

## Selectivity of (Trifluoromethyl)chlorocarbene

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**Abstract:** (Trifluoromethyl)chlorocarbene ( $\text{CF}_3\text{CCl}$ ) was generated by photolysis of 3-(trifluoromethyl)-3-chlorodiazirine and added to eight alkenes affording the corresponding cyclopropanes. Additions to *cis*- and *trans*-butenes were stereospecific. No allylic CH insertion products were observed with any of the substrates. Substrates, reactivities (relative to  $\text{Me}_2\text{C}=\text{CH}_2 = 1.00$ ), and stereoselectivities (syn-Cl/anti-Cl) for the  $\text{CF}_3\text{CCl}$  addition reactions follow:  $\text{Me}_2\text{C}=\text{CMe}_2$ , 0.92, none;  $\text{Me}_2\text{C}=\text{CHMe}$ , 1.17, 1.48;  $\text{Me}_2\text{C}=\text{CH}_2$ , 1.00, none; *cis*- $\text{MeCH}=\text{CHMe}$ , 0.88, 1.65; *trans*- $\text{MeCH}=\text{CHMe}$ , 0.62, none;  $\text{EtCH}=\text{CH}_2$ , 0.48, 1.28; *i*- $\text{PrCH}=\text{CH}_2$ , 0.25, 1.36; *t*- $\text{BuCH}=\text{CH}_2$ , 0.11, 1.66. The reactivity data are analyzed and compared to analogous results for  $\text{CH}_3\text{CCl}$  and  $\text{CCl}_2$ . The carbene selectivity index,  $m_{\text{CXY}}$ , of  $\text{CF}_3\text{CCl}$  is  $\sim 0.19$  ( $m_{\text{CCl}_2} = 1.00$ ), and its steric demand during addition to  $\text{RCH}=\text{CH}_2$  (Taft  $\delta$ ) is 0.41 ( $\delta_{\text{CCl}_2} = 0.88$ ). Relative to  $\text{CH}_3\text{CCl}$ ,  $\text{CF}_3$  strongly destabilizes  $\text{CF}_3\text{CCl}$ . This conclusion follows both from analysis of the experimental data and from ab initio calculations.  $\text{CF}_3\text{CCl}$  is believed to add to alkenes via "early", relatively "open" transition states, in which electronic and steric selectivities are leveled.

The unique polar effects of the trifluoromethyl ( $\text{CF}_3$ ) group have focused much attention on this moiety as a useful probe substituent in mechanistic and spectroscopic investigations.<sup>2</sup> Much progress has been recorded in the areas of heterolytic and homolytic aromatic or aliphatic reaction chemistry,<sup>2</sup> but the influence of the  $\text{CF}_3$  group on the reactivity of carbenic intermediates is poorly characterized from the quantitative standpoint.

Bis(trifluoromethyl)carbene reacts with aromatic and aliphatic substrates, the latter including saturated and unsaturated examples,<sup>3a-d</sup> as well as with carbonyl fluoride (to give an oxirane)<sup>3e</sup> and with alkynes to yield cyclopropenes.<sup>3f</sup> In its reactions with *cis*-butene, *trans*-butene, and cyclohexene,  $(\text{CF}_3)_2\text{C}$  appears to behave as a triplet,<sup>3c</sup> which is known to be the carbene's ground state.<sup>4</sup> Triplet involvement is also apparent in the nonstereospecific addition of (trifluoromethyl)carbene to *cis*-butene.<sup>5</sup>  $\text{CF}_3\text{CH}$  also possesses a triplet ground state,<sup>4</sup> but both singlet and triplets seemed to be involved in its reactions with hydrocarbons. The singlet inserts into CH bonds with very little selectivity, suggesting a destabilizing effect of  $\text{CF}_3$  on a singlet carbenic center.<sup>6</sup> There are also references to reactions of (trifluoromethyl)cyanocarbene<sup>7</sup> and (trifluoromethyl)(carboethoxy)carbene,<sup>8</sup> but these reports do not focus on carbenic reactivity.

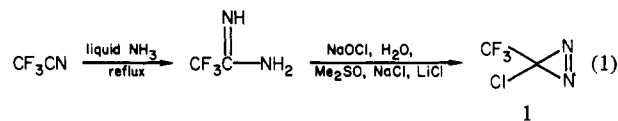
Generally, carbenes bearing halogen atoms directly bonded to the carbenic center are considerably more selective than related carbenes bearing hydrogen or electron-withdrawing substituents.<sup>9</sup> Accordingly,  $\text{CF}_3\text{CHal}$  should be much more amenable to a reactivity study than  $(\text{CF}_3)_2\text{C}$  or  $\text{CF}_3\text{CH}$ . Members of the  $\text{CF}_3\text{CHal}$  class<sup>10</sup> include  $\text{CF}_3\text{CF}$ <sup>11</sup>  $\text{CF}_3\text{CCl}$ ,<sup>12,13</sup> a related species is  $\text{CF}_2\text{H}$ -

$\text{CF}$ .<sup>14</sup>  $\text{CF}_3\text{CF}$  and  $\text{CF}_2\text{HCF}$  are usually generated by pyrolysis ( $\sim 150^\circ\text{C}$ ) of organometallic precursors.<sup>11,14</sup> Selectivity data collected under these conditions would not be directly comparable to the large body of selectivity data now available for other carbenes at  $25^\circ\text{C}$ .<sup>9,15</sup> Similarly,  $\text{CF}_3\text{CCl}$  has been generated by pyrolysis of either  $\text{PhHg}(\text{CF}_3)\text{CBrCl}$  ( $130\text{--}140^\circ\text{C}$ )<sup>12</sup> or 3-(trifluoromethyl)-3-chlorodiazirine ( $120^\circ\text{C}$ ).<sup>13</sup> The latter precursor, however, should also be photochemically labile at  $25^\circ\text{C}$ , making practical a selectivity study of  $\text{CF}_3\text{CCl}$  under mild and normative<sup>9,15</sup> reaction conditions.

Although the carbene-alkene addition reaction is the principal vehicle for the assessment of carbenic selectivity,<sup>15</sup> there are no selectivity studies of  $\text{CF}_3$ -substituted carbenes with simple alkenes. A study of  $\text{CF}_3\text{CCl}$  would bridge this gap and would also provide data directly comparable to analogous results for  $\text{CH}_3\text{CCl}$ .<sup>16</sup> A clear measure of the influence of the  $\text{CF}_3$  group on carbenic selectivity would thus be obtained. We now present the first experimental and theoretical results from a study of  $\text{CF}_3\text{CCl}$  selectivity.

## Results

3-(Trifluoromethyl)-3-chlorodiazirine (**1**)<sup>13</sup> was generated from trifluoroacetamide<sup>13,17</sup> by hypochlorite oxidation<sup>18</sup> and condensed into pentane at  $77\text{ K}$  (eq 1). Portions of the cold pentane solutions

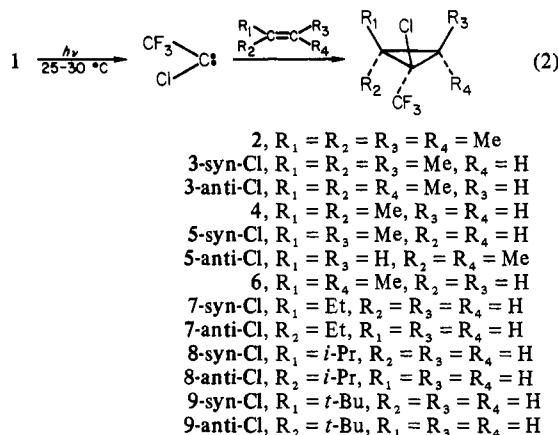


were diluted with various alkenes at  $-78^\circ\text{C}$ , and the dilute diazirine/alkene solutions were then photolyzed for 3 h ( $25\text{--}30^\circ\text{C}$ ) in sealed tubes, using a focused Osram 200-W XE mercury lamp. Products were isolated by preparative GC after careful evaporation of the alkenes. Yields of the isolated cyclopropane products, based

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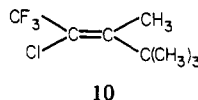
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on trifluoroacetamide, were quite low (2–12%), but the reactions were very clean. The alkenes used were tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, *trans*-butene, 1-butene, isopropylethylene, and *tert*-butylethylene. These afforded cyclopropanes 2–9, respectively, as shown in eq 2.



Photolyses in trimethylethylene, *cis*-butene, and RCH=CH<sub>2</sub> (R = Et, *i*-Pr, *t*-Bu) led to the expected pairs of *syn*/*anti* isomers 3, 5, 7, 8, and 9. The product structures were substantiated by <sup>1</sup>H and <sup>19</sup>F NMR spectra, elemental analysis, mass spectra, and comparisons with literature data for the known compounds 2, 3, 5, and 6.<sup>12</sup> Details of these observations appear in the Experimental Section; however, the differentiation of *syn*/*anti* isomers will be discussed below.

When CF<sub>3</sub>CCl was generated from PhHg(CF<sub>3</sub>)CClBr (130 °C, 54 h) and added to Me<sub>2</sub>C=CMe<sub>2</sub>, cyclopropane 2 and olefin 10

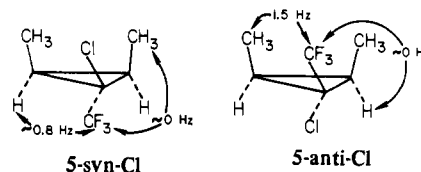


(tentative assignment) were obtained in 58% and 13% yields, respectively.<sup>12</sup> The olefin is most likely a thermal rearrangement product of 2. Thus, we find that *photolysis* of 1 (30 °C, 3 h) in Me<sub>2</sub>C=CMe<sub>2</sub> affords only cyclopropane 2, although thermolysis (120 °C, 3 h) gives both 2 and 10 (NMR<sup>12</sup>) in a GC ratio of 9:1.

**Stereospecificity.** GC permitted the separation of *trans*-butene adduct 6 from isomeric *cis*-butene adducts 5 (conditions: 20 ft × <sup>3</sup>/<sub>16</sub> in. 10% SE-30 on 80/100 Anakrom ABS column at 60 °C; injector, 140 °C; detector, 175 °C; He flow 80 mL/min). Addition of CF<sub>3</sub>CCl (photolytically generated from 1) to *cis*-butene gave only (≥99%) adducts 5, whereas addition of CF<sub>3</sub>CCl to *trans*-butene gave only (≥99%) adduct 6. Control GC experiments demonstrated that 1% of 6 could be readily detected in 99% of 5. The stereospecificity revealed in reactions of CF<sub>3</sub>CCl with *cis*- or *trans*-butene suggests that *singlet*<sup>19</sup>CF<sub>3</sub>CCl is the reactive form of the carbene observed under our reaction conditions. Stereospecific additions of CF<sub>3</sub>CCl to *cis*- and *trans*-butenes were also observed upon thermolysis (135 °C, 10 days) of PhHg(CF<sub>3</sub>)CClBr in these alkenes.<sup>12</sup>

**Stereoselectivity.** CF<sub>3</sub>CCl additions to alkenes which lacked both a center of symmetry and a twofold rotational axis coincident with the double bond afforded isomeric pairs 3, 5, 7, 8, and 9. Excepting the trimethylethylene adducts (3), these were all separable by GC. Assignment of configurations, however, proved very difficult. The case of the *cis*-butene adducts (5) was intensively studied.

The two isomers, 5-*syn*-Cl and 5-*anti*-Cl, were formed in a 1.65:1 ratio (GC) and separated at 70 °C on a 19 ft × 0.25 in. 15% SF-96 on 80/100 Chromsorb W column. Under these conditions, the major product eluted first. At 60 MHz the <sup>1</sup>H NMR spectrum of "major" showed a crude doublet for the Me resonances at δ<sub>CCl<sub>4</sub></sub>



1.10 and a multiplet for the ring protons centered at ~δ 1.53. "Minor" displayed its Me "doublet" and ring CH multiplet at δ 1.27 and 1.67, respectively. In the <sup>19</sup>F NMR spectra (Varian FT-80 spectrometer, equipped with a broad-band probe), major and minor isomers gave signals at 73.6 and 62.6 ppm *upfield* from an internal CCl<sub>3</sub>F reference (in CDCl<sub>3</sub>), respectively.<sup>20</sup>

We assign the major isomer the 5-*syn*-Cl structure and the minor isomer the 5-*anti*-Cl structure on the basis of the long range H–F couplings observed in their high-field <sup>1</sup>H and <sup>19</sup>F NMR spectra. There is strong evidence that long range H–F coupling is largely a "through-space" phenomenon, dependent on spatial proximity of the two nuclei.<sup>21</sup>

In the 300-MHz proton spectrum (Varian SC-300 spectrometer, CDCl<sub>3</sub>) of 5-*syn*-Cl (major), decoupling the ring CH protons reduced the Me resonance to a singlet; there was no (*J* ≤ 0.2 Hz) long-range (anti) CF<sub>3</sub>–CH<sub>3</sub> coupling. On the other hand, the ring CH protons of 5-*syn*-Cl (with Me decoupled) displayed 0.8-Hz residual coupling to the (syn) CF<sub>3</sub> fluorines. These measurements were on 100-Hz width display, 300-MHz spectra, where 1 Hz = 5 mm. In the 188-MHz <sup>19</sup>F NMR spectrum (Varian XL-200 spectrometer), 5-*syn*-Cl displayed the reciprocal 0.75-Hz HF coupling between CF<sub>3</sub> and ring CH atoms. The CF<sub>3</sub> fluorines appeared as a quintet, X<sub>3</sub> of AA'X<sub>3</sub>.

In the 300-MHz proton spectrum of 5-*anti*-Cl (minor), decoupling of the ring CH protons revealed the Me resonances to be a quartet with (syn) CH<sub>3</sub>–CF<sub>3</sub> (<sup>5</sup>J<sub>HF</sub>) = 1.5 Hz. When the Me protons were decoupled and the ring CH protons were observed, however, there was no (≤0.2 Hz) detectable HF coupling. The 188-MHz <sup>19</sup>F NMR spectrum afforded the reciprocal 1.5-Hz H–F coupling between CH<sub>3</sub> and CF<sub>3</sub>. The F resonance was a septet due to coupling to six equivalent methyl protons. The observed long-range coupling constants are summarized in the structural formulas above.

Significant long-range HF coupling between CF<sub>3</sub> and CH<sub>3</sub> or ring CH is observed only when CF<sub>3</sub> is *syn* to the particular proton or protons. In the sense that *syn*-CF<sub>3</sub>–CH or *syn*-CF<sub>3</sub>–CH<sub>3</sub> are the spatially proximate situations,<sup>21</sup> the observed couplings would appear to be consistent only with the suggested configurational assignments.<sup>50</sup>

The stereoselectivity of CF<sub>3</sub>CCl addition to *cis*-butene is therefore preferentially *syn*-Cl (or *anti*-CF<sub>3</sub>). In this, it behaves similarly to CH<sub>3</sub>CCl, for which *syn*-Cl/*syn*-CH<sub>3</sub> stereoselectivity is 2.84:1 at 25–30 °C.<sup>16</sup> In both cases, the major mode of addition opposes the *smaller* (Cl) carbenic substituent to the *cis*-butene Me groups. The kinetically controlled stereoselectivities of CF<sub>3</sub>CCl and CH<sub>3</sub>CCl toward *cis*-butene appear to be mainly determined by relative steric hindrance between carbenic and olefinic substituents in the alternative *syn*-Cl or *anti*-Cl transition states.<sup>22</sup>

On the basis of steric control of CF<sub>3</sub>CCl stereoselectivity, we tentatively assign the stereoselectivities of the other CF<sub>3</sub>CCl addition reactions as indicated in Table I. The *syn*-Cl/*anti*-Cl ratios increase (albeit gently) as R in RCH=CH<sub>2</sub> increases in size. This is in accord with configurational assignments based on relative steric hindrance in kinetically competitive *syn* and *anti* transition states.

We must note, however, that these configurational assignments mean that all of the *syn*-Cl (*anti*-CF<sub>3</sub>) cyclopropanes have *higher* field <sup>19</sup>F chemical shifts than their *anti*-Cl (*syn*-CF<sub>3</sub>) isomers. (See the Experimental Section for <sup>19</sup>F chemical shifts.) This is

(20) All <sup>19</sup>F chemical shifts in this paper are reported in parts per million upfield from internal CCl<sub>3</sub>F in CDCl<sub>3</sub> solvent.

(21) Review: Hilton, J.; Sutcliffe, L. H. *Prog. NMR Spectrosc.* **1975**, *10*, 27.

(22) A fuller discussion appears below.

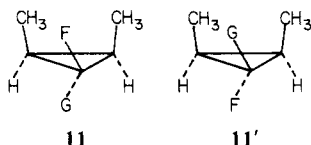
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Table I. Stereoselectivity of CF<sub>3</sub>CCl Additions<sup>a</sup>

alkene	adducts	syn-Cl/ anti-Cl (syn-CF <sub>3</sub> ) <sup>b</sup>
Me <sub>2</sub> C=CHMe	3	1.48 <sup>c</sup>
<i>cis</i> -MeCH=CHMe	5	1.65
EtCH=CH <sub>2</sub>	7	1.28
<i>i</i> -PrCH=CH <sub>2</sub>	8	1.36
<i>t</i> -BuCH=CH <sub>2</sub>	9	1.66

<sup>a</sup> At 25–30 °C; determined by GC analysis of crude reaction mixtures. The GC conditions are described below in the section on relative reactivity experiments. <sup>b</sup> Errors (% a.d.) in repetitive GC analyses were <3%. <sup>c</sup> By integration of the <sup>19</sup>F NMR spectrum of the crude product mixture.

somewhat surprising and contrary to expectations based on compounds such as **11** and **11'** (G = Cl<sup>23</sup> or Ph<sup>24</sup>), where syn-Me



groups shield the syn-cyclopropyl fluorine of **11**, relative to the anti fluorine atom of **11'**. Structural assignments to **5** based on coupling constants thus force us to conclude that CF<sub>3</sub> (in place of F in **11**) is *deshielded* by syn-Me groups. We lack a good explanation for this phenomenon, but we feel that the long-range coupling<sup>21</sup> here constitutes a superior basis for configurational assignments than the less well-rationalized <sup>19</sup>F chemical shifts.

**Relative Reactivity Experiments.** Competitive additions of CF<sub>3</sub>CCl in binary alkene mixtures were carried out in the usual way.<sup>9</sup> Diazirine **1** was photolyzed ( $\lambda > 300$  nm) for 3 h in olefinic solutions (sealed tubes) at 30 °C. Each olefin was present in at least tenfold excess over **1**. Products were stable to the GC conditions selected for quantitative analysis, and the thermal conductivity detector was calibrated by using pure products. Relative reactivities for olefin a vs. olefin b were calculated from expression 3, where  $P_i$  is the mole fraction of product cyclopropanes

$$(k_a/k_b) = (P_a/P_b)(O_b/O_a) \quad (3)$$

and  $O_i$  is the initial mole fraction of olefins.<sup>9</sup> Experimentally determined relative reactivities are collected in Table II.

## Discussion

**Steric Selectivity.** The stereoselectivity of CXY carbenic additions to (e.g.) *cis*-butene depends on the relative energies of the X/Me<sub>2</sub> and Y/Me<sub>2</sub> nonbonded interactions in the alternative syn-X and syn-Y transition states.<sup>9,25</sup> At appropriate internuclear separations, X/Me<sub>2</sub> interactions can be attractive due to van der Waals or London dispersion forces.<sup>25</sup> At large reactant separations, in the early transition states associated with highly exothermic reactions, these interactions may also be attractive due to in-phase secondary orbital interactions between carbenic and olefinic substituents ("steric attraction").<sup>26</sup> Of course, at sufficiently close separations, the X/Me<sub>2</sub> interaction will be net repulsive because of closed-shell repulsions between the carbenic and olefinic substituents ("steric hindrance").<sup>25,26</sup>

CF<sub>3</sub>CCl exhibits syn-Cl (or anti-CF<sub>3</sub>) stereoselectivity toward *cis*-butene with syn-Cl/anti-Cl = 1.65. This seems consistent with both electronic and steric expectations. Chlorine interacts attractively with syn-CH<sub>3</sub> groups in carbenic additions of ClCR to *cis*-butene. For example addition of ClCF to *cis*-butene is syn-Cl stereoselective,<sup>23</sup> although preferential syn-F addition might have been anticipated on the basis of relative steric hindrance (Cl >

F). Dominant electrostatic attraction of the more polarizable Cl for the Me groups in the alternative addition transition states has been held responsible.<sup>23,27</sup> The additions of ClCCH<sub>3</sub>,<sup>16</sup> ClCC<sub>6</sub>H<sub>5</sub>,<sup>28</sup> and ClC-cyclo-C<sub>3</sub>H<sub>5</sub><sup>29</sup> to *cis*-butene are also syn-Cl stereoselective, although, in these latter cases, the greater steric demand of the second carbenic substituent (relative to Cl) must reinforce the syn-Cl-directing attractive forces.

We believe that syn-Cl addition of CF<sub>3</sub>CCl to *cis*-butene is also buttressed by the smaller steric demand of Cl, relative to CF<sub>3</sub>. The differential Taft steric substituent constant,  $\Delta E_s (=E_s^{CF_3} - E_s^{Cl}) = -1.34$ , with CF<sub>3</sub> the sterically more demanding substituent.<sup>30</sup>

Although the stereoselectivity of CF<sub>3</sub>CCl appears (perhaps deceptively) to be readily rationalized, comparison with the stereoselectivity of CH<sub>3</sub>CCl presents a problem. The larger steric demand of CF<sub>3</sub>, relative to CH<sub>3</sub> ( $\Delta E_s = -1.16$ ),<sup>30</sup> suggests that CH<sub>3</sub>CX should exhibit greater syn-CH<sub>3</sub> stereoselectivity (or at least *less* anti-CH<sub>3</sub> stereoselectivity) than would be observed for CF<sub>3</sub> in the corresponding reactions of CF<sub>3</sub>CX. Indeed, it appears that CH<sub>3</sub>CH adds to propene with a small syn-CH<sub>3</sub> preference (1.4:1),<sup>31</sup> whereas, under conditions where its addition to *cis*-butene is reasonably stereospecific, CF<sub>3</sub>CH adds to propene with slight anti-CF<sub>3</sub> stereoselectivity (1.2:1).<sup>32</sup> We might therefore expect CH<sub>3</sub>CCl to be *less* syn-Cl (i.e., more syn-CH<sub>3</sub>) stereoselective than CF<sub>3</sub>CCl. That is, CF<sub>3</sub>CCl should exhibit greater anti-CF<sub>3</sub> stereoselectivity than the anti-CH<sub>3</sub> stereoselectivity shown by CH<sub>3</sub>CCl. The result, however, is the reverse: syn-Cl/syn-CR<sub>3</sub> selectivities for additions to *cis*-butene are 2.84:1 for CH<sub>3</sub>CCl<sup>16</sup> and only 1.65:1 for CF<sub>3</sub>CCl (Table I).

Among several possible explanations, we prefer the following one. CF<sub>3</sub>CCl is a destabilized, highly reactive carbene. Its addition reaction transition states are early and relatively "open", so that differential steric (and electronic) effects are minimized. CH<sub>3</sub>CCl, on the other hand, is a more stabilized, less reactive species, which utilizes later, tighter addition transition states, where differential substituent effects are more developed.

Below, we present calculational and experimental evidence supporting this rationalization. Here, however, we note that a similar conclusion emerges from direct comparison of the "steric selectivities" of CF<sub>3</sub>CCl and CCl<sub>2</sub>. The data of Table II permits calculation of the reactivities of CF<sub>3</sub>CCl in additions to RCH=CH<sub>2</sub>, relative to 1-butene (R = Et). In Table III, we compare these reactivities to analogous CCl<sub>2</sub> data,<sup>33</sup> with all reactivities measured at 25–30 °C. The CF<sub>3</sub>CCl reactivities may also be *partitioned*<sup>34</sup> so as to incorporate the experimental syn/anti preferences (Table I). The resulting partial relative reactivities appear in Table III.

Inspection of the  $k_{rel}$  values indicates that CF<sub>3</sub>CCl experiences *less* steric retardation than CCl<sub>2</sub> in additions to RCH=CH<sub>2</sub> as a consequence of the increasing size of R, despite the anticipated greater steric demand of CF<sub>3</sub>CCl. This conclusion is reinforced by correlating the logarithms of the  $k_{rel}$  data with  $E_s$ ,<sup>30</sup> the correlation slopes ( $\delta$ ) are also shown in Table III. Note that  $\delta_{CF_3CCl}$  (0.41), which represents the susceptibility of CF<sub>3</sub>CCl to steric hindrance during its addition reactions, is *less* than  $\delta_{CCl_2}$  (0.88) for CCl<sub>2</sub> additions to the same substrates under comparable conditions. This is so whether we examine  $\delta_{CF_3CCl}$  on the basis of the overall relative reactivities of CF<sub>3</sub>CCl ( $\delta = 0.41$ ) or use the partial relative reactivities ( $\delta_{CF_3CCl}^{syn-Cl} = 0.39$ ;  $\delta_{CF_3CCl}^{syn-CF_3} = 0.47$ ). Addition of CF<sub>3</sub>CCl to RCH=CH<sub>2</sub> in the syn-CF<sub>3</sub> mode is

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Table II. Experimentally Observed Relative Reactivities of CF<sub>3</sub>CCl (30 °C)

case	olefin a	olefin b	GC condtns		$k_a/k_b^b$
			column <sup>a</sup>	$T, ^\circ\text{C}$	
1	<i>cis</i> -MeCH=CHMe	Me <sub>2</sub> C=CH <sub>2</sub>	A	60	0.88 ± 0.02
2	<i>trans</i> -MeCH=CHMe	<i>cis</i> -MeCH=CHMe	A	55	0.71 ± 0.01
3	Me <sub>2</sub> C=CHMe	Me <sub>2</sub> C=CH <sub>2</sub>	A	70	1.17 ± 0.05
4	Me <sub>2</sub> C=CMe <sub>2</sub>	Me <sub>2</sub> C=CHMe	A	85	0.72 ± 0.03
5	Me <sub>2</sub> C=CMe <sub>2</sub>	<i>cis</i> -MeCH=CHMe	A	65, 95 <sup>c</sup>	1.12 ± 0.01
6	<i>i</i> -PrCH=CH <sub>2</sub>	EtCH=CH <sub>2</sub>	B	60	0.52 ± 0.02
7	<i>t</i> -BuCH=CH <sub>2</sub>	<i>i</i> -PrCH=CH <sub>2</sub>	B	70	0.44 ± 0.02
8	<i>i</i> -PrCH=CH <sub>2</sub>	Me <sub>2</sub> C=CH <sub>2</sub>	B	60	0.25 ± 0.01

<sup>a</sup> Column A: 19 ft × 0.25 in 15% SF-96 on 80/100 Chromosorb W; injector, 140–150 °C; detector, 170 °C; He flow, 80 mL/min (85 mL/min in case 4). Column B: 20 ft × 3/16 in 10% SE-30 on 80/100 Anakrom ABS; injector, 135 °C; detector, 175 °C; He flow, 60 mL/min (65 mL/min in case 7). <sup>b</sup> Where applicable, relative reactivities were based on composites of syn + anti isomeric cyclopropane products. Errors represent the average deviations of two experiments. <sup>c</sup> Programmed from 65 to 95 °C at 4 °C/min after 18 min at 65 °C.

Table III. Comparative Relative Reactivities of CF<sub>3</sub>CCl and CCl<sub>2</sub><sup>a</sup>

substrate (R in RCH= CH <sub>2</sub> )	$(k_R/k_{\text{iso}})_{\text{CCl}_2}^b$	$(k_R/k_{\text{iso}})_{\text{CF}_3\text{CCl}}$		
		overall <sup>c</sup>	syn-Cl <sup>d</sup>	syn-CF <sub>3</sub> <sup>e</sup>
Et	1.00	1.00	1.12	0.88
<i>i</i> -Pr	0.48	0.52	0.60	0.44
<i>t</i> -Bu	0.051	0.23	0.28	0.17
$\delta^f$	0.88 <sup>g</sup>	0.41	0.39	0.47

<sup>a</sup> EtCH=CH<sub>2</sub> is the standard substrate; 25–30 °C. <sup>b</sup> From ref 33. <sup>c</sup> The overall  $k_{\text{rel}}$  is the sum of both syn-Cl and anti-Cl (=syn-CF<sub>3</sub>) additions of CF<sub>3</sub>CCl to RCH=CH<sub>2</sub>. The  $k_{\text{rel}}$  values are normalized to EtCH=CH<sub>2</sub> = 1.00 from the data in Table II. <sup>d</sup> Relative reactivities for addition of CF<sub>3</sub>CCl in the syn-Cl mode, calculated from the overall  $k_{\text{rel}}$  values and the syn-Cl/anti-Cl stereo-selectivities of Table I.  $k_{\text{rel}}^{\text{syn-Cl}}$  values have been multiplied by 2.0 to put them on the same scale as the CCl<sub>2</sub> and overall CF<sub>3</sub>CCl  $k_{\text{rel}}$ 's. <sup>e</sup> Relative reactivities for addition of CF<sub>3</sub>CCl in the syn-CF<sub>3</sub> mode; cf. footnote d. <sup>f</sup> Slopes of log  $k_{\text{rel}}$  vs.  $E_s$ .<sup>30</sup> <sup>g</sup> From ref 33.

somewhat more sterically demanding than addition in the syn-Cl mode, but both  $\delta$  values are considerably less than  $\delta_{\text{CCl}_2}$ .<sup>35</sup> This point remains valid even if our syn/anti structural assignments (see above) are reversed.

Thus, the larger CF<sub>3</sub>CCl behaves as a less sterically demanding carbene than the smaller CCl<sub>2</sub>. This is consistent with the idea that CF<sub>3</sub>CCl additions proceed through an earlier, more open transition state than the analogous addition reactions of CCl<sub>2</sub>.

**Discrimination.** The CF<sub>3</sub>CCl relative reactivities of Table II, adjusted to an isobutene standard ( $k_{\text{rel}} = 1.00$ ), are collected in Table IV, together with analogous results for CH<sub>3</sub>CCl<sup>16</sup> and CCl<sub>2</sub>.<sup>36</sup> Clearly, CF<sub>3</sub>CCl is considerably less discriminating across our standard set<sup>15</sup> of olefinic substrates than either CH<sub>3</sub>CCl or CCl<sub>2</sub>. Notice that CF<sub>3</sub>CCl appears to be less reactive toward Me<sub>2</sub>C=CMe<sub>2</sub><sup>37</sup> than toward Me<sub>2</sub>C=CHMe, in contrast to the behavior of typical electrophilic carbenes.<sup>15</sup> It might be suggested that this represents a differential steric effect operating against the tetrasubstituted alkene. This is unlikely, however, because CCl<sub>2</sub>, which exhibits a greater steric demand than CF<sub>3</sub>CCl (see above), shows no evidence of steric discrimination against Me<sub>2</sub>C=CMe<sub>2</sub>.

The most generally applicable way to quantitatively measure the olefinic discrimination of an electrophilic carbene is to determine a "carbene selectivity index",  $m_{\text{CXY}}$ , defined as the

(35) Correlations of the  $k_{\text{rel}}$  data of Table III using DeTar's revised  $E_s$  values afford  $\delta$ 's which differ by <3% from the tabulated values obtained with Taft's  $E_s$  parameters;<sup>30</sup> cf. DeTar, D. F. *J. Org. Chem.* **1980**, *45*, 5166 and references therein.

(36) See ref 9, p 221.

(37) The relative reactivity ratio for CF<sub>3</sub>CCl with Me<sub>2</sub>C=CMe<sub>2</sub> vs. Me<sub>2</sub>C=CH<sub>2</sub> could not be determined directly because Me<sub>2</sub>C=CMe<sub>2</sub> and adduct 4 had similar volatilities and GC behavior.  $k_{\text{Me}_2\text{C}=\text{CMe}_2}/k_{\text{Me}_2\text{C}=\text{CH}_2}$  was therefore calculated indirectly in two different ways; cf. Table IV, footnote d. Although the estimated error in the final value is ~9%, there is little doubt that Me<sub>2</sub>C=CMe<sub>2</sub> is not more reactive, and probably somewhat less reactive, toward CF<sub>3</sub>CCl than is Me<sub>2</sub>C=CHMe.

Table IV. Relative Reactivities of XCCl toward Olefins

olefin	X		
	CF <sub>3</sub> <sup>a</sup>	CH <sub>3</sub> <sup>b</sup>	Cl <sup>c</sup>
Me <sub>2</sub> C=CMe <sub>2</sub>	0.92 <sup>d</sup>	3.87	8.98
Me <sub>2</sub> C=CHMe	1.17 <sup>e</sup>	2.44 <sup>e</sup>	3.12
Me <sub>2</sub> C=CH <sub>2</sub>	1.00	1.00	1.00
<i>cis</i> -MeCH=CHMe	0.88 <sup>e</sup>	0.74 <sup>e</sup>	0.27
<i>trans</i> -MeCH=CHMe	0.62 <sup>f</sup>	0.52	0.18
EtCH=CH <sub>2</sub>	0.48 <sup>e,g</sup>		
<i>i</i> -PrCH=CH <sub>2</sub>	0.25 <sup>e</sup>		
<i>t</i> -BuCH=CH <sub>2</sub>	0.11 <sup>e,h</sup>		

<sup>a</sup> This work, 30 °C. <sup>b</sup> Reference 16, 25–30 °C. <sup>c</sup> Reference 36, 25 °C. <sup>d</sup> This is the mean of the reactivities calculated from Table II, cases 4 and 3 ( $k_{\text{Me}_2\text{C}=\text{CMe}_2} = 0.84$ ) and cases 5 and 1 ( $k_{\text{Me}_2\text{C}=\text{CHMe}} = 0.99$ ). The error associated with the mean is estimated to be ±0.08 (~9%). <sup>e</sup> Composite of syn and anti modes of addition to this olefin. <sup>f</sup> Calculated from Table II, cases 2 and 1. <sup>g</sup> Calculated from Table II, cases 6 and 8. <sup>h</sup> Calculated from Table II, cases 7 and 8.

least-squares slope of log  $(k_i/k_o)_{\text{CXY}}$  vs. log  $(k_i/k_o)_{\text{CCl}_2}$ .<sup>15,38</sup> Applied to CH<sub>3</sub>CCl, this procedure leads to  $m_{\text{CH}_3\text{CCl}} = 0.50$ , on a scale where  $m_{\text{CCl}_2} = 1.00$ .<sup>38</sup> The CF<sub>3</sub>CCl data cannot readily be treated in this way because of the obvious lack of linearity between the CF<sub>3</sub>CCl and CCl<sub>2</sub> (log)  $k_{\text{rel}}$  data. If the Me<sub>2</sub>C=CMe<sub>2</sub> substrate is omitted, however, a four-point  $m_{\text{CF}_3\text{CCl}}$  value of 0.19 can be derived from the logarithms of the remaining CF<sub>3</sub>CCl and CCl<sub>2</sub> relative reactivities. This correlation is still rather poor,  $r = 0.91$ , significant only at the 90% confidence level.

Previously, we showed that the experimentally determined  $m_{\text{CXY}}$  values of nine carbenes could be correlated by eq 4,<sup>15,38</sup> in which

$$m_{\text{CXY}} = -1.10\sum_{\text{X,Y}}\sigma_{\text{R}}^+ + 0.53\sum_{\text{X,Y}}\sigma_{\text{I}} - 0.31 \quad (4)$$

$\sum_{\text{X,Y}}$  represents the sum of the appropriate  $\sigma$  constants<sup>39</sup> for the substituents of CXY. Using<sup>39</sup>  $(\sigma_{\text{R}}^+)_{\text{CF}_3} = +0.08$  and  $(\sigma_{\text{I}})_{\text{CF}_3} = +0.45$ , together with appropriate  $\sigma$  constants for Cl,<sup>39</sup> we calculate  $m_{\text{CF}_3\text{CCl}} = 0.48$  from eq 4. This predicts that CF<sub>3</sub>CCl should be similar in olefinic selectivity to CH<sub>3</sub>CCl ( $m = 0.50$ ), despite our prejudice that the very different electronic properties of the CF<sub>3</sub><sup>2</sup> and CH<sub>3</sub> substituents should confer rather different olefinic selectivities on their respective chlorocarbene derivatives. If we employ revised<sup>40a</sup> values of  $(\sigma_{\text{R}}^+)_{\text{CF}_3} = +0.20$  and  $(\sigma_{\text{I}})_{\text{CF}_3} = 0.38$ , we calculate  $m_{\text{CF}_3\text{CCl}} = 0.31$ , significantly less selective than CH<sub>3</sub>CCl, but still more selective than the admittedly imprecise experimental value of ~0.19.

(38) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.

(39) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(40) (a) Private communication from Professor M. Charton, Pratt Institute, Brooklyn, N.Y. These revised  $\sigma$  values are normalized to the Ehrenson et al. scale<sup>39</sup> and are based on the compilation by: Charton, M. *Prog. Phys. Org. Chem.*, in press. We thank Professor Charton for making this information available to us in advance of publication. (b) Weeks, G.; Horák, V. *J. Org. Chem.* **1980**, *45*, 2068.

We also examined an extended form of eq 4 which included a term in  $\sigma^-$  to cope with the strongly electron-withdrawing  $\text{CF}_3$  substituent; cf. eq 4a. Equations of this form have been shown

$$m_{\text{CXY}} = -1.70\sum_{\text{X,Y}}\sigma_{\text{R}}^+ + 0.76\sum_{\text{X,Y}}\sigma_{\text{I}} + 0.64\sum_{\text{X,Y}}\sigma_{\text{R}}^- - 0.66 \quad (4a)$$

to effectively deal with wide variations of electronic effects.<sup>40b</sup> As before,<sup>38</sup> multiple linear regression analysis of the dependence of  $m_{\text{CXY}}^{\text{obsd}}$  for our nine base carbenes on  $(\sum_{\text{X,Y}}\sigma_{\text{I}})$ ,  $\sigma_{\text{R}}^+$ , and  $\sigma_{\text{R}}^-$  (A)<sup>39</sup> defined the coefficients of the new correlation equation. Equation 4a correlated the selectivities of the base carbenes better than did eq 4; the standard deviation of differences ( $\Delta m = m^{\text{obsd}} - m^{\text{calcd}}$ ) was 0.070 for eq 4a vs. 0.089 for eq 4. Similarly,  $f$ , the root mean square of the  $\Delta m$ 's/root mean square of the experimental  $m$ 's, was 0.077 for eq 4a vs. 0.092 for eq 4; correlations of acceptable precision have  $f < 0.1$ .<sup>39</sup> Calculation with eq 4a, using revised<sup>40a</sup>  $\text{CF}_3$  values of  $\sigma_{\text{R}}^+$ ,  $\sigma_{\text{I}}$ , and  $\sigma_{\text{R}}^-$  (+0.23), gave  $m_{\text{CF}_3\text{CCl}} = 0.25$ , in reasonably good agreement with  $m_{\text{CF}_3\text{CCl}}^{\text{obsd}} \approx 0.19$ .

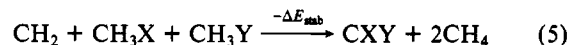
It is apparent that the olefinic discrimination of  $\text{CF}_3\text{CCl}$  is unusual. The carbene does not display the normal linearity<sup>15</sup> for  $\log k_{\text{rel}}$  vs.  $\log (k_{\text{rel}})_{\text{CCl}_2}$ , and simulation of its approximate  $m$  value requires revision of our correlation equation.<sup>38</sup> However, its observed selectivity is significantly less than that of  $\text{CH}_3\text{CCl}$ , which is both reassuring and intuitively consonant with the expected destabilization of a singlet  $\text{XCCl}$  by a strongly electron-withdrawing group such as  $\text{CF}_3$ .<sup>41</sup> On the other hand,  $\text{CF}_3\text{CCl}$  is *not completely unselective*; disregarding the  $\text{Me}_2\text{C}=\text{CMe}_2$  data in Table IV, we note a clear decrease in  $\text{CF}_3\text{CCl}$  relative addition rates as we progress from tri- to di- to monosubstituted alkenes.

Qualitatively, the expressed selectivity of  $\text{CF}_3\text{CCl}$  places it between  $\text{HCCOOEt}$  and  $\text{BrCCOOEt}$ .<sup>38</sup> The latter ( $m^{\text{obsd}} = 0.29$ ,  $m^{\text{calcd}} = 0.26$ )<sup>38</sup> is a well-behaved electrophilic carbene, less selective than  $\text{CH}_3\text{CCl}$  ( $m^{\text{obsd}} = 0.50$ ,  $m^{\text{calcd}} = 0.58$ ),<sup>38</sup> but now seen to be more selective than  $\text{CF}_3\text{CCl}$  ( $m^{\text{obsd}} \approx 0.19$ ). On the other hand,  $\text{HCCOOEt}$  is less selective than  $\text{CF}_3\text{CCl}$ . It too fails to exhibit linearity of  $k_{\text{rel}}$  vs.  $(k_{\text{rel}})_{\text{CCl}_2}$ , but, in addition, it undergoes allylic C—H insertion competitively with addition to  $\text{C}=\text{C}$ ,<sup>38</sup> which  $\text{CF}_3\text{CCl}$  does not do.

Again, the data are consistent with a highly reactive, quite unselective, singlet electrophilic  $\text{CF}_3\text{CCl}$ . Recently, we showed that the *absolute* rate constant for addition of  $\text{PhCCl}$  to  $\text{Me}_2\text{C}=\text{CMe}_2$  was  $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>42</sup> Because  $\text{PhCCl}$  ( $m^{\text{obsd}} = 0.83$ ) is considerably *more* discriminating toward alkenes and presumably substantially less reactive than  $\text{CF}_3\text{CCl}$ ,<sup>43</sup> it is reasonable to believe that  $k_{\text{abs}}$  for  $\text{CF}_3\text{CCl}$  addition to  $\text{Me}_2\text{C}=\text{CMe}_2$  is greater than  $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Conceivably, the rate of this reaction might approach diffusion control. If so, " $k_{\text{rel}}$ " for  $\text{Me}_2\text{C}=\text{CMe}_2$  could well be out of line with expectations based upon the reactivities of less substituted, less reactive alkenes. Alternatively, the compensation between differential enthalpies and entropies of activation, upon which the observed relationships<sup>15</sup> between carbene/alkene structure and reactivity probably rest,<sup>45</sup> may well fail for carbenes as reactive as  $\text{CF}_3\text{CCl}$  or  $\text{HCCOOEt}$ .

Additional support for the experimental picture of a highly reactive, quite unselective  $\text{CF}_3\text{CCl}$  emerges from ab initio calculations. The geometry and orbital energies (HOMO and LUMO) of  $\text{CF}_3\text{CCl}$  were calculated by STO-3G/4-31G procedures.<sup>46</sup> The C—C and C—Cl bond lengths and the CCl angle of  $\text{CF}_3\text{CCl}$  were optimized by using the STO-3G basis set; the  $\text{CF}_3$  geometry was fixed by using standard values. Next, the

frontier molecular orbital energies were calculated by using the 4-31G basis set. The 4-31G orbital energies of the singlet carbene were found to be  $-0.33 \text{ eV}$  (LUMO or p) and  $-11.96 \text{ eV}$  (HOMO or  $\sigma$ ). Next, we calculated the *carbene stabilization energy*,  $\Delta E_{\text{stab}}^{\text{CXY}}$ , the stabilization of CXY relative to the corresponding substituted methane according to the isodesmic reaction (5). The



negative of the 4-31G energy of eq 5 is defined as  $\Delta E_{\text{stab}}^{\text{CXY}}$ .<sup>46</sup> The  $\Delta E_{\text{stab}}$  of  $\text{CF}_3\text{CCl}$  was found to be  $1.40 \text{ kcal/mol}$ , a much lower stabilization energy than those of 12 previously studied carbenes.<sup>44</sup>  $\Delta E_{\text{stab}}$  of  $\text{CH}_3\text{CCl}$ , for example, was calculated as  $29.3 \text{ kcal/mol}$ . Obviously, the exchange of  $\text{CF}_3$  ( $\text{CF}_3\text{CCl}$ ) for  $\text{CH}_3$  ( $\text{CH}_3\text{CCl}$ ) greatly destabilizes the carbene.

There is a direct relation between  $\Delta E_{\text{stab}}$  and carbenic selectivity. Indeed,  $\Delta E_{\text{stab}}$  and  $m_{\text{CXY}}$  afford linear correlation 6.<sup>44</sup> The very

$$m_{\text{CXY}}^{\text{calcd}} = 0.035\Delta E_{\text{stab}} - 0.449 \quad (6)$$

low calculated  $\Delta E_{\text{stab}}$  for  $\text{CF}_3\text{CCl}$  thus indicates a very unselective carbene. There are some problems with the calculations, however. The calculated C—C bond length ( $1.630 \text{ \AA}$ ) is obviously too long, and we suspect that  $\Delta E_{\text{stab}}$  is too low. Indeed, correlation 6 predicts  $m_{\text{CF}_3\text{CCl}} = -0.4$  (based on  $\Delta E_{\text{stab}}^{\text{obsd}} = 1.40$ ), an impossible value. Put the other way, taking  $m_{\text{CF}_3\text{CCl}}^{\text{obsd}} \approx 0.19$ , the  $\Delta E_{\text{stab}}/m_{\text{CXY}}$  correlation gives  $\Delta E_{\text{stab}}^{\text{CF}_3\text{CCl}} \approx 18 \text{ kcal/mol}$ . Although much larger than the 4-31G  $\Delta E_{\text{stab}}$  for  $\text{CF}_3\text{CCl}$ , this value is  $11 \text{ kcal/mol}$  less than  $\Delta E_{\text{stab}}$  calculated for  $\text{CH}_3\text{CCl}$  and still corresponds to significant carbenic destabilization due to the  $\text{CF}_3$  substituent.

In summary, all experimental results, as well as a brief theoretical study, describe  $\text{CF}_3\text{CCl}$  as a highly reactive, unselective carbene which adds to alkenes via early, relatively open transition states. This behavior reflects the destabilizing character of the strongly electron-withdrawing  $\text{CF}_3$  substituent.<sup>2,41</sup> Despite its low selectivity,  $\text{CF}_3\text{CCl}$  adds stereospecifically to the 2-butenes and, with simple alkenes, does not insert into allylic C—H bonds competitively with C=C addition.  $\text{CF}_3\text{CCl}$  is the most unselective carbene for which an  $m$  value has been even approximately defined, and its reactions should serve as a good model for those of other poorly stabilized (or destabilized), singlet, disubstituted carbenes.

## Experimental Section

**General Data.** Proton NMR spectra were normally recorded with a Varian T-60 spectrometer; chemical shifts are reported in  $\delta$  units. Fluorine NMR spectra were normally recorded with a Varian FT-80 spectrometer (broad-band probe); chemical shifts are reported in parts per million upfield from an internal  $\text{CCl}_3\text{F}$  reference. Gas chromatography employed Varian Aerograph Model 90P and 1700 instruments. Mass spectra were determined with a Hewlett-Packard Model 5985 GC-MS system. Microanalyses were performed by Robertson Laboratory, Florham Park, N.J.

**3-Chloro-3-(trifluoromethyl)diazirine (1).**<sup>13,17</sup> Anhydrous ammonia (50 g) was condensed into a 100-mL three-neck flask, equipped with a magnetic stirring bar and cooled in a Dry-Ice/acetone bath. To this stirred solution was added 10 g (105 mmol) of trifluoroacetone nitrile (Columbia Organics) slowly via a gas inlet tube over 2.5 h at  $-60$  to  $-70$  °C. After addition, the solution was refluxed (Dry-Ice/acetone condenser) for 30 min. Excess ammonia was removed by evaporation at 20 °C, and residual ammonia was removed by three freeze/pump/thaw cycles ( $-30$  °C ( $<1 \text{ mmHg}$ )). The product, trifluoroacetimidine, was obtained in about 90% yield and was generally used without further purification. Alternatively, the crude product could be fractionated under reduced pressure (bp  $34$ – $35$  °C ( $11 \text{ mmHg}$ )) (lit.<sup>47</sup> bp  $35$ – $36$  °C ( $11 \text{ mmHg}$ )).

Oxidation was carried out by Graham's procedure.<sup>13,18</sup> To a cooled ( $0$  °C) solution of 6.72 g (60 mmol) of trifluoroacetimidine and 11.6 g of  $\text{LiCl}$  in 200 mL of  $\text{Me}_2\text{SO}$  was quickly added 500 mL of aqueous sodium hypochlorite solution,<sup>48</sup> saturated with  $\text{NaCl}$ . The reaction solution was rapidly stirred during addition and continuously evacuated ( $P < 1 \text{ mmHg}$ ) through a train composed of a U-tube filled with  $\text{NaOH}$

(41) For examples and leading references to destabilizing effects of the  $\text{CF}_3$  group, see: Greenberg, A.; Liebman, J. F.; Van Vechten, D. *Tetrahedron* **1980**, *36*, 1161.

(42) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

(43) Carbene-alkene addition reactions appear to follow the reactivity-selectivity principle.<sup>44</sup>

(44) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *103*, 1770.

(45) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

(46) Details and leading references for these procedures may be found in ref 44.

(47) Reilly, W. L.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6032.

(48) Commercial liquid "pool chlorine", 12.4% sodium hypochlorite by weight, was used.

pellets, followed by three traps. The first trap was cooled to  $-77^{\circ}\text{C}$ , while the second and third traps were cooled to 77 K with liquid nitrogen. The last trap contained 1 mL of pentane. Diazirine **1** which collected in the second trap was cautiously distilled under vacuum at  $25^{\circ}\text{C}$  into the third trap. The final pentane solution of **1** was used without further purification. The yield was  $\sim 45\%$ , and the spectral characterization of **1** has been reported.<sup>13,49</sup> *Caution:* Diazirine **1** is potentially explosive.

**Synthesis of Cyclopropanes. General Procedure.** About 15 mL of the desired alkene was added (or condensed) into a screw-top (Pyrex) Carius tube, which also contained a small magnetic stirring bar. The alkene was cooled to  $-78^{\circ}\text{C}$ , and the pentane/diazirine solution was added. The tube was sealed and warmed to  $25^{\circ}\text{C}$ , and the contents were stirred and photolyzed for 3 h at  $25\text{--}30^{\circ}\text{C}$  by using a focused Osram 200-W Xe mercury lamp. After photolysis, the reaction solution was cooled to  $-78^{\circ}\text{C}$ , the tube was opened, and the alkene was cautiously evaporated by warming. Crude products were then subjected to GC for product isolation and analysis. Yields of GC-isolated cyclopropanes ranged from 2 to 12% on the basis of (trifluoromethyl)acetamide ( $\sim 4$  to 27% on the basis of diazirine **1**).

**1-Chloro-1-(trifluoromethyl)-2,2,3,3-tetramethylcyclopropane (2).**<sup>12</sup> This product was formed from  $\text{CF}_3\text{CCl}$  and  $\text{Me}_2\text{C}=\text{CMe}_2$  and was isolated by GC on an 11 ft  $\times$  0.25 in. 15% SF-96 on 80/100 Chromosorb W column at  $85^{\circ}\text{C}$  (injector,  $135^{\circ}\text{C}$ ; detector,  $170^{\circ}\text{C}$ ; He flow, 60 mL/min). The retention time was 15.3 min. The proton NMR spectrum ( $\delta$ ,  $\text{CCl}_4$ ) showed overlapping singlets at 1.25 (lit.,<sup>12</sup> 1.23). Mass spectrum:  $m/e$  200, 202,  $\text{M}^+$ ; base peak,  $\text{M}^+ - \text{Cl}$ .

**1-Chloro-1-(trifluoromethyl)-2,2,3-trimethylcyclopropanes (3-*syn*-Cl and 3-*anti*-Cl).**<sup>12</sup> These products were formed from  $\text{CF}_3\text{CCl}$  and trimethylethylene. They were isolated as a mixture by GC, using the column described for **2**, at  $80^{\circ}\text{C}$  (injector,  $150^{\circ}\text{C}$ ; detector,  $170^{\circ}\text{C}$ ; He flow, 60 mL/min): retention times, 18.1 and 19.2 min; NMR ( $\delta$ ,  $\text{CCl}_4$ ) 0.95–1.50 (m) (lit.,<sup>12</sup> 0.97–1.57);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ) major isomer, 63.9, minor isomer, 59.8;<sup>20</sup> ratio, 1.48:1. Mass spectrum,  $m/e$  186, 188,  $\text{M}^+$ , base peak,  $\text{M}^+ - \text{Cl}$ .

**1-Chloro-1-(trifluoromethyl)-2,2-dimethylcyclopropane (4).** This product was formed from isobutene and  $\text{CF}_3\text{CCl}$ . It was isolated on column A (Table II) at  $70^{\circ}\text{C}$  (injector,  $150^{\circ}\text{C}$ ; detector,  $170^{\circ}\text{C}$ ; He flow, 60 mL/min): retention time, 14.3 min; proton NMR ( $\delta$ ,  $\text{CCl}_4$ ) 1.0 (m, 1 H, cyclopropyl H), 1.37, 1.43 (2"s" + m, 7 H,  $\text{CH}_3$ 's + cyclopropyl H); mass spectrum,  $m/e$  172, 174,  $\text{M}^+$ , base peak,  $\text{M}^+ - \text{Cl}$ .

**1-Chloro-1-(trifluoromethyl)-*cis*-2,3-dimethylcyclopropanes (5-*syn*-Cl and 5-*anti*-Cl).**<sup>12</sup> These products were formed from  $\text{CF}_3\text{CCl}$  and *cis*-butene and were isolated by GC on column A (Table II) at  $70^{\circ}\text{C}$  (conditions as for **4**). The major isomer eluted first (15.7 min), followed by the minor isomer (18 min). The 60-MHz NMR spectrum of **5-*syn*-Cl**

(major) showed ( $\delta$ ,  $\text{CCl}_4$ ) 1.10 ("d",  $\text{CH}_3$ 's) and 1.23–1.77 (m, cyclopropyl). The minor isomer (**5-*anti*-Cl**) showed 1.27 ("d",  $\text{CH}_3$ 's) and 1.50–1.93 (m, cyclopropyls). The GC isomer ratio was 1.65:1. Detailed discussions of the  $^1\text{H}$  and  $^{19}\text{F}$  NMR appear in the Results. Mass spectrum (each isomer): ( $m/e$ ) 172, 174,  $\text{M}^+$ .

**1-Chloro-1-(trifluoromethyl)-*trans*-2,3-dimethylcyclopropane (6).**<sup>12</sup> This product was formed from  $\text{CF}_3\text{CCl}$  and *trans*-butene and was isolated by GC on the column used for **2** at  $60^{\circ}\text{C}$  (injector,  $135^{\circ}\text{C}$ ; detector,  $170^{\circ}\text{C}$ ; He flow, 60 mL/min): retention time, 10.1 min; NMR ( $\delta$ ,  $\text{CCl}_4$ ) 1.17 (b s,  $\text{CH}_3$ 's) and 1.70–1.57 (m, cyclopropyl H's) (lit.,<sup>12</sup> 1.11, 0.97–1.44); mass spectrum,  $m/e$ , 172, 174,  $\text{M}^+$ ; base peak,  $\text{M}^+ - \text{Cl}$ .

**1-Chloro-1-(trifluoromethyl)-2-ethylcyclopropanes (7-*syn*-Cl and 7-*anti*-Cl).** These isomers were formed from  $\text{CF}_3\text{CCl}$  and 1-butene and were separated on column B (Table II) at  $60^{\circ}\text{C}$  (injector,  $125^{\circ}\text{C}$ ; detector,  $175^{\circ}\text{C}$ ; He flow, 50 mL/min): retention times, 10 min, 50 s (major) and 12 min, 12 s (minor); GC isomer ratio, 1.28;  $^1\text{H}$  NMR (isomer mixture,  $\delta$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ) 0.73–1.80;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ) 72.82 (major), 65.85 (minor).<sup>20</sup> Anal. C, H, Cl.

**1-Chloro-1-(trifluoromethyl)-2-isopropylcyclopropanes (8-*syn*-Cl and 8-*anti*-Cl).** These isomers were formed from  $\text{CF}_3\text{CCl}$  and isopropylethylene and were separated on column B (Table II) at  $60^{\circ}\text{C}$ , using the conditions described for **7**: retention times, 22 min (major) and 23 min, 30 s (minor); GC isomer ratio, 1.36;  $^1\text{H}$  NMR (isomer mixture,  $\delta$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ) 1.0 ("d",  $J = 5$  Hz, *i*-Pr methyls), 1.13–1.60 (m, cyclopropyl + carbonyl H's);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ) 74.75 (major), 67.59 (minor).<sup>20</sup> Anal. C, H, Cl.

**1-Chloro-1-(trifluoromethyl)-2-*tert*-butylcyclopropanes (9-*syn*-Cl and 9-*anti*-Cl).** These isomers were formed from  $\text{CF}_3\text{CCl}$  and *tert*-butylethylene and were separated on column B (Table II) at  $85^{\circ}\text{C}$  (injector,  $125^{\circ}\text{C}$ ; detector,  $175^{\circ}\text{C}$ ; He flow, 65 mL/min): retention times, 11 min, 49 s (major) and 12 min, 56 s (minor); GC isomer ratio, 1.66;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ , mixture of isomers) 1.07, 1.12 (singlets, 9 H, *t*-Bu's of minor and major adducts, respectively), 1.23–1.73 (m, 3 H, cyclopropyl H's);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ,  $\text{CFCl}_3$ ) 75.4 (major), 65.4 (minor).<sup>20</sup> Anal. C, H, Cl.

**Competition Experiments.** These were run on carefully weighed binary mixtures of olefins, using diazirine **1** prepared from 20 mmol of trifluoroacetamide (see above). Details of procedure and analysis appear in the Results. See Table II for tabulated results and analytical conditions.

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(49) We observed UV maxima for **1** at 333 and 318 nm (pentane,  $-63^{\circ}\text{C}$ ) (lit.,<sup>13</sup>  $\lambda_{\text{max}} = 318$  (gas phase)).

(50) Both **5-*syn*-Cl** and **5-*anti*-Cl** were subjected to heteronuclear decoupling NMR experiments in which their methyl protons were irradiated and their  $\text{CF}_3$  resonances were observed. Significant nuclear Overhauser effects were observed in neither compound.