.3	1	0	1	44
10	2.7	1	0.7	1	0	1	22
11	6	1	1	1	0	0.5	41
12	1	1	1	1	0	0.5	43
13	0.33	1	1	1	0	0.5	85

[a] All yields except entry 13 based on $CFCl_3$ as the limiting reagent.

Table V. Variation of the Solvent Using 3 equiv of α-Methylstyrene

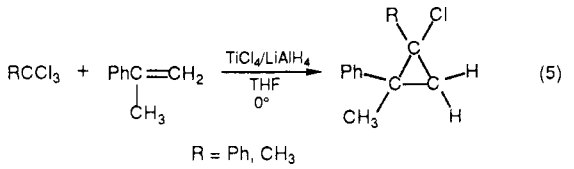
run	solvent	yield,[d] %
1	benzene[a]	0
2	ethyl ether	5
3	dimethoxyethane	17
4	tetrahydrofuran	40
5	THF/CH_3CN[b]	4
6	THF/TMEDA[c]	33

[a] Catalytic THF added so that reduction would occur. [b] Acetonitrile added after reduction of $TiCl_4$. [c] Tetramethylethylenediamine added before reduction of $TiCl_4$. [d] Yield based on $CFCl_3$ employed.

along with variation of the temperature and time of reaction, did not significantly increase the yield (see Table IV). In addition, variation of the solvent showed that THF was the best solvent (Table V).

We concluded from these experiments that the maximum production of chlorofluorocarbene from $CFCl_3$ was only about 40%. However, we found it possible to obtain good yields of cyclopropanes, based upon *alkene* as the limiting reactant, by using a 3-*fold excess* of $CFCl_3$ and reduced titanium. This strategy has the advantage of being very efficient in terms of alkene used. It was also found that acidic hydrolysis of the reaction mixture avoids formation of a gelatinous precipitate, thus greatly facilitating the workup.

In view of this synthetic success with $CFCl_3$, it was decided to explore the scope of the reaction with respect to the use of different halocarbons (eq 5). The results of



(5)

R = Ph, CH_3

these experiments are presented in Table VI, and it can be seen that the reaction clearly works best when there are *four* halogens on the methane. While little effort was made to maximize the conditions of these reactions, it can be seen that reduced titanium is effective to various degrees in the formation and synthetic utilization of phenylchlorocarbene, methylchlorocarbene, dichlorocarbene, and difluorocarbene. It, unfortunately, would seem to have *no* potential for the effective generation of *mono*halocarbenes (i.e., CHX).

In conclusion, we have presented a new method for generation of chlorofluorocarbene by reaction of $CFCl_3$ with reduced titanium. The synthetic procedure is easy to carrry out and can be used without drying the solvent. Good yields of chlorofluorocyclopropane are obtained with

Table VI. Reactions of Halocarbons with Reduced Titanium in the Presence of 3 equiv of an Alkene

entry	alkene	halocarbon	yield,[a] %
1		CCl_4	60[10]
2		$PhCCl_3$	58[b]
3		CF_2Br_2	45[c]
4		CH_3CCl_3	15
5		CF_3CCl_3	0[d]
6		$CHCl_3$	0
7		$CHFBr_2$	0[d]
8		$CHFI_2$	0[d]

[a] NMR yields using internal standards. [b] Byproduct also formed. [c] Inverse addition. [d] Many products in low yield; no cyclopropane produced.

most alkenes. It appears that the reaction invovles "free" chlorofluorocarbene and not a "carbenoid" species.

Experimental Section

General Comments. Proton, fluorine, and carbon spectra were determined on a Varian VXR-300 spectrometer at 300, 282, and 75 MHz, respectively. The proton chemical shifts are reported in ppm downfield from TMS. The fluorine chemical shifts are reported in ppm upfield of internal $CFCl_3$. The carbon shifts are reported in ppm downfield of TMS. Initially, the THF was distilled from $LiAlH_4$ and the reactions were performed under argon; however, it was later discovered that drying the solvent did not increase the yields. All reactions where products were isolated were performed under nitrogen with THF that was not dried. All alkenes and $CFCl_3$ were used as received. GC analysis was performed on a 3 m × 3 mm o.d. column packed with 20% QF-1 on Chromosorb WHP 100/120 at 100 °C.

General Procedure A. Synthesis and Isolation of 1-Chloro-1-fluorocyclopropanes. A 1000-mL, three-necked, round-bottom flask was equipped with magnetic stirrer, thermometer, rubber septum with nitrogen inlet needle, and a pressure-equalizing addition funnel with outlet stopcock. The system was flushed with nitrogen and 300 mL of THF was added. The flask was cooled in a salt–ice bath and then 43.3 g (0.228 mol) of titanium tetrachloride was carefully added over a period of 13 min at such a rate that the temperature remained below 5 °C. The addition was exothermic. A white vapor was produced and a yellow precipitate was formed. A solution of 9.11 g (0.228 mol) of 95% lithium aluminum hydride in 200 mL of THF was carefully added over a period of 25 min at such a rate that the temperature remained below 15 °C. The reaction was exothermic and hydrogen was evolved. The reaction mixture turned dark brown. The

salt–ice bath was removed and the dark brown mixture was allowed to stir as it slowly warmed to 19 °C over a period of 40 min.

The flask was cooled again in a salt–ice bath. When the temperature had fallen to 0 °C, 0.0760 mol of alkene was added. Then a solution of 31.3 g (0.228 mol) of fluorotrichloromethane in 100 mL of THF was added over a period of 32 min at such a rate that the temperature remained at 0 °C. The mixture was allowed to stir at 0 °C for 30 min.

The cold, dark brown mixture was carefully poured into a mixture of 800 mL of 10% aqueous hydrochloric acid and 400 mL of crushed ice in a 3000-mL beaker. Rapid stirring was maintained during this hydrolysis. Gas was evolved and the mixture came rapidly to room temperature. After gas evolution had ceased, the upper, dark brown organic layer was separated from the dark brown aqueous layer. The aqueous layer was extracted once with 300 mL of methylene chloride and twice with 200 mL of methylene chloride. The combined organic layers were washed with 200 mL of 10% aqueous sodium bicarbonate and their dark brown color gradually faded to give a clear, pale-yellow-tinted organic solution. The organic layer was dried over anhydrous sodium sulfate.

The bulk of the solvent was removed by distillation at ambient pressure on a 50-cm Vigreux column. The residue was further concentrated by distillation on a 15-cm Vigreux column. The product was obtained by fractional distillation at reduced pressure on a 15-cm Vigreux column. The syn/anti ratios were determined by integration of the ^{19}F NMR spectrum.

General Procedure B. NMR Yield of 1-Chloro-1-fluorocyclopropanes. A 100-mL, three-necked, round-bottom flask was equipped with magnetic stirrer, thermometer, rubber septum with argon inlet needle, and a pressure-equalizing addition funnel with an outlet stopcock. The system was flushed with dry argon and 30 mL of dry THF was added. The flask was cooled in a salt–ice bath and then 4.33 g (22.8 mmol) of titanium tetrachloride was carefully added over a period of 10 min at such a rate that the temperature remained below 5 °C. The addition was very exothermic and a white vapor was produced along with a yellow precipitate.

A solution of 0.911 g (22.8 mmol) of 95% lithium aluminum hydride in 20 mL of dry THF was carefully added over a period of 12 min at such a rate that the temperature remained below 10 °C. The reaction was exothermic and gas was evolved. Upon addition, a brown color was produced that disappeared again. The reaction mixture became green and finally dark brown. The salt–ice bath was removed and the mixture was allowed to stir as it slowly warmed to 20 °C over a period of 30 min.

The flask was cooled again in a salt–ice bath. When the temperature had fallen to 0 °C, 7.60 mmol of alkene was added. Then, a solution of 3.13 g (22.8 mmol) of fluorotrichloromethane in 10 mL of dry THF was added over a period of 22 min at such a rate that the temperature remained at or below 0 °C. The mixture was allowed to stir at 0 °C for 30 min.

The cold mixture was carefully poured into 100 mL of 10% aqueous hydrochloric acid, containing some ice, in a 600-mL beaker. Rapid stirring was maintained during this hydrolysis. Gas was evolved and the mixture came rapidly to room temperature. The brown aqueous mixture was extracted three times with 25-mL portions of methylene chloride. The combined organic layers were brown in color. They were washed with 25 mL of 10% aqueous sodium bicarbonte, upon which they became pale yellow in color. The organic solution was dried over anhydrous sodium sulfate and concentrated by distillation at ambient pressure on a 30-cm Vigreux column. The methylene chloride and THF distilled off at 40–65 °C. The clear, pale amber liquid residue was added to a vial containing 100 mg (0.5375 mmol) of hexafluorobenzene as internal standard and the ^{19}F NMR spectrum was taken. The NMR yield was determined by integration of the product resonances relative to the internal standard resonance. Syn/anti ratios were determined by integration of the syn isomer relative to the anti isomer.

1-Chloro-2,2-dimethyl-3-(1,1-dimethylethyl)-1-fluorocyclopropane. By following procedure A, 8.53 g (0.0760 mol) of 2,4,4-trimethyl-2-pentene gave 11.32 g (83%) of clear, colorless liquid product, bp 60 °C/22 mm. Analysis by GC indicated a purity of 96%. The syn/anti ratio before distillation was 5.65. The syn/anti ratio after distillation was 6.11. ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (m), 1.18 (m). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −128.0 (d, J = 23.6 Hz, syn isomer), −151.6 (d, J = 7.6 Hz, anti isomer).

1-Chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane. By following procedure A, 6.40 g (0.0760 mol) of 2,3-dimethyl-2-butene gave 7.55 g (66%) of clear, coloress liquid product, bp 60 °C/65 mm (lit.[11] bp 55–60 °C/60 mm). Analysis by GC indicated a purity of 98%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (d, J = 1.6 Hz, 6 H), 1.13 (d, J = 2.1 Hz, 6 H). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −148.1 (m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 104.6 (d, J_{CF} = 294.3 Hz), 27.4 (d, J_{CF} = 9.5 Hz), 18.8 (d, J_{CF} = 1.6 Hz), 15.5 (d, J_{CF} = 9.0 Hz).

1-Chloro-1-fluoro-2,2,3-trimethylcyclopropane. Procedure A was followed except that the combined organic layers were washed five times with an additional 500 mL of water. The bulk of the solvent was distilled off slowly on a 50-cm Vigreux column until the residue had a volume of 200 mL. The residue was washed with 400 mL of water, 200 mL of water, 75 mL of water, and 40 mL of water; then the organic layer was dried over anhydrous sodium sulfate. Distillation at ambient pressure on a 15-cm Vigreux column gave the desired product. Starting from 5.33 g (0.0760 mol) of 2-methyl-2-butene, there were obtained 5.42 g (52%) of clear, colorless liquid, bp 103–108 °C (lit.[18] bp 107–108 °C). Analysis by GC indicated a purity of 99.6%. The syn/anti ratio before distillation was 2.22. The syn/anti ratio after distillation was 2.20.

7-Chloro-7-fluoro-2-oxabicyclo[4.1.0]heptane. By following procedure A, 6.39 g (0.0760 mol) of 3,4-dihydro-2*H*-pyran gave 8.88 g (78%) of clear, colorless liquid product, bp 68 °C/17 mm (lit.[19] bp 70 °C/14 mm). Analysis by GC indicated a purity of 95%. The syn/anti ratio before distillation was 1.51. The syn/anti ratio after distillation was 1.29.

(2-Chloro-2-fluoro-1-methylcyclopropyl)benzene. By following procedure A, 8.98 g (0.0760 mol) of α-methylstyrene gave 11.13 g (79%) of clear, colorless liquid product, bp 66–69 °C/3 mm (lit.[7] bp 69–70 °C/5 mm). The syn/anti ratio was 1.02 before distillation. The syn/anti ratio was 0.97 after distillation. Analysis by GC indicated a purity of 97%.

1-Chloro-2,2-diethyl-1-fluorocyclopropane. By following procedure A, 6.40 g (0.0760 mol) of 2-ethyl-2-butene gave 8.28 g (72%) of clear, colorless liquid, bp 62 °C/60 mm (lit.[20] bp 43–45 °C/25 mm). Analysis by GC indicated a purity of 98%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.54 (m, 4 H), 1.14 (dd, J_{HH} = 7.3, J_{HF} = 17.1 Hz, 1 H), 0.97 (t, J = 7.4 Hz, 6 H), 0.89 (t, J = 6.9 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −141.6 (dm, J_{HF} = 17.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 99.6 (d, J_{CF} = 288.7 Hz, CFCl), 34.2 (d, J_{CF} = 8.8 Hz, quat.), 26.6 (d, J_{CF} = 10.2 Hz, CH_2), 25.3 (d, J_{CF} = 1.8 Hz, CH_2), 22.0 (d, J_{CF} = 8.5 Hz, CH_2), 10.5 (s, CH_3), 10.1 (d, J_{CF} = 1.5 Hz, CH_3).

2-Butoxy-1-chloro-1-fluorocyclopropane. By following procedure A, 7.61 g (0.0760 mol) of *n*-butyl vinyl ether gave 7.25 g (57%) of clear, colorless liquid, bp 69 °C/31 mm (lit.[21] bp 55 °C/16 mm). Analysis by GC indicated a purity of 96%. The syn/anti ratio was 1.62 before distillation. The syn/anti ratio was 1.66 after distillation. ^1H NMR (300 MHz, $CDCl_3$): δ 3.75–3.54 (complex m), 3.44 (m), 1.70–1.50 (complex m), 1.48–1.29 (complex m), 0.93 (m). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −138.0 (m, syn isomer) and −159.6 (dd, J_{HF} = 8.7 and J_{HF} = 19.3 Hz, anti isomer).

7-Chloro-7-fluorobicyclo[4.1.0]heptane. By following procedure A, 6.24 g (0.0760 mol) of cyclohexene gave 6.01 g (53%) of clear, colorless liquid, bp 56–58 °C/17 mm (lit.[4] bp 53–54 °C/15 mm). Analysis by GC indicated a purity of 93%. The syn/anti ratio before distillation was 2.23. The syn/anti ratio was 2.10 after distillation.

(2-Chloro-2-fluorocyclopropyl)benzene. By following procedure A, 7.92 g (0.0760 mol) of styrene gave 5.40 g (42%) of clear, colorless liquid, bp 56–58 °C/1.6 mm (lit.[6] bp 67–68 °C/9 mm). Analysis by GC indicated a purity of 93%. The syn/anti

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ratio was 1.31 before distillation. The syn/anti ratio was 1.33 after distillation.

***N*-(2-Chloro-2-fluorocyclopropyl)pyrrolidinone.** Procedure A was used except that the reduced titanium mixture was added to a solution of 8.45 g (0.0760 mol) of 1-vinylpyrrolidinone and $CFCl_3$ in THF at 0 °C. A total of 1.63 g (12%) of clear, colorless liquid product was obtained, bp 67–69 °C/0.05 mm. The product was not stable to GC conditions. It was also evident from the ^1H NMR spectrum that some decomposition had occurred during distillation. The syn/anti ratio was 2.81 before distillation. The syn/anti ratio was 11.0 after distillation. ^1H NMR (300 MHz, $CDCl_3$): δ 3.53 (m, 1 H), 3.40 (m, 1 H), 3.26 (m, 1 H), 2.42 (m, 2 H), 2.12–1.95 (m, 3 H), 1.84 (m, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −138.4 (m, syn isomer) and −153.2 (dd, J_{HF} = 9.2 and J_{HF} = 17.9 Hz, anti isomer).

2-Butyl-1-chloro-1-fluorocyclopropane. By following procedure A, 19.2 g (0.228 mol) of 1-hexene gave 4.32 g (13%) of clear, colorless liquid, bp 53–55 °C/33 mm. Analysis by GC indicated a purity of 90%. The syn/anti ratio was 1.37 before distillation. The syn/anti ratio was 1.32 after distillation. ^1H NMR (300 MHz, $CDCl_3$): δ 1.58–1.27 (complex m), 1.06 (m), 0.92 (m), 0.79 (m). ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −130.7 (m, syn isomer), −152.1 (m, anti isomer).

(1-Chloro-2,2,3,3-tetramethylcyclopropyl)benzene. Procedure B was followed, using 3.84 g (45.6 mmol) of 2,3-dimethyl-2-butene and 4.46 g (22.8 mmol) of α,α,α-trichlorotoluene. After concentration by distillation, the clear, amber liquid residue was added to a vial containing 500 mg (8.19 mmol) of nitromethane as internal standard. Integration of the nitromethane resonance at 4.27 ppm versus the methyl resonances at 1.38 and 1.03 ppm indicated the yield of cyclopropane product to be 58%. The chemical shifts of the methyl groups are nearly identical with the literature values of 1.37 and 1.03 ppm.[21]

1-Chloro-1,2,2,3,3-pentamethylcyclopropane. Procedure B was followed, using 3.84 g (45.6 mmol) of 2,3-dimethyl-2-butene and 3.04 g (22.8 mmol) of 1,1,1-trichloroethane. After concentration by distillation, the clear, colorless liquid residue was added to a vial containing 500 mg (8.19 mmol) of nitromethane as internal standard. Integration of the nitromethane resonance at 4.32 ppm versus the methyl resonances of the product indicated that the yield was 15%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.56 (s, 3 H), 1.16 (s, 6 H), 1.03 (s, 6 H).

(2,2-Difluoro-1-methylcyclopropyl)benzene. Procedure B was followed, with the exception that the reduced titanium mixture was added to a solution of 7.37 g (62.4 mmol) of α-methylstyrene and 4.78 g (22.8 mmol) of dibromodifluoromethane in 10 mL of THF over a period of 45 min at 0 °C. After an additional hour at 0 °C, the mixture was hydrolyzed as before. After concentration by distillation, the liquid residue was added to a vial containing 200 mg (1.075 mmol) of hexafluorobenzene as internal standard and the ^{19}F NMR was taken. Integration of the hexafluorobenzene resonance at −162.4 ppm versus the product resonances indicated that the yield was 45%. ^{19}F NMR (282 MHz, $CDCl_3$): ϕ −132.9 (dddq, 1 F, J^2_{FF} = 150.2, J^4_{HF} = 3.0, J^3_{HF} = 4.5, J^3_{HF} = 13.5 Hz), −137.9 (dddq, 1 F, J^2_{FF} = 150.2, J^4_{HF} = 1.8, J^3_{HF} = 12.4, J^3_{HF} = 3.6 Hz).

Competition Reaction with 2,3-Dimethyl-2-butene and 2-Methyl-2-butene. Procedure B was followed, using 9.59 g (114 mmol) of 2,3-dimethyl-2-butene and 8.00 g (114 mmol) of 2-methyl-2-butene. The addition of $CFCl_3$ was carried out at −10 °C. The reaction mixture was analyzed by ^{19}F NMR before hydrolysis and the product resonances were integrated. A value of 3.53 was obtained for the ratio of 1-chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane to 1-chloro-1-fluoro-2,2,3-trimethylcyclopropane. Thus, the relative reactivity of 2,3-dimethyl-2-butene to 2-methyl-2-butene is 3.53. When the concentration of all reactants was halved and the amount of THF kept the same, a relative reactivity of 4.00 was obtained.

Acknowledgment. Support of this research in part by the National Science Foundation is gratefully acknowledged by the authors.

Registry No. *tBuCH*=$C(CH_3)_2$, 107-40-4; $(CH_3)_2C$=$C(CH_3)_2$, 563-79-1; $(CH_3)_2C$=$CHCH_3$, 513-35-9; $PhCH_3C$=CH_2, 98-83-9; $(CH_3CH_2)_2C$=CH_2, 760-21-4; nBuOCH=CH_2, 111-34-2; PhCH=CH_2, 100-42-5; nBuCH=CH_2, 592-41-6; tBuCH=CH_2, 558-37-2; $CFCl_3$, 75-69-4; $CFBr_2Cl$, 353-55-9; $FCCl_2COCCl_2F$, 79-51-6; CCl_4, 56-23-5; $PhCCl_3$, 98-07-7; CF_2Br_2, 75-61-6; CH_3CCl_3, 71-55-6; CF_3CCl_3, 354-58-5; $CHCl_3$, 67-66-3; $CHFBr_2$, 1868-53-7; $CHFI_2$, 1493-01-2; Ti, 7440-32-6; FClC:, 1691-88-9; PhClC:, 19807-41-1; F_2C:, 2154-59-8; Cl_2C:, 1605-72-7; H_3CClC:, 31304-51-5; 2*H*-3,4-dihydropyran, 110-87-2; cyclohexene, 110-83-8; *N*-vinyl-2-pyrrolidinone, 88-12-0; *syn*-1-chloro-2,2-dimethyl-3-(1,1-dimethylethyl)-1-fluorocyclopropane, 124155-55-1; *anti*-1-chloro-2,2-dimethyl-3-(1,1-dimethylethyl)-1-fluorocyclopropane, 124155-56-2; 1-chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane, 1727-63-5; *syn*-1-chloro-1-fluoro-2,2,3-trimethylcyclopropane, 16496-04-1; *anti*-1-chloro-1-fluoro-2,2,3-trimethylcyclopropane, 16496-05-2; *syn*-7-chloro-7-fluoro-2-oxabicyclo[4.1.0]heptane, 17301-37-0; *anti*-7-chloro-7-fluoro-2-oxabicyclo[4.1.0]heptane, 17301-36-9; *syn*-(2-chloro-2-fluoro-1-methylcyclopropyl)benzene, 62360-19-4; *anti*-(2-chloro-2-fluoro-1-methylcyclopropyl)benzene, 62360-18-3; 1-chloro-2,2-diethyl-1-fluorocyclopropane, 41641-21-8; *syn*-2-butoxy-1-chloro-1-fluorocyclopropane, 101944-73-4; *anti*-2-butoxy-1-chloro-1-fluorocyclopropane, 101944-74-5; *syn*-7-chloro-7-fluorobicyclo[4.1.0]heptane, 16646-94-9; *anti*-7-chloro-7-fluorobicyclo[4.1.0]heptane, 16646-93-8; *syn*-(2-chloro-2-fluorocyclopropyl)benzene, 35694-71-4; *anti*-(2-chloro-2-fluorocyclopropyl)benzene, 35694-73-6; *syn*-*N*-(2-chloro-2-fluorocyclopropyl)pyrrolidinone, 124155-57-3; *anti*-*N*-(2-chloro-2-fluorocyclopropyl)pyrrolidinone, 124155-58-4; *syn*-2-butyl-1-chloro-1-fluorocyclopropane, 121825-07-8; *anti*-2-butyl-1-chloro-1-fluorocyclopropane, 121825-08-9; 1,2-dichloro-2-methyl-2-phenylcyclopropane, 3591-42-2; 1-chloro-1-phenyl-2,2,3,3-tetramethylcyclopropane, 3141-40-0; 1,1-difluoro-2-methyl-2-phenylcyclopropane, 59164-24-8; 1-chloro-1,2,2,3,3-pentamethylcyclopropane, 21181-48-6.