

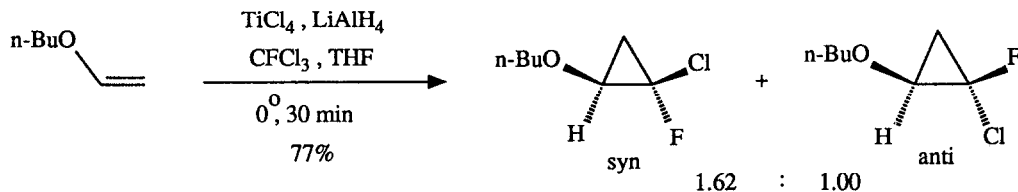
**Generation of Chlorofluorocarbene by Dehalogenation  
of Fluorotrichloromethane with Reduced Titanium.  
A New Synthesis of 1-Chloro-1-fluorocyclopropanes.**

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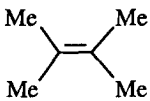
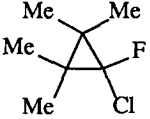
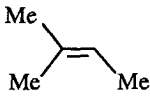
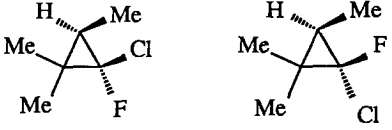
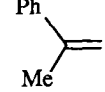
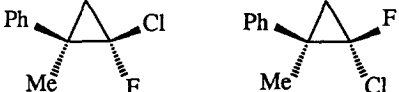
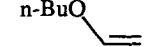
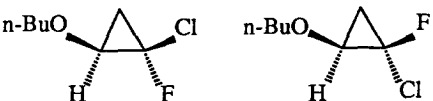


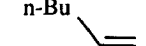
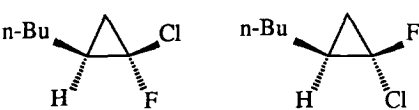
**Abstract:** Reaction of fluorotrichloromethane with reduced titanium at 0° produces chlorofluorocarbene which adds to alkenes, giving 1-chloro-1-fluorocyclopropanes in good yield

Previous attempts to prepare chlorofluorocyclopropanes by reaction of  $\text{CFCl}_3$  with alkyl lithiums,<sup>1</sup> or with phosphines,<sup>2</sup> in the presence of an alkene, have given disappointingly low yields. We now wish to report that chlorofluorocarbene is produced by the reaction of  $\text{CFCl}_3$  with reduced titanium, prepared by reduction of titanium tetrachloride with lithium aluminum hydride.<sup>4</sup> The chlorofluorocarbene has been successfully trapped with various alkenes, providing a new, high-yield synthesis of chlorofluorocyclopropanes.



This new procedure has several advantages over previous methods for generating chlorofluorocarbene.<sup>5</sup> The  $\text{CFCl}_3$  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 non-volatile by-products are produced, facilitating isolation of pure material.

Table 1. Reactions of Alkenes with Chlorofluorocarbene

Alkene	Products	% yield <sup>a</sup>	syn/anti <sup>b</sup>
		90	—
		89	2.22
		85	1.02
		77	1.62
		52	2.23
		12	1.37

a) Yields determined by integration of the  $^{19}\text{F}$  NMR spectrum at 282 MHz with hexafluorobenzene as internal standard. b) Ratios determined by integration of the  $^{19}\text{F}$  NMR for the reaction mixture.

Initial, exploratory reactions of  $\text{CFCl}_3$  with excess  $\alpha$ -methylstyrene gave a yield of only 40%. It was found, however, that it was possible to obtain good yields by using a three-fold excess of  $\text{CFCl}_3$  and titanium, thus basing the yield on the alkene as the limiting reactant. This strategy has the added advantage of being very efficient in terms of alkene used. It was also found that acidic hydrolysis of the reaction mixture will prevent formation of a gelatinous precipitate, thus greatly facilitating the work-up.

We believe that this reaction in all probability involves a free carbene rather than a "carbenoid" species. This conclusion is based upon the fact that the syn/anti product ratios

which we observe are very close to those reported for various other unrelated methods of addition of chlorofluorocarbene to alkenes. Specifically, in base-induced reactions, 2-methyl-2-butene is reported to give a syn/anti ratio of 2.35 when  $\text{CFCl}$  is generated from tetrachlorodifluoroacetone,<sup>12</sup>  $\alpha$ -methylstyrene gave a ratio of 1.0 using  $\text{CFCl}_2\text{CO}_2\text{Et}$ ,<sup>13</sup> and cyclohexene gave a ratio of 2.2 using  $\text{CHFCl}_2$ .<sup>8</sup> These ratios compare well with our observed syn/anti ratios of 2.22, 1.02, and 2.23, respectively. In cases where carbenoids are known to be involved, syn/anti ratios can vary quite dramatically. For example, "free" fluorocarbene gives a syn/anti ratio of 1.0 with cyclohexene,<sup>14</sup> while the copper and zinc carbenoids give values of 2.4<sup>15</sup> and 5.7,<sup>16</sup> respectively.

As can be seen from Table 1, the yields of chlorofluorocyclopropanes decrease with decreasing reactivity of the alkene with chlorofluorocarbene. Monoalkyl-substituted alkenes are the least reactive and give very low yields as has generally been observed for chlorofluorocarbene in the past.<sup>12,8</sup> However, as one might have expected, when the mono-substituted alkene bears an electron-donating substituent, such as in the case of n-butyl vinyl ether, reactivity is enhanced and a good yield can be obtained.

It has also been found that bromofluorocarbene can be generated in a like manner from fluorotribromomethane, and that difluorocarbene can be generated from dibromodifluoromethane, although the latter reaction is only useful for cyclopropanations of more-reactive alkenes. Work on these and related systems is currently in progress and will be reported in due course.

#### Typical Experimental Procedure

A flask containing 300 mL THF under nitrogen was cooled to 0°C and 43.3 g (0.228 mol)  $\text{TiCl}_4$  were carefully added over 9 minutes. To the yellow mixture was carefully added a solution of 9.11 g (0.228 mol) 95%  $\text{LiAlH}_4$  in 200 mL THF over 20 minutes. The dark brown mixture was allowed to stir without cooling for 30 minutes.

The flask was cooled again and 7.61 g (0.0760 mol) n-butyl vinyl ether were added. Then a solution of 31.3g (0.228 mol)  $\text{CFCl}_3$  in 100 mL THF was added at 0°C over 42 minutes. After 30 minutes at 0°C, the mixture was carefully poured into 800 mL 10% HCl containing 400 mL crushed ice. The upper organic layer was separated, then the aqueous layer was extracted once with 300 mL  $\text{CH}_2\text{Cl}_2$  and twice with 200 mL  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with 200 mL 10%  $\text{NaHCO}_3$  and dried over  $\text{Na}_2\text{SO}_4$ .

The solvent was removed by distillation using a 50-cm Vigreux column. Further distillation at reduced pressure using a 15-cm column gave 7.25 g (57%) clear, colorless liquid (bp 69°C at 31 mm). Analysis by GLC indicated a purity of 95%. The 2-butoxy-1-chloro-1-fluorocyclopropane was obtained as a mixture of syn and anti isomers in the ratio of 1.66 to 1.00, as determined by integration of the  $^{19}\text{F}$  NMR spectrum.

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## References and Footnotes

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