# Reaction of bis(trifluoromethyl)diazomethane with trimethyl-3,3,3-trifluoropropynyltin, trimethyltin hydride, and related compounds

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Bis(trifluoromethyl)diazomethane (1) reacts with the compounds  $(CH_3)_3MC \equiv CCF_3$  (M = Ge, Sn)

to give the cyclopropenes  $(CH_3)_3MC = C(CF_3)C(CF_3)_2$ . Cyclopropenes are also obtained from the reaction of 1 with the acetylenes  $RC = CCF_3$  (R = H,  $CF_3$ ) but the main products are the isopyrazoles

 $RC = C(CF_3)N = N - C(CF_3)_2$ . Compound 1 reacts easily with  $(CH_3)_3SnH$  to give  $(CH_3)_3SnC(CF_3)_2H$ and a similar insertion reaction takes place with  $(CH_3)_2A_3H$ . Compound 1 does not insert into Si-H, Ge-H, Ge-Br, Ge-Ge bonds. It reacts with  $(CH_3)_2A_3 - A_3(CH_3)_2$  to give  $(CH_3)_2A_3C(CF_3)_2H$ . Bis(trifluoromethyl)diazirine also reacts with  $(CH_3)_3GeC = CCF_3$  to give the cyclopropene.

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The reaction of a diazomethane RR 'CN<sub>2</sub> with an inorganic compound has proved to be a useful means of inserting a one-carbon fragment into an M—X bond (X = H, halogen, oxygen) (eq. [1]).

$$[1] \qquad M = X + RR'CN_2 \rightarrow M = C = X + N_2$$

The earlier literature has been reviewed by Seyferth (1), and since 1955 a number of investigations of this "insertion" reaction have been made (e.g. 2-7). Moreover, there has been considerable interest in the reactions of diazomethanes with organometallic systems in the hope of preparing novel compounds (e.g. 6, 8-10).

Bis(trifluoromethyl)diazomethane (1) has recently been reported (11) and a few of its reactions have been studied (6, 7, 11–14). Those reactions that have been investigated have been interpreted in three ways: (a) as attack by the diazo compound acting as a 1,3-dipolar reagent, (6, 12); (b) as involving bis(trifluoromethyl)carbene (6, 11, 12) the main intermediate in both the thermal and photolytic decompositions of 1; or (c) as radical attack on the terminal nitrogen of 1 (13). The diazo compound was of primary interest in the present investigation as a 1,3dipolar reagent and as a source of the carbene  $C(CF_3)_2$ .

#### Experimental

Volatile reactants and products were manipulated in a vacuum system. Unless otherwise indicated reactions were carried out in thick-walled Pyrex Carius tubes. Vapor-phase chromatography (v.p.c.) separations were carried out using an Aerograph A-90-P gas chromatograph. The columns used for a particular separation are given in the experimental details below. Molecular weights were determined using Regnault's method. Nuclear magnetic resonance (n.m.r.) spectra were run using Varian A-60 (<sup>1</sup>H spectra in p.p.m. with respect to external TMS), and Varian HA-100 (<sup>19</sup>F spectra in p.p.m. with respect to internal CFCl<sub>3</sub>) spectrometers; positive values of chemical shift being to higher field. Infrared (i.r.) spectra were recorded using a PE 457 spectrometer.

Microanalyses were performed by Mr. Peter Borda of this Department.

Bis(trifluoromethyl)diazomethane and bis(trifluoromethyl)diazirine were prepared from hexafluoroacetone (the kind gift of the Allied Chemical Company) according to the methods described by Gale *et al.* (11). The purity of the diazomethane was checked by i.r. spectroscopy and by its molecular weight of 177 (Calcd. for  $C_3F_6N_2$ : 178). The diazirine was found to be only 95% pure on the basis of its <sup>19</sup>F n.m.r. spectrum but was used without further purification.

#### 1) Reaction with 3,3,3-Trifluoropropyne

3,3,3-Trifluoropropyne (1.395 g, 14.8 mmoles) and bis(trifluoromethyl)diazomethane (1.187 g, 6.66 mmoles) were heated for 20 h at 150°. The v.p.c. separation (20% SE-30 at 55°) of the volatile fraction which condensed at  $-78^{\circ}$  showed five components but only the second and third fractions could be collected and identified. The first eluted major component was identified as 3,3,5-tris(trifluoromethyl)isopyrazole (0.776 g), micro b.p. 52° (atm).

Anal. Calcd. for  $C_6HF_9N_2$ : C, 26.45; H, 0.37; F, 62.90. Found: C, 26.58; H, 0.43; F, 62.50.

The i.r. spectrum (vapor): 3060 (w), 2009 (w), 1738 (vw), 1323 (m), 1300 (m), 1281 (s), 1271 (s), 1231 (w), 1200 (s), 1180 (m), 1120 (m), 978 (m), 973 (m), 852 (w), 805 (vw) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a complex but well defined multiplet at -5.99 p.p.m. (see Fig. 1). The <sup>19</sup>F n.m.r. spectrum showed two peaks, each a doublet, centered at 61.39 (=CCF<sub>3</sub>) ( $J_{F-H}$  =

5.7 c.p.s.) (area 1) and 61.81 p.p.m.  $(-C(CF_3)_2)(J_{F-H} =$ 

2.4 c.p.s.) (area 2).



The <sup>1</sup>H n.m.r. spectrum of the isopyrazole FIG. 1. obtained from the reaction of HC=CCF<sub>3</sub> with  $(CF_{3})_{2}CN_{2}.$ 

The second component was identified as 1,3,3-tris(trifluoromethyl)cyclopropene (0.201 g), micro b.p. 56.9° (atm)

Anal. Calcd. for C<sub>6</sub>HF<sub>9</sub>: C, 29.53; H, 0.41; F, 70.01. Found: C, 29.55; H, 0.62; F, 69.66.

The i.r. spectrum: 3185 (w), 1814 (w), 1321 (s), 1291 (m), 1262 (s), 1246 (m(sh)), 1215 (s), 1195 (s), 1005 (w), 961 (m), 772 (w), 708 (m) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a poorly defined complex multiplet at -7.02p.p.m. The <sup>19</sup>F n.m.r. spectrum showed two multiplets centered at 62.0 p.p.m. (=CCF<sub>3</sub>) ( $J_{F-H} = 1.3$  c.p.s.;

 $J_{F-F} = 1.2$  c.p.s.) (area 1) and 67.65 p.p.m. (-C(CF\_3)\_2)

 $(J_{\rm F-H} = 1.0 \text{ c.p.s.})$  (area 2) (see Fig. 2). The fraction which passed through the  $-78^{\circ}$  bath was identified as slightly impure 3,3,3-trifluoropropyne (0.728 g).

In another reaction, the trifluoropropyne and the diazo compound were heated at 150° for 21 h and then examined to determine the ratio of the products. From the v.p.c. and <sup>1</sup>H n.m.r. integrations of the  $-78^{\circ}$  fraction, it was determined that the isopyrazole and the cyclopropene together comprised 30% of the products based on propyne consumed, and that the ratio isopyrazole:cyclopropene was 2.45:1.

When the reaction was carried out under ultraviolet (u.v.) light (450 W u.v. source) for 21 h the n.m.r. spectrum indicated that the isopyrazole and cyclopropene comprised 65.5% of the products, based on propyne consumed, and that the ratio isopyrazole:cyclopropene was 2.04:1.

2a) Reaction with Hexafluorobutyne-2

Hexafluorobutyne-2 (0.424 g, 2.66 mmoles) and bis(tri-

fluoromethyl)diazomethane (0.466 g, 2.62 mmoles) were heated at 150° for 20 h. A small amount of the starting butyne (0.086 g) was recovered. The fraction which condensed at  $-78^{\circ}$  was separated by v.p.c. into 5 components (20% silicone GE-SS-96 at 51°). Only the first and third eluted fractions were identified. The first (~0.07 g) was identified as tetrakis(trifluoromethyl)cyclopropene (see section 2b below).

The second fraction was identified as 3,3,4,5-tetrakis-(trifluoromethyl)isopyrazole (0.262 g, 35% yield) micro b.p. 81° (atm).

Anal. Calcd. for C<sub>7</sub>F<sub>12</sub>N<sub>2</sub>: C, 24.72; F, 67.04. Found: C, 24.92; F, 66.6.

The i.r. spectrum (vapor): 2392 (vw), 1672 (vw), 1356 (s), 1302 (s), 1269 (vw), 1227 (vw), 1197 (vs), 1149 (m), 1050 (w), 1004 (w), 980 (m), 952 (s), 941 (w), 772 (w), 755 (vw), 737 (m), 672 (w) cm<sup>-1</sup>. The <sup>19</sup>F n.m.r. spectrum showed an  $A_3M_3X_6$  pattern where  $A_3$  was the 4-position CF<sub>3</sub> group ( $\delta(A) = 56.2$  p.p.m.), M<sub>3</sub> was the 5-position CF<sub>3</sub> group ( $\delta(M) = 63.25$  p.p.m.), and X<sub>6</sub> was the two, 3-position CF<sub>3</sub> groups ( $\delta(X) = 64.45$  p.p.m.)  $(J_{A-M} = 8.5 \text{ c.p.s.}; J_{A-X} = 6 \text{ c.p.s.})$  (see Fig. 3).

# 2b) Pyrolysis of 3,3,4,5-Tetrakis(trifluoromethyl)pyrazole

The pyrazole (0.903 g, 2.68 mmoles) was heated at 300° for 72 h. The product, tetrakis(trifluoromethyl)cyclopropene (0.764 g, 92% yield), was purified by repeated passes through a trap at  $-78^{\circ}$ .

Anal. Calcd. for  $C_7F_{12}$  (mol. wt. 312): C, 26.93; F, 72.90. Found (308): C, 27.23; F, 72.60.

The i.r. spectrum: 1919 (w), 1321 (s), 1303 (s(sh)), 1246 (s), 1225 (s), 1200 (s), 1030 (m), 961 (m), 765 (vw), 709 (m), 666 (m), 641 (w) cm<sup>-1</sup>. The <sup>19</sup>F n.m.r. spectrum showed two septets, at 61.2 p.p.m.  $(CF_3C = CCF_3)$  and

67.5 p.p.m. (--C(CF<sub>3</sub>)<sub>2</sub>) ( $J_{F-F} = 1.15$  c.p.s.). A linear

plot of log p against  $10^3/T$  was extrapolated to give a b.p. of 34.9° (760 mm).

3) Reaction with 3,3,3-Trifluoropropynyltrimethylgermane 3,3,3-Trifluoropropynyltrimethylgermane (0.779 g, 3.69 mmoles) and bis(trifluoromethyl)diazomethane (1.076 g, 6.05 mmoles) were heated at 150° for 29 h. A noncondensible gas, presumably nitrogen, was produced. The fraction which condensed at  $-78^{\circ}$  was examined by v.p.c. (20% Kel-F grease at 72°). The two major components were identified as, in order of their elution: 3,3,5-tris(trifluoromethyl)isopyrazole, of known i.r. spectrum (see 1 above) and 2,3,3-tris(trifluoromethyl)cyclopropenyltrimethylgermane (0.179 g, 12.3% yield), micro b.p. 124.5° (atm).

Anal. Calcd. for C<sub>9</sub>H<sub>9</sub>F<sub>9</sub>Ge: C, 29.95; H, 2.50. Found: C, 29.37; H, 2.46.

The i.r. spectrum (vapor): 2995 (w), 2915 (w), 1837 (w), 1420 (vw), 1358 (w), 1320 (vs), 1295 (s), 1269 (vs), 1228 (s(sh)), 1209 (vs), 1183 (vs), 1163 (s(sh)), 1104 (vw), 1080 (vw), 997 (w), 958 (s), 841 (s), 841 (m), 768 (w), 710 (m) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a singlet at -0.35 p.p.m. The <sup>19</sup>F n.m.r. spectrum showed a septet and quartet centered at 62.0 p.p.m. and 66.9 p.p.m. with J = 1.2 c.p.s. in both splitting patterns. The area ratio of the low field to high field absorptions was 1:2 (Calcd. 1:2).

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FIG. 2. The <sup>19</sup>F n.m.r. spectrum of the cyclopropene obtained from the reaction of HC=CCF<sub>3</sub> with (CF<sub>3</sub>)<sub>2</sub>CN<sub>2</sub>.



FIG. 3. The <sup>19</sup>F n.m.r. spectrum of the isopyrazole obtained from the reaction of  $CF_3C \equiv CCF_3$  with  $(CF_3)_2CN_2$ .

# 4) Reaction with 3,3,3-Trifluoropropynyltrimethyltin

3,3,3-Trifluoropropynyltrimethyltin (1.178 g, 4.59 mmoles) and bis(trifluoromethyl)diazomethane (1.424 g, 8.02 mmoles) were heated at 165° for 29 h. There was considerable decomposition. No free propyne was detected but a non-condensible gas, presumably nitrogen, was produced. The  $-78^{\circ}$  fraction was separated by v.p.c. (20% Kel-F grease at 100°) into many components but only the last eluted component could be collected as a single, uncontaminated product. It was identified as 2,3,3-tris(trifluoromethyl)cyclopropenyltrimethyltin (0.140 g, 7% yield). The i.r. spectrum (vapor): 3000 (vw), 2925 (vw), 1820 (w), 1358 (w), 1321 (s), 1290 (m), 1266 (s), 1209 (s), 1181 (s), 1000 (vw), 982 (vw), 958 (m), 788 (vw),

763 (vw) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a singlet at -0.3 p.p.m. with tin satellite peaks ( $J_{1175n-CH_3} =$ 58.2 c.p.s.;  $J_{1195n-CH_3} = 61.0$  c.p.s.). The <sup>19</sup>F n.m.r. spectrum showed two sets of peaks: a septet at 62.55 p.p.m. (--CF<sub>3</sub>) and a quartet at 66.9 p.p.m. (--C(CF<sub>3</sub>)<sub>2</sub>)

 $(J_{F-F} = 1.25 \text{ c.p.s.})$ , (area ratio, septet:quartet = 1:2 (Calcd. 1:2)). The compound decomposed in a glass isotenoscope at  $\sim 67^{\circ}$ . The b.p. is estimated from the data collected below this temperature to be  $\sim 99^{\circ}$ .

## 5) Reaction with Trimethylsilane

Trimethylsilane (0.40 g, 5.4 mmoles) and bis(trifluoromethyl)diazomethane (0.250 g, 1.4 mmoles) did not

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appear to react after 1 day at 20°. The mixture was heated at 100° for 72 h after which the volatiles were examined by <sup>1</sup>H n.m.r. spectroscopy. The spectrum showed only one multiplet at -3.25 p.p.m. (J = 3.7 c.p.s.) which corresponded with the original trimethylsilane.

#### 6) Reaction with Trimethylgermane

Trimethylgermane (0.356 g, 3.0 mmoles) and bis(trifluoromethyl)diazomethane (0.761 g, 4.27 mmoles) did not appear to react after 1 day at 20°. The mixture was heated at 135° for 50 h. The <sup>1</sup>H n.m.r. spectrum of the volatiles showed three high field absorptions and a septet centered at -2.64 p.p.m. (J = 9.5 c.p.s.). However, the <sup>1</sup>H n.m.r. spectra of the major v.p.c. separated products (20% Kel-F grease at 90°) showed that the septet was due to a compound which did not have any high field methyl absorptions and thus, not due to (CH<sub>3</sub>)<sub>3</sub>GeC(CF<sub>3</sub>)<sub>2</sub>H. The v.p.c. separated products were not further studied.

#### 7) Reaction with Trimethyltin Hydride

Trimethyltin hydride (0.633 g, 4.0 mmoles) and bis(trifluoromethyl)diazomethane (0.741 g, 4.2 mmoles) reacted upon warming to 20° with evolution of gas and loss of color. A white precipitate had formed after 2 h. After 3 days a brown decomposition product was observed. After 3 weeks at 20° the volatiles were fractionated by trap-to-trap distillation. The fraction which condensed at  $-78^{\circ}$  was purified by v.p.c. (20% Kel-F grease at 95°) and identified as 1,1,1,3,3,3-hexafluoroisopropyltrimethyltin (0.611 g, 51% yield), micro b.p. 129.5° (atm).

Anal. Calcd. for  $C_6H_9F_7Sn$ : C, 22.89; H, 3.20; F, 36.21. Found: C, 23.06; H, 3.20; F, 35.91.

The i.r. spectrum (vapor): 3000 (w), 2939 (w), 1766 (w), 1363 (s), 1282 (vs), 1250 (m), 1220 (vs(br)), 1195 (s), 1130 (w), 1079 (m), 1050 (m), 970 (vw), 900 (w), 870 (w), 787 (m), 674 (w) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a singlet at -0.30 p.p.m. (-CH<sub>3</sub>) with tin satellite peaks  $(J_{1175n-CH_3} = 51.5$  c.p.s.;  $J_{1195n-CH_3} = 56.5$  c.p.s.) and a septet at -2.54 p.p.m. (-CH(CF<sub>3</sub>)<sub>2</sub>) ( $J_{F-H} = 11.5$  c.p.s.). The two absorptions integrated in the ratio 9.3:1, respectively (Calcd. 9:1). The <sup>19</sup>F n.m.r. spectrum showed a doublet of septets centered at 56.1 p.p.m. ( $J_{F-CH_3} =$ 0.5 c.p.s.).

The material which passed through the  $-78^{\circ}$  bath was identified as mostly perfluoropropene by its known i.r. spectrum.

#### 8) Reaction with Trimethylgermanium Bromide

Trimethylgermanium bromide (0.713 g, 3.60 mmoles) and bis(trifluoromethyl)diazomethane were miscible at 20°. The mixture was opaque after 1 day. After 48 h at 100° a brown decomposition product had formed. A small amount of perfluoropropene (<0.1 g) was isolated. The fraction which condensed at  $-78^{\circ}$  was separated into two major components by v.p.c. (20% silicone GE-SS-96 at 90°). The first fraction (0.110 g) showed i.r. absorptions at 7.9, 8.05, and 13.81  $\mu$ .<sup>1</sup> It was not identified. The second component was identified as trimethylgermanium bromide (0.278 g) by comparison of its i.r. and <sup>1</sup>H spectra with that of a known sample.

## 9) Reaction with Dimethylarsine

Dimethylarsine (0.374 g, 3.54 mmoles) and bis(tri-

<sup>1</sup>This spectrum was run on a Perkin-Elmer Infracord.

fluoromethyl)diazomethane (0.799 g, 4.48 mmoles) were miscible at 20°. No evidence of reaction was observed after two days. After 48 h at 100° a brown decomposition product had formed. The fraction which condensed at  $-78^{\circ}$  was purified by v.p.c. (20% Kel-F grease at 95°) and identified as the insertion product, 1,1,1,3,3,3-hexafluoroisopropyldimethylarsine (0.605 g, 67% yield), micro b.p. 110.5° (atm).

Anal. Calcd. for  $C_5H_7F_6As$ : C, 23.45; H, 2.75; F, 44.52. Found: C, 23.63; H, 2.84; F, 44.22.

The i.r. spectrum (vapor): 3025 (w), 3000 (w), 2939 (w), 1424 (w(br)), 1358 (s), 1296 (vs), 1241 (vs), 1213 (s), 1142 (m), 1090 (s), 1075 (s(sh)), 909 (m), 975 (w), 960 (w), 679 (m) cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum showed a broad singlet and a septet at -1.0 p.p.m. (CH<sub>3</sub>) and -2.67 p.p.m. ( $-CH(CF_3)_2$ ), respectively ( $J_{F-H} = 10$  c.p.s.). The <sup>19</sup>F n.m.r. spectrum displayed a doublet of septets centered at 55.90 p.p.m. ( $J_{F-CH_3} = 0.95$  c.p.s.). The lower boiling fraction was identified by i.r. spectroscopy as a mixture of starting diazo compound and perfluoropropene.

#### 10) Reaction with Hexamethyldigermane

Hexamethyldigermane (0.726 g, 3.09 mmoles) and bis(trifluoromethyl)diazomethane (0.742 g, 4.17 mmoles) were miscible at 20°. There was no visible evidence of any reaction after one day at 20°. The mixture was heated at 100° for 24 h. The fraction which condensed at  $-78^{\circ}$  was examined by v.p.c. (20% silicone GE-SS-96 at 132°), and found to be 82% hexamethyldigermane.

Anal. Calcd. for  $C_6H_{18}$ Ge:  $\overline{C}$ , 30.85; H, 7.72. Found: C, 30.63; H, 7.65.

The fraction which passed through the  $-78^{\circ}$  bath was found by its i.r. spectrum to be a mixture of tetramethylgermane, perfluoropropene, and the starting diazo compound.

#### 11) Reaction with Tetramethyldiarsine

Tetramethyldiarsine (0.940 g, 4.5 mmoles) and bis(trifluoromethyl)diazomethane (0.893 g, 5.0 mmoles) were miscible at 20°. No evidence of reaction was observed after two days at 20°. The mixture was heated at 100° for 48 h. The volatile fractions which condensed at  $-63^{\circ}$ were combined and separated by v.p.c. (20% Kel-F grease at 100°). One of the two major components was identified as 1,1,1,3,3,3-hexafluoroisopropyldimethylarsine (0.185 g). This was the last compound to elute from the column and was characterized by comparing its i.r. spectrum with that of a known sample (see section 9 above).

#### Reaction of Bis(trifluoromethyl)diazirine with 3,3,3-Trifluoropropynyltrimethylgermane

Bis(trifluoromethyl)diazirine (0.924 g, 5.17 mmoles)and 3,3,3-trifluoropropynyltrimethylgermane (0.683 g, 3.24 mmoles) were heated at 165° for 13 h. The fraction of the reaction mixture which condensed at  $-78^{\circ}$  was examined by v.p.c.  $(20\% \text{ Kel-F grease at } 72^{\circ})$ . The major component was identified as 2,3,3-tris(trifluoromethyl)cyclopropenyltrimethylgermane (0.241 g, 20% yield) by its i.r. spectrum (see section 3 above). A small amount of 3,3,5-tris(trifluoromethyl)isopyrazole was also identified by its known i.r. spectrum (see section 1 above). CULLEN AND WALDMAN: BIS(TRIFLUOROMETHYL)DIAZOMETHANE



# **Results and Discussion**

## Reactions with Acetylenes

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The 1,3-dipolar nature of diazo compounds in general, and of 1 in particular, arises from the fact that the structure of a diazo compound can be represented as a number of canonical forms, 1a-1d. In the case of 1 it is predicted that the canonical forms 1b and 1c (a 1,3-dipole) will predominate due to the stabilizing effect of the strongly electron-withdrawing trifluoromethyl groups.

Numerous investigations of 1,3-dipolar additions of diazo compounds to alkynes have been reported (15); however, only one reaction of 1with an alkyne has been described (12) (eq. [2]).

[2] 
$$(CF_3)_2CN_2 + CH_3C \equiv CCH_3 \rightarrow CH_3 \longrightarrow N$$

The isopyrazole<sup>2</sup> eliminates nitrogen at  $400^{\circ}$  to give the cyclopropene according to eq. [3].



We have now found that bis(trifluoromethyl)diazomethane reacts with 3,3,3-trifluoropropyne either at 150° or under the influence of u.v. light  $(\lambda > 2850 \text{ Å})$  to give as major products: 3,3,5tris(trifluoromethyl)isopyrazole (2) and 1,3,3tris(trifluoromethyl)cyclopropene (3) (eq. [4]). When the reactants are heated at 150°, 2 and 3 together comprise 30% of the products based on propyne consumed and are in the ratio 2:3 = 2.45:1. Under photolytic conditions a slightly lower ratio, 2.04:1, is obtained; however, the overall yield is higher, namely, 65.5%.

<sup>2</sup>The ring structure  $\bigvee_{N}^{N}$  has the parent name "pyrazole"; however, no systematic nomenclature has yet been accepted for the ring structure  $\bigvee_{N}^{N}$ . This latter structure has been called  $\Delta^{1,3}$ -pyrazole (16), pyrazolenine (17), 3-*H*-pyrazole (12), and isopyrazole (18). In this paper the parent name isopyrazole will be used. The structure of the isopyrazole **2** is indicated mainly by its n.m.r. spectra. Thus by using the coupling constants derived from the <sup>19</sup>F spectrum the complex multiplet displayed in the <sup>1</sup>H spectrum can be satisfactorily assigned as shown in Fig. 1. This isopyrazole is apparently the only one formed (1,3-addition (15) could take place in the opposite direction to give a second isomer) and the direction of addition corresponds with addition of **1**c to the acetylene polarized in the

direction  $HC = C \rightarrow CF_3$ . This polarization has been observed in other studies (19). It is interesting to note that 3,3,3-trifluoropropyne reacts with 2,2,2-trifluorodiazoethane to give two isomeric pyrazoles, the predominant one corresponding to addition in the same sense as 2 (16).

The structure of the cyclopropene 3 is confirmed by its i.r. and n.m.r. spectra. The  ${}^{1}H$  n.m.r. spectrum shows a single complex peak at

-7.02 p.p.m. similar to that of HC == C(CF<sub>3</sub>)CF<sub>2</sub> (-7.37 p.p.m.) (20). A small upfield shift might be expected in the present case since the vinylic fluorine atoms have been replaced by less electronwithdrawing CF<sub>3</sub> groups. The <sup>19</sup>F n.m.r. spectrum shows two sets of peaks as shown in Fig. 2 and the coupling constants can all be assigned on a first order basis.

In a similar way 1 reacts with hexafluorobutyne-2 to give 3,3,4,5-tetrakis(trifluoromethyl)isopyrazole (4) and a small amount of tetrakis-(trifluoromethyl)cyclopropene (5) (eq. [5]). Under the conditions studied, 4 and 5 comprise 50% of the products (based on butyne consumed) and are in the ratio 4:5 = 3.8:1. As in the reaction described by eq. [3], 4 loses nitrogen on heating (300°) to give the cyclopropene 5. The structure of 4 is shown immediately by its <sup>19</sup>F n.m.r. spectrum, Fig. 3, and confirmed by elemental analysis for carbon and fluorine. The three peaks in the <sup>19</sup>F n.m.r. spectrum integrate in the ratio 1:1:2, as expected, and the splitting patterns can be completely analyzed on a first order basis. The structural proof of the cyclopropene 5 is provided by its <sup>19</sup>F n.m.r. spectrum which shows two septets (J = 1.15 c.p.s.) of

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# CANADIAN JOURNAL OF CHEMISTRY. VOL. 48, 1970 TABLE 1

	Infrared spectra of cyclopropene derivatives RC=C(CF <sub>3</sub> )C(CF <sub>3</sub> ) <sub>2</sub> *												
Derivative	-				Pea	ak values	(cm <sup>-1</sup> )						
R/H	3185	1814	1321	1291	1262	1215	1195	1005	961	772	708		
CF <sub>3</sub>		1919	1321	1303	1246	1225	1200	1030	961		709	666	
(CH <sub>3</sub> ) <sub>3</sub> Ge		1837	1320	1295	1269	1209	1183	997	958	841	710		
(CH <sub>3</sub> ) <sub>3</sub> Sn		1820	1321	1290	1266	1209	1181		958				

\*Main bands only.

$$(CF_{3})_{2}\bar{C}-N=N^{+}$$
 +



HC≡CCF<sub>3</sub>

[6]

equal intensity at chemical shift values similar to those of the cyclopropene 3 (Table 2). The i.r. frequency associated with the C=C stretching vibration occurs at  $1914 \text{ cm}^{-1}$  and is the second highest recorded C=C frequency of a cyclopropene. The highest frequency,  $1945 \text{ cm}^{-1}$ , occurs in perfluorocyclopropene (21). These i.r. spectra are further discussed below.

The reaction of 1 with the Group IV trifluoropropynyl derivatives at 165° gives the corresponding Group IV 2,3,3-tris(trifluoromethyl)cyclopropenyl derivative (eq. [6]). A small amount of 2 is also produced in the reaction involving the propynyl germanium derivative which probably results from the reaction of 1 with  $HC \equiv CCF_3$ . The latter has been detected in the products of thermal reactions involving (CH<sub>3</sub>)<sub>3</sub>GeC = CCF<sub>3</sub> (22).

The proposed structures of the compounds 6(M = Ge, Sn) are based primarily on the similarity of their i.r. and n.m.r. spectra to those of

 $HC = C(CF_3)C(CF_3)_2$  (Tables 1 and 2). Analytical data for the germanium compound are

somewhat over the margin of experimental error. However the proposed structure is confirmed by the finding that the i.r. spectrum of the major product of the reaction of (CH<sub>3</sub>)<sub>3</sub>GeC=CCF<sub>3</sub> and bis(trifluoromethyl)diazirine  $(CF_3)_2$ -

6

 $CF_3$ 

C-N=N is identical with the spectrum of the germanium derivative produced in the reaction given by eq. [6]. Thermal decomposition of the diazirine at temperatures  $\ge 150^\circ$  is known to produce only  $C(CF_3)_2$  as a reactive species (12)

and thus  $(CH_3)_3$  GeC =  $C(CF_3)C(CF_3)_2$  is the expected product. It is notable that some of the isopyrazole 2 is also produced in the reaction of  $(CH_3)_3GeC = CCF_3$  with the diazirine. This is surprising since the diazirine is not expected to produce isopyrazole products; however, the diazirine used was only 95% pure and one of the impurities may have been 1.

The cyclopropenes 3, 5, and 6, could have been formed either by elimination of nitrogen from the corresponding isopyrazoles or by the direct addition of  $C(CF_3)_2$  to the C $\equiv$ C bonds. Neither

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[4]

#### CULLEN AND WALDMAN: BIS(TRIFLUOROMETHYL)DIAZOMETHANE

Nuclear magnetic resonan	nce parameters	of some cycle	opropene der	ivatives	
	111				
	-Π (δ)	δ(F <sup>a</sup> )	δ(F <sup>b</sup> )	J <sub>F<sup>a</sup>-F<sup>b</sup></sub>	
H CF <sub>3</sub> CF <sub>3</sub>	-7.02	62.0	67.65	1.2	
CF <sub>3</sub> CF <sub>3</sub> CF <sub>3</sub> CF <sub>3</sub>		61.2	67.5	1.15	
(CH <sub>3</sub> ) <sub>3</sub> Ge CF <sub>3</sub> CF <sub>3</sub> CF <sub>3</sub>	-0.35	62.0	66.9	1.2	
(CH <sub>3</sub> ) <sub>3</sub> Sn CF <sub>3</sub> CF <sub>3</sub>	-0.30	62.55	66.9	1.25	

TABLE 2

possibility can be excluded with the present experimental results. However, in one experiment which we have been unable to repeat, the product from the reaction of 1 with the trifluoropropynylgermane was the isopyrazole (14) which suggests that this might be the intermediate.

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The i.r. spectra of all the cyclopropenes show a weak high frequency C=C stretching band and a very similar pattern of bands in the C-F stretching region (Table 1). Although it is recognized that the C=C stretching vibration of cyclopropenes is not a very "pure" vibration (23) it is worth noting the frequency increase of this vibration as more electronegative groups are substituted in the vinylic positions. Thus we have

for series  $(CF_3)_2C - CX = CY : X = Y = CH_3$ , 1745 cm<sup>-1</sup> (12); X = H, Y = CF<sub>3</sub>, 1814 cm<sup>-1</sup>; X = Y = CF<sub>3</sub>, 1919 cm<sup>-1</sup>; and for the series

 $F_2C$ —CX=CY: X = H, Y = CF<sub>3</sub>, 1730 cm<sup>-1</sup>  $(20); X = Y = CF_3, 1820 \text{ cm}^{-1}(20); X = Y = F,$ 1945 cm<sup>-1</sup> (21). This is probably due to coupling with the C-F or C-CF<sub>3</sub> stretching vibrations.

The n.m.r. parameters listed in Table 2 also show a high degree of internal consistency.

# "Insertion" Reactions

Bis(trifluoromethyl)diazomethane (1) reacts easily with dimethylarsine and trimethyltin hydride (eqs. [7] and [8]). Nitrogen is eliminated and the  $C(CF_3)_2$  group is inserted into the M—H bond giving the 1,1,1,3,3,3-hexafluoroisopropyl

$$[7] \quad (CH_3)_2AsH + (CF_3)_2CN_2 \rightarrow (CH_3)_2AsC(CF_3)_2H + N_2 \\ 7 \\ [8] \quad (CH_3)_3SnH + (CF_3)_2CN_2 \rightarrow (CH_3)_3SnC(CF_3)_2H + N_2 \\ \end{tabular}$$

8

derivatives. The <sup>1</sup>H n.m.r. spectra of both products show broad singlets due to the CH<sub>3</sub> groups and a septet  $(J_{H-F} \approx 11 \text{ c.p.s.})$  due to the isopropyl hydrogen atoms. The broadness of the CH<sub>3</sub> absorption is due to coupling with the fluorine atoms since the <sup>19</sup>F spectra show a doublet of septets for 7 ( $J_{CH_3-F} \approx 1$  c.p.s.) and a doublet of multiplets (at least 7) ( $J_{CH_3-F} \approx$ 

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0.5 c.p.s.) for 8. Similar insertion products have been obtained from the reaction of 1 with pentacarbonyl(hydrido)manganese (20°) and a platinum hydride (120°) (6). The low temperature reactions (20°) probably proceed via attack of a molecule of 1 to form an intermediate complex which then rearranges with elimination of nitrogen to give the final product (1). It is possible that the platinum and arsenic hydride reaction involves the free carbene (6). Compound 1 does not react with trimethylsilane (100°), trimethylgermane (135°), or trimethylgermanium bromide (110°) with insertion into the Si-H, Ge-H, or Ge-Br bonds. It does, however, insert into the Pd—Cl bond of  $(C_6H_5CN)_2PdCl_2$  (7). The carbene CF<sub>3</sub>CH, from CF<sub>3</sub>CHN<sub>2</sub>, inserted into the Si—H and C—H bonds of  $(CH_3)_3SiH(3)$ .

Dicobaltoctacarbonyl reacts with 1 at 20° as indicated by eq. [9] (6). This reaction can be regarded as an initial addition of 1 across the Co-Co bond followed by loss of CO and N<sub>2</sub> and formation of a new Co-Co bond. Therefore it was of interest to see what would happen if a compound such as tetramethyldiarsine which contains a very reactive As—As bond (24) were mixed with 1. One of the main products of this facile reaction is the isopropyl derivative 7, indicating that any intermediate adduct is not very stable. A similar reaction occurs when 1 is heated with  $[\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sub>2</sub> (eq. [10]). In this case the additional hydrogen atom comes from the solvent (6). Hexamethyldigermane does not react easily or cleanly with 1 at 100°. The analogous ditin compound would be expected to be more easily cleaved.

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