drastic change of mechanism on going from DMSO to H_2O as solvent.

Experimental Section

Materials. Ethyl vinyl ether and dimethyl sulfoxide were obtained commercially and were purified by distillation. The latter was stored under dry nitrogen after distillation at 0.2 mm from calcium hydride. Standard hydrochloric acid and sodium hydroxide solutions were prepared in the usual manner.[23] Deuterium chloride was prepared from benzoyl chloride and D_2O.[24] The acidified aqueous dimethyl sulfoxide solutions were prepared gravimetrically. Each reaction mixture was titrated potentiometrically for acid after the completion of measurements.

Isotopic Product Studies. Each product collection with ethyl vinyl ether as a substrate was accompanied by one in which acetaldehyde itself was used as substrate under otherwise identical conditions. In a typical experiment a solution of 0.6 ml of ethyl vinyl ether (or 0.35 ml of acetaldehyde) in 40 ml of aqueous DMSO (5 ml of H_2O/100 ml of solution) containing 9.1×10^{-3} M HCl and $\sim 10^{-2}$ mCi of tritium was maintained at 25° for 4.5 hr. The reaction mixture was added to 0.8 g of 4-phenylsemicarbazide and allowed to stand at 25° for 1 hr. Dilution with 200 ml of H_2O and chilling induced crystallization. The white needles were filtered and recrystallized from aqueous methanol (mp 147.5–148.5°, lit.[2,25] mp 151–152°). Before addition of the substrate a small portion of the aqueous DMSO had been set aside for later counting. The semicarbazone products and the aqueous DMSO were analyzed for tritium.[26] The correction for the incorporation of tritium by the acetaldehyde by exchange is given in eq 11. The subscripts

$$\frac{r_e}{n_e} = \left[\frac{r_a/t_a}{n_a}\right]\left[t_e - \frac{1 - \exp\{k_2(\mathrm{H}^+)t_e\}}{k_2(\mathrm{H}^+)}\right] \tag{11}$$

a and e refer to acetaldehyde and vinyl ether experiments, respectively. The counting rate due to exchange is r. (This is the total counting rate in the case of r_a.) The incubation period is t, and n is the number of moles of derivative counted.

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[23] I. M. Kolthoff and E. B. Sandell, "Textbook of Qualitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1943.

[24] H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2223 (1942).

[25] P. P. T. Sah and T. S. Ma, *J. Chinese Chem. Soc.*, **2**, 34 (1934).

[26] A. R. Friedman and E. Leete, *J. Am. Chem. Soc.*, **85**, 2141 (1963).

Anomalous Reactions of Bis(trifluoromethyl)diazomethane and Bis(trifluoromethyl)diazirine with Saturated Hydrocarbons[1]

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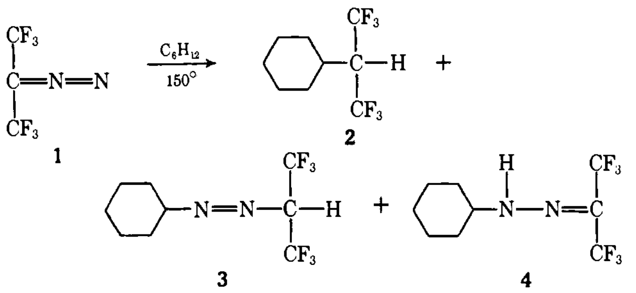
Abstract: Bis(trifluoromethyl)diazomethane (**1**) reacted anomalously with cyclohexane to give a hydrazone (**4**) and an azo compound (**3**) as the major products in addition to the expected carbene insertion product (**2**). Evidence for a radical chain mechanism is presented. Bis(trifluoromethyl)diazirine (**8**) also reacted abnormally with cyclohexane, but the major product was an unexpected imine (**9**) rather than the adducts obtained with bis(trifluoromethyl)diazomethane. Hexafluoroacetone azine (**14**) gave the normal insertion product (**2**) with cyclohexane. Reactions with other hydrocarbons are discussed in light of possible mechanisms.

The thermal reactions of aliphatic and aromatic diazo compounds with saturated hydrocarbons have been intensively investigated.[2] Such reactions normally give carbene insertion products and are frequently used to help establish the reactivity of the intermediate carbene. In no case have other primary products derived from the diazo compound and the saturated hydrocarbon been reported. This also appears to be true of the reactions of diazirines (cyclic diazo compounds) with saturated hydrocarbons, although these compounds have been less thoroughly investigated.[3]

We have found that unexpected reactions occur when either bis(trifluoromethyl)diazomethane (**1**)[4] or its cyclic isomer, bis(trifluoromethyl)diazirine (**8**)[4] is heated with a saturated hydrocarbon.

Bis(trifluoromethyl)diazomethane (1). When **1** was heated at 150° for 8 hr in excess cyclohexane, only a small amount of the expected carbene insertion product, [2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (**2**), was obtained. The major products were an azo compound (**3**) and a hydrazone (**4**) (95% combined yield of **2**, **3**, and **4**). These addition products of the diazo compound **1** with cyclohexane were obtained even though the reaction was run at a temperature shown to be sufficiently high to generate a carbene, from **1**.[4]



The structures of the products suggested that adducts **3** and **4** were formed from a common intermediate by the radical chain mechanism given by reactions 1–3. Additional experiments were conducted to test this

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[1] A portion of this work was communicated earlier [D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965)].

[2] J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964.

[3] E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, **3**, 333 (1964).

[4] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.* **88**, 3617 (1966).

$$C_6H_{12} + R\cdot \longrightarrow C_6H_{11}\cdot + RH \qquad (1)$$

$$C_6H_{11}\cdot + (CF_3)_2CN_2 \longrightarrow \underset{\mathbf{5}}{C_6H_{11}{-}\dot{N}{=}N{-}C(CF_3)_2} \longleftrightarrow \underset{\mathbf{5}}{C_6H_{11}N{=}N{-}\dot{C}(CF_3)_2} \qquad (2)$$

$$\mathbf{5} + C_6H_{12} \longrightarrow \mathbf{3} \text{ or } \mathbf{4} + C_6H_{11}\cdot \qquad (3)$$

mechanism (Table I). In the presence of hydroquinone, a radical trap, insertion product **2** was the major component of the reaction mixture. When the radical sources benzoyl peroxide and *t*-butyl peroxide were added, the reaction proceeded at a lower temperature and the proportion of **2** was slightly reduced. The reaction appears to be temperature dependent, which implies a fair activation energy for one or more of the chain steps.

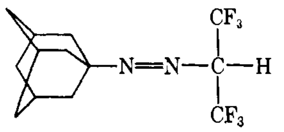
Table I. Reaction Products from Bis(trifluoromethyl)diazomethane and Cyclohexane

Temp, °C	Time, hr	Catalyst	Composition, % 2	3	4	*b*
60	16	$N_2[C(CH_3)_2CN]_2$	No reaction			
90	16	Benzoyl peroxide[a]	6	44	39	12
135	16	*t*-Butyl peroxide	6	59	33	2
150	6	None	8	60	30	2
150	8	None	12	52	36	<1
200	8	None	10	40	47	3
150	8	Hydroquinone	61	26	13	<1

[a] The yield for this reaction was only one-sixth of the usual, starting material being recovered. [b] Unknown.

The small amount of **2** formed in this reaction comes mainly, if not entirely, from direct carbene insertion as a competing reaction and not from the thermal decomposition of the azo product **3**. At 200°, our highest reaction temperature, **3** was stable to pyrolysis over quartz; at 300° it partially decomposed, but no **2** could be detected. The conversion of **3** to **2** was first indicated at 400°, and was complete at 500°.

Adamantane also forms addition products with **1**. The two major products of the reaction, **6** and **7**, indicate that substitution occurs preferentially at the tertiary bridgehead hydrogen, a further indication of the radical nature of the reaction.



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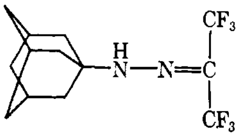

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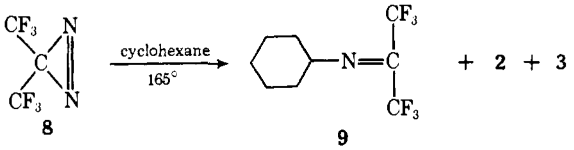
Bis(trifluoromethyl)diazirine (8). When cyclohexane was heated with **8** at 165° in an inert solvent (CF_2Cl-$CFCl_2$), neither the expected carbene insertion product **2** nor an adduct, such as **3**, **4**, or **13**, was the major product. Instead, a product containing only one nitrogen atom per molecule, the imine **9**, was favored. The results of several experiments are listed in Table II.



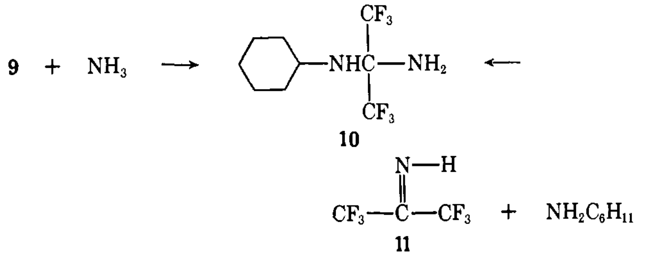
When the reaction was carried out in the absence of a mutual solvent for cyclohexane and **8**, or when the radical-trap hydroquinone or phenothiazine was added to the reaction mixture, the ratio of carbene insertion product **2** to imine **9** increased. However, the addition of the radical source, *t*-butyl peroxide, appeared to reverse the ratio of products. In all cases, a small amount of the azo compound **3** was also formed.

Table II. Reaction of Bis(trifluoromethyl)diazirine (10 g) and Cyclohexane

Cyclohexane, g	Catalyst or solvent	Temp, °C	Composition of product, % 9	2	3
25	CCl_2FCF_2Cl (50 ml)	165	69	30.5	0.5
25	Phenothiazine	165	30	69	1
25	Hydroquinone	165	42	55	3
25	None	165	40	58	2
25	*t*-Butyl peroxide	135	50	49	1
125	None	165	47	47	6
10[a]	None	165	60	39	1
50	None	165	50	49	1

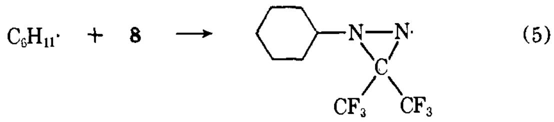
[a] The yield of this reaction was only one-half of the usual.

The structure of the imine **9** was verified by its ^{19}F nmr spectrum, which showed two quartets at 25° that coalesced to a singlet at 150°, and by hydrolysis to cyclohexylamine. Imine **9** was also converted to diamine **10** by addition of ammonia. An authentic sample of **10** was prepared by reaction of cyclohexylamine with hexafluoroacetone imine (**11**).



The mechanism remains in doubt because we have not been able to identify all the products of the reaction of **8** with cyclohexane. To balance any equation, the elements of NH (or $N_2 + H_2$) must be lost. At least part of the missing nitrogen appears to be incorporated in a small amount of intractable residue that is relatively rich in nitrogen. Numerous attempts to isolate other nitrogen-containing products have been unsuccessful. A possible radical chain mechanism is given by reactions 4–8. Such a mechanism would account for some of the features of the reaction, but is

$$C_6H_{12} + R\cdot \longrightarrow C_6H_{11}\cdot + RH \qquad (4)$$



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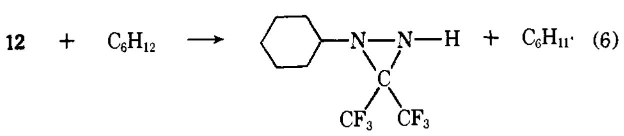

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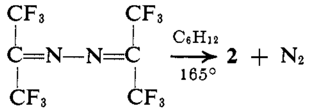
$$\mathbf{13} \longrightarrow \mathbf{9} + [NH] \qquad (7)$$

$$[NH] + C_6H_{12} \longrightarrow R\cdot + tar \qquad (8)$$

probably an oversimplification. Since more than one radical would be generated in each sequence (4–8), small amounts of radical traps or radical sources would have little effect, and the reaction of NH with cyclohexane could account for the tar formation. The coupling of an intermediate such as **12** with subsequent loss of N_2 appears to be unlikely, since this would terminate the chain. Other paths for the formation of **9**, which involve the formation of $CF_3CH_2CF_3$, hexafluoroacetone imine (**11**), or azine (**14**), also appear unlikely. Both the imine **11** and $CF_3CH_2CF_3$ were shown to be stable to the reaction conditions and should have been found in the reaction product if they were formed. The azine **14**, which is known to be formed from the pyrolysis of **8**,[4] reacts with cyclohexane at 165° to give **2** as the major product. Thus **14** may be the best source of bis(trifluoromethyl)carbene for an addition reaction with saturated hydrocarbons. However, this reaction may not involve formation of the free carbene, since **14** did not react with benzene at 165°. Benzene reacts normally with both **1**[4] and **8** at 165° or less to give only carbene addition products.

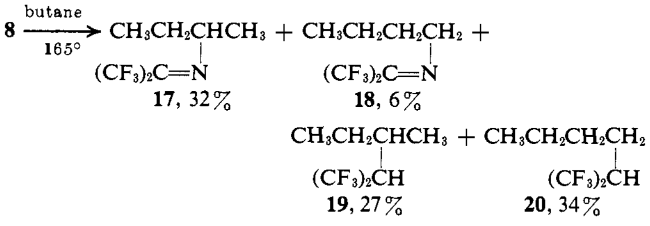


$$(CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \xrightarrow[165^\circ]{C_6H_{12}} \mathbf{2} + N_2$$

14

Reactions of **8** with other saturated hydrocarbons support the free-radical nature of imine formation. With neopentane, which contains only primary hydrogens, the carbene insertion product **15** was the major product (56%), while the imine **16** was the minor product (44%). With butane, which contains both primary and secondary hydrogens, two different imines, **17** and **18**, and two different carbene insertion products, **19** and **20**, were formed. The statistically corrected ratio of imine products derived from replacement of a secondary hydrogen (**17**) as compared to replacement of a primary hydrogen (**18**) is 8:1, which shows the required high degree of selectivity for a radical reaction. Moreover, the corrected ratio of secondary (**19**) to primary (**20**) insertion products is only 1.2:1, in good agreement with the behavior expected of a highly reactive carbene.[2]

$$C(CH_3)_4 + \mathbf{8} \longrightarrow \underset{\mathbf{15}}{(CH_3)_3CCH_2C(CF_3)_2H} + \underset{\mathbf{16}}{(CH_3)_3CCH_2N{=}C(CF_3)_2}$$



$$\mathbf{8} \xrightarrow[165^\circ]{\text{butane}} \underset{\mathbf{17},\ 32\%}{CH_3CH_2CH(N{=}C(CF_3)_2)CH_3} + \underset{\mathbf{18},\ 6\%}{CH_3CH_2CH_2CH_2N{=}C(CF_3)_2} + \underset{\mathbf{19},\ 27\%}{CH_3CH_2CH(CH(CF_3)_2)CH_3} + \underset{\mathbf{20},\ 34\%}{CH_3CH_2CH_2CH_2CH(CF_3)_2}$$

Experimental Section[5]

Reaction of Bis(trifluoromethyl)diazomethane (1) with Cyclohexane. In a typical run, 9.8 g of the diazo compound was heated in an autoclave with 100 ml (78 g) of cyclohexane for 8 hr at 150°. Gas chromatographic analysis (silicone grease column) showed three products (12:52:36). (Table I gives the product compositions under various other conditions.) On distillation, 12.7 g (95%) of reaction product was obtained. The products were separated by spinning-band fractionation or by preparative gas chromatography (silicone oil).

[2,2,2-Trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (2) was obtained as a colorless liquid: bp 72° (72 mm); n^{25}D 1.3668; ^{19}F nmr (neat) δ 64.7 (d, J = 9 Hz); H^1 nmr (neat) τ 7.28 (septet, J = 9 Hz to d, J = 2 Hz, C(CF$_3$)$_2$*H*), 8–9 (m, 11 H).

Anal. Calcd for $C_9H_{12}F_6$: C, 46.17; H, 5.17; F, 48.68. Found: C, 46.37; H, 5.31; F, 48.62.

2-(Cyclohexylazo)-1,1,1,3,3,3-hexafluoropropane (**3**) was obtained as a colorless liquid: bp 79° (50 mm); n^{25}D 1.3690; ir (liquid) 1570 cm^{-1} (–N=N–); ^{19}F nmr (neat) δ 71.0 (d, J = 7 Hz); H^1 nmr (neat) τ 5.75 (septet, J = 7 Hz, C(CF$_3$)$_2$*H*), 6.35 (broad, C*H*–N), 8.88 (m, 10 H).

Anal. Calcd for $C_9H_{12}F_6N_2$: C, 41.21; H, 4.62; F, 43.30; N, 10.68. Found: C, 41.46; H, 4.77; F, 43.38; N, 10.78.

The cyclohexylhydrazone of hexafluoroacetone (**4**) was obtained as a colorless oil: bp 104° (50 mm); n^{25}D 1.4023; ir (liquid) 3450 (NH), 1600 cm^{-1} (N=C); ^{19}F nmr (neat) δ 67.2 (quartet, J = 6 Hz, 3 F), 68.0 (quartet, J = 6 Hz, 3 F); H^1 nmr (neat) τ 2.86 (m, N*H*), 6.65 (m, C*H*–N), 8–9 (m, 10 H).

Anal. Calcd for $C_9H_{12}F_6N_2$: C, 41.21; H, 4.62; F, 43.30; N, 10.68. Found: C, 41.47; H, 4.88; F, 43.42; N, 10.88.

Pyrolysis of 3. Samples of the azo compound **3** were pyrolyzed over 20-mesh quartz chips (gas chromatography–pyrolysis setup) at temperatures from 200 to 500° (see text). At 500° the major peak (>95%) except for nitrogen was collected and shown to be **2** by direct infrared comparison with an authentic sample.

Reaction of Bis(trifluoromethyl)diazomethane with Adamantane. A 25-g sample of the diazo compound, 180 ml of 1,1,2-trichloro-1,2,2-trifluoroethane, and 100 mg of *t*-butyl peroxide were heated together at 135° for 16 hr. The reaction mixture was distilled to give a mixture of products (28 g, 56%), bp 64–95° (2–0.8 mm). The fraction boiling at 64° (2 mm) was rich in the isomer shown to be the azo compound **6**. Purification by preparative gas chromatography (fluorosilicone column) gave **6** as a colorless liquid: n^{25}D 1.4198; ^{19}F nmr (neat) δ 73.3 (d, J = 7 Hz); H^1 nmr (neat) δ 73.3 (d, J = 7 Hz); H^1 nmr (neat) τ 5.75 (septet, J = 7 Hz, C(CF$_3$)$_2$*H*), 7.8 (m, 3 bridgehead H), 8.2 (m, 12-methylene H); mass spectrum (70 eV) *m/e* 314 (parent), 135 (adamantyl carbonium ion).

Anal. Calcd for $C_{13}H_{16}F_6N_2$: C, 49.68; H, 5.14; F, 36.27; N, 8.91. Found: C, 50.17; H, 5.33; F, 36.02; N, 9.19.

The higher boiling fractions, mainly at 83° (2 mm), solidified when cooled with a seed (obtained by preparative gc), and the hydrazone **7** was isolated by recrystallization from ethanol–water to give colorless crystals: mp 38–40°; ^{19}F nmr (CCl$_3$F) δ 64.6 (A$_3$B$_3$ pattern); H^1 nmr (CCl$_3$F) τ 4.3 (s, N*H*), 5.6 (m, ≡CH, 3 H) 6.1 (m, C*H*$_2$–C–N, 6 H), 6.5 (m, C*H*$_2$–C–C); ir (KBr) 3345 (NH), 1595 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* 314 (parent), 135 (adamantyl carbonium ion).

Anal. Calcd for $C_{13}H_{16}F_6N_2$: C, 49.68; H, 5.14; F, 36.27; N, 8.91. Found: C, 49.01; H, 5.26; F, 35.66; N, 8.72.

Reaction of Bis(trifluoromethyl)diazirine (8) with Cyclohexane. In a typical run, 10.0 g of the diazirine, 25 ml of cyclohexane, and 50 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (solvent) were heated in a 240-ml autoclave at 165° for 12 hr. The ^{19}F nmr spectrum of the crude reaction mixture indicated that two major (69 and 30.5%) and one minor (0.5%) fluorine-containing products were present. (Table II gives the product composition under various conditions.) Distillation gave 8.05 g of colorless liquid, bp 132–139°. The two major products were separated by preparative glpc (fluorosilicone column). The 69% component was eluted first and identified as N-cyclohexylhexafluoroisopropylidenimine (**9**): bp 135°; ^{19}F nmr (25°, neat) δ 64.2 (quartet, J_{FF} = 7.5 Hz to d, J_{FH} = 2.2 Hz), 71.2 (quartet, J_{FF} = 7.5 Hz); ^{19}F nmr (150°, neat) δ 67.8 (s); H^1 nmr (neat) τ 6.0 (m, C*H*–N), 8.3 (m, 10 H).

Anal. Calcd for $C_9H_{11}F_6N$: C, 43.73; H, 4.48; F, 46.12; N, 5.67. Found: C, 43.92; H, 4.51; F, 45.78; N, 5.79.

The 30.5% component was eluted second and identified as (2,2,2-trifluoro-1-trifluoromethyl)cyclohexane (**2**) by comparison of its ir and nmr spectra with those of an authentic sample. The 0.5% component was identified as compound **3** by comparison of its ir and nmr spectra with those of an authentic sample.

Reaction of Bis(trifluoromethyl)diazirine with Neopentane. A mixture of 10.0 g (0.056 mol) of bis(trifluoromethyl)diazirine and

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(5) Proton nmr spectra were obtained with a Varian A-60 spectrometer. Peak center positions for protons are reported as τ values (10 − δ in parts per million). Fluorine nmr spectra were obtained with a Varian A56-60 spectrometer. Peak center positions for fluorine are reported in parts per million upfield from CFCl$_3$ used as an internal standard.

25 g of neopentane was heated at 165° for 12 hr in a 240-ml bomb. The bomb was cooled and vented, and the contents were distilled to give 5.7 g of a colorless liquid, bp 95–100°, and 0.75 g of a black residue. Analysis of the residue indicated that it contained 5.25% N and 9.42% F. Gas chromatographic analysis on a silicone column of the distillate indicated two main components in the ratio 56:44. These components were separated on a preparative glpc column (fluorosilicone column). The principal component, having the longer retention time, was 1,1,1-trifluoro-2-(trifluoromethyl)-4,4-dimethylpentane (**15**): bp 101–102°; $n^{25}\mathrm{D}$ 1.3301; ^{19}F nmr (neat) δ 6.83 (d, J = 8.4 Hz); H^1 nmr (neat) τ 9.05 (s, 3 CH_3), 8.29 (d, J = 4.5 Hz, C–CH_2–C), 7.18 (m, $\mathrm{C(CF_3)_2}H$).

Anal. Calcd for $C_8H_{12}F_6$: C, 43.24; H, 5.45; F, 51.31. Found: C, 43.41; H, 5.49; F, 51.01.

The other component, with the shorter retention time, was 2,2-dimethyl-N-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1-propylamine (**16**): bp 96–97°; $n^{25}\mathrm{D}$ 1.3303; ^{19}F nmr (neat) δ 64.7 (quartet, J = 7.4 Hz to t, J = 2.7 Hz, 3 F) and 71.0 (quartet, J = 7.4 Hz to t, J = 2.0 Hz, 3 F); H^1 nmr (neat) τ 9.00 (s, 3 CH_3) and 6.45 (m, C–CH_2–N).

Anal. Calcd for $C_8H_{11}F_6N$: C, 40.86; F, 48.46; N, 5.96; H, 4.72. Found: C, 40.99; F, 48.58; N, 6.01; H, 4.69.

Reaction of Bis(trifluoromethyl)diazirine with Butane. A mixture of 15 g (0.084 mol) of bis(trifluoromethyl)diazirine and 40 g of *n*-butane was heated at 165° for 12 hr in a 400-ml stainless-steel bomb. The bomb was cooled and vented, and the contents were distilled to give 11.08 g of colorless liquid, bp 81–92°. Gas chromatographic analysis and ^{19}F nmr indicated four principal products present in the ratio 32:27:34:6 (by ^{19}F nmr integration). Preparative glpc (fluorosilicone column) gave the following compounds in order of retention time.

1-Methyl-N-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]propylamine (**17**) was the original 32% component: bp 82–83°; ^{19}F nmr (neat) 63.4 ppm (quartet, J_{FF} = 7.7 Hz to d, J_{FH} = 2 Hz, 3 F) and 71.0 ppm (quartet, J = 7.7 Hz, 3 F).

Anal. Calcd for $C_7H_9F_6N$: C, 38.01; H, 4.10; F, 51.55; N, 6.34. Found: C, 38.31; H, 4.30; F, 51.72; N, 6.43.

1,1,1-Trifluoro-2-(trifluoromethyl)-3-methylpentane (**19**) was the original 27% component: bp 88–89°; ^{19}F nmr (neat), two pentets (probably overlapping quartets with J_{FF} and J_{FH} = *ca.* 8.5 Hz) centered at 62.1 ppm.

Anal. Calcd for $C_7H_{10}F_6$: C, 40.39; H, 4.84; F, 54.77. Found: C, 40.51; H, 4.92; F, 55.00.

1,1,1-Trifluoro-2-(trifluoromethyl)hexane (**20**) was the original 34% component: bp 88–89°; ^{19}F nmr (neat) 67.9 ppm (d, J = 8.1 Hz).

Anal. Calcd for $C_7H_{10}F_6$: C, 40.39; H, 4.84; F, 54.77. Found: C, 40.47; H, 4.90; F, 54.92.

N-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]butylamine (**18**) was the original 6% component: ^{19}F nmr (neat) 64.6 ppm (quartet, J_{FF} = 7.5 Hz to t, J_{FH} = 2.3 Hz, 3 F) and 71.1 ppm (quartet, J_{FF} = 7.5 Hz to t, H_{FH} = 1.6 Hz, 3 F).

Anal. Calcd for $C_7H_9F_6N$: C, 38.01; H, 4.10; F, 51.55; N, 6.34. Found: C, 38.32; H, 4.40; F, 51.60; N, 6.44.

Reaction of Hexafluoroacetone Azine (14) with Cyclohexane. A mixture of 25 ml of cyclohexane and 10.0 g of hexafluoroacetone azine was heated at 165° for 12 hr in a 145-ml bomb. The bomb was cooled and vented. Gas chromatographic analysis indicated only one major peak in addition to cyclohexane. Distillation gave 5.64 g (40%) of 2,2,2-trifluoro-1-(trifluoromethyl)ethylcyclohexane (**2**), bp 57–58° (25 mm), which was identified by comparison of its ir and nmr spectra with those of an authentic sample.

N-Cyclohexyl-1,1,1,3,3,3-hexafluoro-2,2-propanediamine (10). Method 1. Hexafluoroacetone imine, 25 ml, was distilled into 19.8 g (0.182 mol) of stirred cyclohexylamine over 45 min. Distillation at reduced pressure gave 35.1 g (70%) of the diamine **10** as a colorless liquid: bp 54–55° (4.4 mm); $n^{25}\mathrm{D}$ 1.3903; ^{19}F nmr (neat) δ 80.2 (s).

Anal. Calcd for $C_9H_{14}F_6N_2$: C, 40.91; H, 5.34; F, 43.15; N, 10.61. Found: C, 40.97; H, 5.16; F, 43.35; N, 10.53.

Method 2. A mixture of 5 g of ammonia and 25 g of a 50:50 mixture of compounds **9** and **2** (prepared from cyclohexane and **8**) was heated at 100° in 8 hr in a 145-ml bomb. Distillation gave 6.77 g of **2**, bp 135°, and 6.70 g of the diamine **10**, bp 62–63° (3.8 mm). Both products were identified by comparison of their ir spectra with those of authentic samples.

Reaction of Bis(trifluoromethyl)diazirine with Benzene. A mixture of 50 ml of benzene and 10 g of bis(trifluoromethyl)diazirine was heated at 165° for 12 hr in a 240-ml stainless-steel bomb. The bomb was cooled and vented, and the contents were distilled to give 11.21 g (85%) of colorless liquid, bp 132–141°. Gas chromatographic analysis indicated the product was composed of 85% 7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene[4] and 15% [2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzene.[4]

A New Synthesis of Olefins from Carbonyl Compounds and Phoshonic Acid Bis Amides

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Abstract: The reaction of α-lithio phosphonamide derivatives with aldehydes and ketones affords β-hydroxy phosphonamides by carbonyl addition in excellent yields. Thermal decomposition of these adducts in benzene or toluene solution at reflux leads to olefins by elimination of the elements of the corresponding phosphoric acid amide. β-Hydroxy phosphonamides can also be synthesized by reduction of β-keto phosphonamides, which in turn are available by the reaction of α-lithio phosphonamides with carboxylic esters. Methods for the stereoselective synthesis of a number of *cis* and *trans* olefins are described. The phosphonamide route to olefins is complementary to the Wittig and Horner–Emmons–Wadsworth methods, having certain general advantages which are discussed herein.

The discovery that β-hydroxy sulfinamides undergo thermal decomposition to olefins, amines, and sulfur dioxide (eq 1) suggested that the analogous trans-

$$\mathrm{R_2C(OH)CH_2SONHR'} \xrightarrow{\Delta} \mathrm{R_2C{=}CH_2} + \mathrm{SO_2} + \mathrm{R'NH_2} \quad (1)$$

formation of β-hydroxy phosphonamides **3** to olefins and phosphoric acid bis amides might also occur.[1] As reported in a preliminary communication,[2] β-hydroxy phosphonamides **3** in fact do decompose readily in refluxing benzene to form olefins. This reaction, in conjunction with the carbonyl addition reaction illustrated

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(1) (a) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966); (b) E. J. Corey and T. Durst, *ibid.*, **90**, 5548 (1968).

(2) (a) E. J. Corey and G. T. Kwiatkowski, *ibid.*, **88**, 5652, 5653 (1966); (b) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).