calibration factor for λ'. This term was measured graphically. The second product term in the numerator corresponds to the unit spectral area at time T. The spectral distribution and therefore the unit spectral area did not change appreciably during an experiment so that this was a constant factor for an experiment. This term can be calculated graphically from the area of a plot of $C_\lambda I_\lambda{}^T / C_{\lambda'} I_{\lambda'}{}^T$ vs. λ, but was actually determined with a Burroughs Datatron 205 computer, programmed with the calibration data.

Procedure for Chemiluminescence Experiments. The light measurement experiments were carried out by combining appropriate aliquots of standardized stock solutions of hydrogen peroxide, DPA, and water in ether or dimethyl phthalate with appropriate aliquots of solvent in a 3.0-ml magnetically stirred cylindrical cuvette attached to the radiometer. The stirrer was positioned vertically against the rear, flat side of the cuvette and provided efficient, rapid mixing. The shutter to the radiometer was opened, the recorder was started, and an aliquot of standarized oxalyl chloride was injected from an all-glass syringe. The intensity of emission of a 5-mμ-wide wavelength segment, usually selected at the spectral maximum, was recorded as a function of time from the point of oxalyl chloride injection. Spectral distributons were determined for representative experiments at several times during a single experiment. The time required for spectral scan was short relative to the intensity decay rate; however, the intensities were corrected for intensity decay. The spectral distributions did not change with time during an experiment under the conditions studied. Corrections of the spectra for reabsorption of emitted light was not necessary with DPA concentrations below 1×10^{-3} M; at 1×10^{-3} M, however, minor reabsorption was noted as a relative loss of intensity at short wavelength. The experiments were not thermostated but were run at room temperature, 25°, which was constant within 1°. Exotherms were not observed at the low reactant concentrations used in several experiments where the temperature was followed with a thermocouple. Typical spectra are shown in Figures 1 and 2. A typical intensity decay plot is is shown in Figure 4.

Stability of Fluorescers in Oxalyl Chloride–Hydrogen Peroxide Chemiluminescent Systems. In a typical experiment, the fluorescence spectrum of 2.95 ml of a solution containing 1×10^{-4} M DPA and 0.1 M H_2O_2 in ether was recorded. A 0.05-ml aliquot of 1.5×10^{-1} M ethereal oxalyl chloride was injected to provide an oxalyl chloride concentration of 2.5×10^{-8} M. After 10 min the chemiluminescence emission decayed essentially to zero and the fluorescence spectrum was again measured. Similarly both perylene and rubrene spectra before and after chemiluminescent reaction were obtained. The results are summarized in Table XIII. Ultraviolet absorption spectra of a reaction of 1.5×10^{-2} M oxalyl chloride, 2.0×10^{-1} M hydrogen peroxide, 1.2×10^{-2} M water, and 6.7×10^{-5} M DPA in ether also indicated essentially no change in fluorescer concentration following the reaction.

Perfluorodiazo Compounds

David M. Gale, William J. Middleton, and Carl G. Krespan

Contribution No. 1167 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware. Received March 12, 1966

Abstract: Members of a new class of perfluoroalkyldiazomethanes $(R_f)_2CN_2$ and the first member of the class of perfluoroalkyldiazirines have been prepared by lead tetraacetate oxidation of the corresponding hydrazones and diaziridine, respectively. The chemistry of these compounds has been investigated with emphasis on the formation and chemistry of carbenes $(R_f)_2C:$, which are sufficiently electrophilic to add to benzene. The ultraviolet spectrum of tropylidene XXVI suggests that the ring is very nearly planar.

Perfluoroalkyldiazomethanes or diazirines have not been reported previous to the start of this investigation.[1-4] Detailed studies of the reactions of the dihalocarbenes have revealed that they are less electrophilic than methylene.[5] This lower electrophilicity has been attributed to a resonance stabilization by the halogen of the electron-deficient carbon, which offsets any inductive destabilization.[6] The method of generation may also be an important consideration in carbene reactivity; for example, chlorocarbene generated from chlorodiazomethane is more reactive than "chlorocarbene" generated in solution from methylene chloride and an organolithium reagent.[7] Recent studies[8] of partly fluorinated carbenes (containing a hydrogen and perfluoroalkyl group attached to the electron-deficient carbon) have led to examples of addition to haloolefins. In the present study, it was hoped that the decomposition of a bis(perfluoroalkyl)diazomethane or diazirine

(1) A preliminary communication describing a portion of this work has appeared: D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, 87, 657 (1965). While this work was in progress, reports of the synthesis of bis(trifluoromethyl)diazomethane[2] and bis-(trifluoromethyl)diazirine[3] by alternate routes have appeared. The properties and chemistry of difluorodiazirine have been reported.[4] See ref 1–4 for a summary of the literature of partly fluorinated diazo compounds.

(2) E. P. Mochalina and B. L. Dyatkin, *Akad. Nauk SSSR Ser. Khim.* 5, 926 (1965).

(3) R. B. Minasyan, E. M. Rokhlin, N. P. Gambaryan, Yu. V. Zeifman, and I. L. Knunyants, *ibid.*, 4, 761 (1965).

(4) R. A. Mitsch, *J. Heterocyclic Chem.*, 1, 59 (1964); *J. Am. Chem. Soc.*, 87, 758 (1965).

(5) For recent reviews, see J. Hine, "Divalent Carbon," Ronald Press New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(6) J. Hine and P. B. Ehrenson, *J. Am. Chem. Soc.*, 80, 824 (1958).

(7) G. L. Closs and J. J. Coyle, *ibid.*, 84, 4350 (1962); 87, 4270 (1965). The reactive species generated from methylene chloride may not be free chlorocarbene.

(8) R. Fields and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1964); *Proc. Chem. Soc.*, 22 (1960).

would give a carbene of unusual reactivity because (1) the electron-deficient carbon would be made more electrophilic through the inductive pull of the fluorine atoms (with little or no opposite effect through resonance stabilization), and (2) excess energy might be imparted to the carbene during generation. Of particular interest were the adducts with benzene because of their possible bearing on the tropylidene–norcaradiene question.[9] The noncarbene chemistry of perfluoroalkyldiazomethanes and diazirines was also of interest because of their relationship to nonfluorinated analogs.

Bis(perfluoroalkyl)diazomethanes I and II were prepared by lead tetraacetate oxidation of the corresponding hydrazones[10] in benzonitrile solution at 0 to 25°. Acetic acid, formed as the reaction proceeds, does not

$$(R_f)_2C{=}NNH_2 + Pb(OAc)_4 \longrightarrow (R_f)_2CN_2 + Pb(OAc)_2 + 2HOAc$$
$$I,\ R_f\ =\ CF_3$$
$$II,\ R_f\ =\ C_2F_5$$
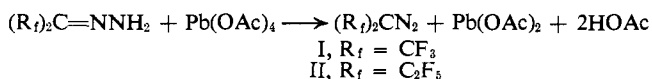
decompose the products. This behavior is in contrast to that of nonfluorinated diazomethanes, which are commonly used to esterify organic acids.[11] Diazo compounds I and II are pale yellow liquids boiling at 13 and 57°, respectively. Bis(trifluoromethyl)diazirine (III), a colorless liquid boiling at −12°, was prepared in a similar manner by the oxidation of bis(trifluoromethyl)diaziridine.[10] An improved synthesis for its diaziridine precursor is given in the Experimental Section.

III
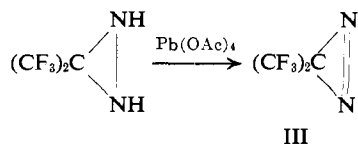
Diazo compounds I and II react with nucleophiles to give linear adducts such as IV and V from triphenylphosphine and piperidine, respectively. The diazirine III is much less reactive toward nucleophiles, for it does not react with triphenylphosphine or piperidine even under more forcing conditions.


IVa, R_f = CF$_3$
b, R_f = C$_2$F$_5$

V
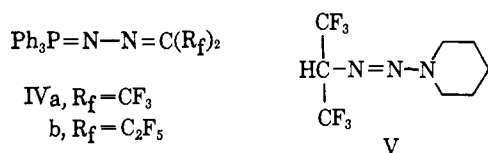
Cyclic adducts VI and VII were prepared from I and acrylonitrile at 60° and dimethylacetylene at 150°, respectively. The later adduct was pyrolyzed to the stable cyclopropene VIII, which could be synthesized directly from dimethylacetylene and diazirine III. Cyclopropene VIII does not readily decolorize bromine in carbon tetrachloride solution; this result is probably due to unfavorable steric requirements in the transition state in going from olefin to would-be addition product.

Bis(trifluoromethyl)diazomethane (I) is neither impact nor static sensitive and is stable to long storage at

(9) E. Ciganek, J. Am. Chem. Soc., 87, 652, 1149 (1965), has found that the adduct of dicyanocarbene and benzene is a norcaradiene and that cyanotrifluoromethylcarbene gives a mixture of norcaradiene and tropylidene.

(10) W. J. Middleton and C. G. Krespan, J. Org. Chem., 30, 1398 (1965).

(11) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 69.

VII   VIII

VI
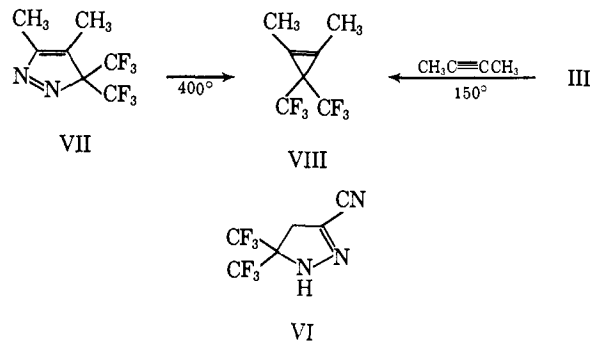
−78°; however, it partly decomposes with loss of nitrogen after several weeks at room temperature. Pyrolysis of I over quartz at 250° (in a helium flow system set up for direct gas chromatographic analysis) gave hexafluoropropene and tetrakis(trifluoromethyl)ethylene (see the Experimental Section for a procedure for preparing the ethylene) as the major products in about equal amounts. In contrast, when the pyrolysis was carried out at low concentrations of I (flow system under high vacuum), hexafluoropropene was essentially the sole product. The intermediacy of bis(trifluoro-

$$I \xrightarrow[\Delta]{-N_2} CF_3CF{=}CF_2 + (CF_3)_2C{=}C(CF_3)_2$$
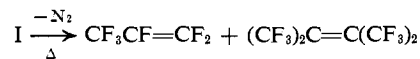
methyl)carbene, $(CF_3)_2C{:}$, which can rearrange by 1,2-fluoride migration[8] to form hexafluoropropene or react with another molecule of I to give the ethylene, was gleaned from the nature of the products and the marked variation in product composition with diazo concentration.[12] The intermediacy of bis(trifluoromethyl)carbene was confirmed with trapping experiments described below.

Bis(trifluoromethyl)diazirine (III) can be stored in a steel cylinder at 25° and shows no tendency to detonate. Pyrolysis of III over quartz at 300° (helium flow system) gave hexafluoroacetone azine[10] and hexafluoropropene as the major products. No tetrakis(trifluoromethyl)ethylene could be detected. The loss of nitrogen from

$$III \xrightarrow[\Delta]{-N_2} CF_3CF{=}CF_2 + (CF_3)_2C{=}NN{=}C(CF_3)_2$$
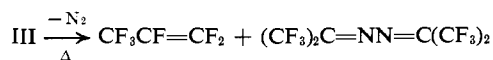
III to give $(CF_3)_2C{:}$ which can either rearrange or react with substrate is, as with the pyrolysis of I, the major reaction path. The absence of tetrakis(trifluoromethyl)ethylene in the pyrolysis of III is evidence that the carbene has little or no tendency to dimerize, thus confirming the suggested reaction path for formation of the ethylene during the pyrolysis of I. The reaction of the carbene with I probably does not lead to azine because attack is at the nucleophilic carbon of the diazo compound. Canonical form Ib may predominate over Ia due to inductive stabilization by the CF$_3$ groups. In the case of III, however, carbene

Ia   Ib
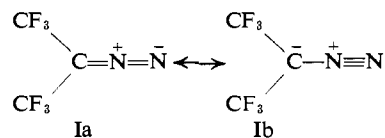
attack may be at the nitrogen–nitrogen double bond and the azine is the observed product.

(12) The possibility that the products are formed from completely concerted decompositions of one and two molecules of the diazo compound is remote but cannot be excluded.

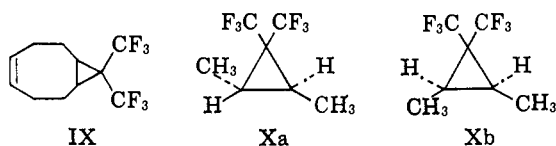III + (CF$_3$)$_2$C: → [structure] → azine
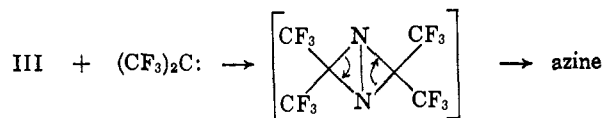
Decomposition of I in an autoclave at 150° with excess *cis,cis*-1,5-cyclooctadiene gave cyclopropane IX in 36% yield. A similar reaction with *trans*-2-butene gave *trans*-1,2-dimethyl-3,3-bis(trifluoromethyl)-

IX   Xa   Xb

cyclopropane (Xa) in 53% yield with none of the *cis* epimer (Xb) detected. The stereochemistry of Xa was established by a sharp singlet at −5.50 ppm in its F^{19} nmr spectrum. Because the fluorine atoms are equivalent, no splitting is observed.[13] Decomposition of I at 150° in the presence of *cis*-2-butene gave (in 57% combined yield) *cis*-cyclopropane Xb (39%), *trans*-cyclopropane Xa (8%), ethylene XI (49%), and minor unidentified components (4%). As expected, Xb showed

XI
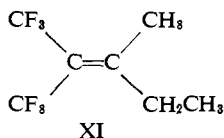
a pair of quartets at +0.84 and −9.83 ppm ($J = 8$ cps) in its F^{19} nmr spectrum due to splitting of the nonequivalent CF$_3$ groups. The ethylene product (XI) was identified on the basis of a strong band at 1647 cm^{-1} in its infrared spectrum (carbon–carbon double bond) and a characteristic ethyl absorption in its H^1 nmr spectrum. The marked difference in product distribution found in the reactions of I with the 2-butenes may be explained on the basis of diradical intermediates A and B which differ in their ability to close to cyclopropanes because of steric repulsions. In the case of
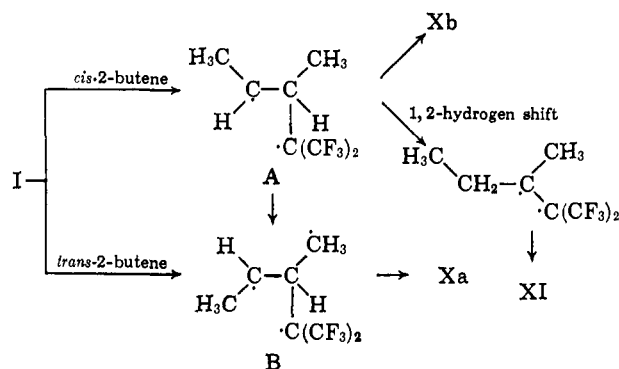

diradical A, in which two methyl groups oppose the bulky trifluoromethyl group, rotation to give B (and subsequently Xa) and 1,2-hydrogen abstraction (leading to XI) can compete favorably with ring closure to give *cis*-cyclopropane Xb. For diradical B, the ring closure is more sterically favorable, and *trans*-cyclopropane Xa is formed relatively without difficulty. Products Xb and XI were shown to be stable to the

(13) The H^1 nmr spectra of Xa and Xb show multiplets at τ 8.5–9.2, probably due to complex AA'B$_3$B$_3$' absorptions with possibly slight broadening from the fluorine atoms.

reaction conditions and in the reaction of I with *cis*-2-butene (in excess) essentially no *trans*-2-butene was present in the recovered olefin. Hydrogen shift during the reaction of diazo compounds with olefins has been observed by other workers.[5]

The reaction of diazirine III with cyclohexene gave three products, XII (47%), XIII (44%), and XIV (9%).

XII   XIII   XIV
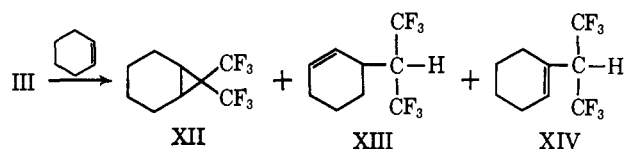
The reaction probably involves a singlet bis(trifluoromethyl)carbene which is fairly indiscriminant (although not completely so, because no product resulting from insertion in the β positions was found). The nature of the products observed from the reaction of III with *cis*- and *trans*-2-butene supports this conclusion, the stereospecific addition to form Xb and Xa, respectively, predominating. It is clear also that in the reaction of I with the butenes, the same carbene intermediate is not involved because little or no allylic or vinylic insertion products were observed for that case; it seems reasonable, therefore, that intermediates A and B could be derived from pyrazolines and that these reactions of I need not involve a carbene.[14] It may be noted that the minor product (XI) in the reaction of III with *cis*-2-butene is the same as the major product in the reaction of I with the same olefin; while the isomerization of III to I to some small extent has not been excluded, a more appealing explanation (accounting for Xa also) is that a diradical intermediate like, but not identical with, intermediate A is formed by addition of a triplet carbene to the olefin. This intermediate might lead to XI and Xa (as would A) but in different ratios. That the singlet carbene should want to undergo singlet–triplet collisional decay is not unreasonable in view of evidence that the triplet is the ground state.[15] Pyrolysis of III in the presence of 2,3-dimethylbutadiene gave carbene addition product XIX.
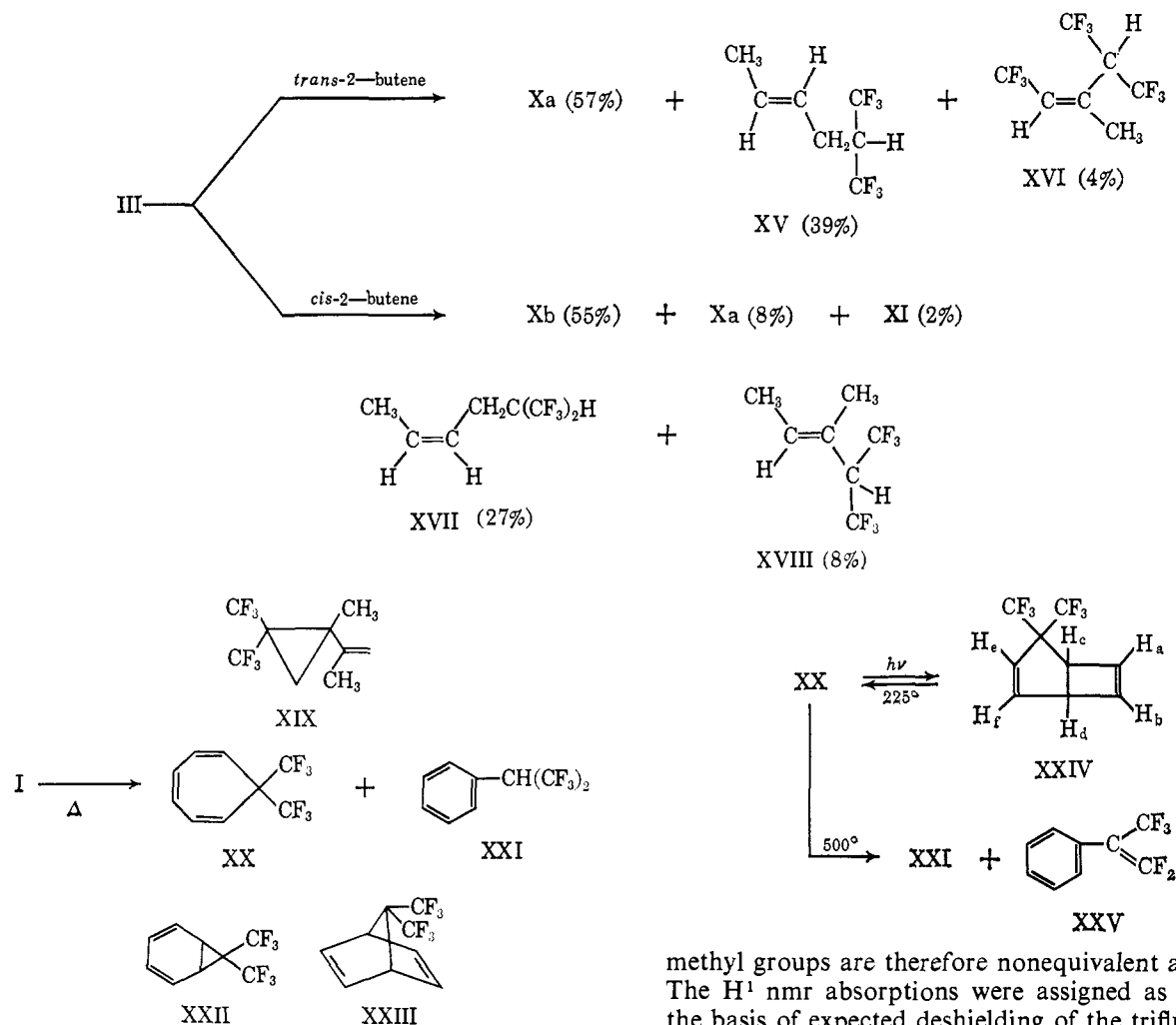
Pyrolysis of I at 200° (or at 150°) in excess benzene gave 7,7-bis(trifluorormethyl)-1,3,5-cycloheptatriene (XX, 88%) and hexafluoroisopropylbenzene[16] (XXI, 12%) in 70% combined yield. This reaction constitutes the first example of the addition of a perhalocarbene to benzene.[17] The tropylidene structure of XX, rather than the valence-tautomeric norcaradiene XXII, was assigned on the basis of nmr data. A sharp singlet at 4.42 ppm was observed for the F^{19} nmr signal, and this resonance remained essentially unchanged from about −120 to 140°. Except for the remote possibility that both CF$_3$ groups have identical chemical shifts, structure XXII with nonequivalent CF$_3$ groups is excluded for the temperature range examined. The H^1 nmr

(14) With less electron-rich olefins, carbene formation from I probably competes with pyrazoline formation. A brief investigation of the reaction of I with 1-butene reveals (from the number of products which appear as doublets in the F^{19} nmr spectrum of the crude reaction mixture) evidence for insertion reactions.

(15) E. Wasserman, to be published. We thank Dr. Wasserman for communicating his results to us prior to publication.

(16) Compounds XXI and XXV were prepared previously: W. A. Sheppard, to be published.

(17) Dichlorocarbene has been added to activated aromatics: W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Am. Chem. Soc.*, 83, 603 (1961). Chlorocarbene has been added to benzene: G. L. Closs and L. E. Closs, *Tetrahedron Letters*, No. 10, 38 (1960).

trans-2—butene → Xa (57%)

cis-2—butene → Xb (55%) + Xa (8%) + XI (2%)

III

XV (39%)

XVI (4%)

XVII (27%)

XVIII (8%)

XIX

I → XX + XXI
Δ

XXII   XXIII

XX ⇌ XXIV
hν / 225°

500° → XXI + XXV

spectrum of XX exhibited multiplets at τ 3.6 (4 H) and 4.6 (2 H) which is in keeping with the tropylidene structure; the hypothetical XXII would be expected to give rise to cyclopropane resonance at higher field.[9] Catalytic hydrogenation of XX gave 1,1-bis(trifluoromethyl)cycloheptane as the only product. The ultraviolet spectrum of XX ($\lambda_{max}^{ethanol}$ 276 mμ (ϵ 3200), $\lambda_{max}^{cyclohexane}$ 277 mμ (ϵ 3300), $\lambda_{max}^{acetonitrile}$ 276 mμ (ϵ 3180)) excludes the possibility of bicycloheptatriene XXIII as the correct structure. The higher-than-usual ultraviolet maxima[18] may reflect a high degree of planarity, possibly due to transannular repulsions by the bulky trifluoromethyl groups. A complete analysis of the H[1] nmr spectrum of XX confirms our structural assignments and independently suggests a high degree of ring planarity.[11]

Photolysis of I in benzene gave a 28% combined yield of XX (40%), XXI (5%), and photodiene XXIV (55%). The photodiene, probably formed from XX during the photolysis, was characterized by its infrared (bands at 1565 and 1618 cm⁻¹ for cyclobutene and cyclopentene, respectively, and saturated CH at 2950 cm⁻¹), ultraviolet (no ϵ >35), and nmr spectra. The F[19] nmr showed a pair of quartets at 5.96 and 1.5 ppm ($J = 9.5$) with the low-field quartet split further; the trifluoro-

methyl groups are therefore nonequivalent as required. The H[1] nmr absorptions were assigned as follows on the basis of expected deshielding of the trifluoromethyl groups and on the observed spin–spin coupling constants[20] (τ values): 3.58 (H_a), 3.95 (H_b), 6.12 (H_c), 6.27 (H_d), 3.58 (H_e), 4.48 (H_f); $J_{ab} = 2.5$ cps, $J_{ef} = 6.0$ cps, all other $J_S \cong 0$ cps; it was necessary to decouple H_f from H_e by the double-resonance technique to analyze this spectrum because of the overlap of H_a and H_e.[21] The formation of the diene (XXIV) on direct photolysis of tropylidene XX was demonstrated; on heating at 225° the reaction is reversed. Pyrolysis of XX at 500°, however, gives benzene derivatives XXI and XXV.

The decomposition of diazo compound II in benzene at 150° led to 7,7-bis(pentafluoroethyl)-1,3,5-cycloheptatriene (XXVI) in 22% yield. It is noteworthy that the probable carbene intermediate, bis(pentafluoroethyl)carbene, adds to benzene before rearrangement by
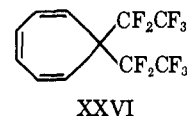
XXVI

migration of either a fluorine atom or fluoroalkyl group. Tropylidene XXVI had a H[1] nmr spectrum almost identical with that of tropylidene XX. The F[19] nmr

(18) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963). This paper summarizes ultraviolet spectra of substituted tropylidenes. Values range from 255 to 269 mμ.

(19) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965).

(20) A recent compilation of vinyl coupling constants in *cis*-cyclo-olefins is in accord with our J values of 2.5 and 6.0 cps found for the cyclobutene and cyclopentene rings, respectively: O. L. Chapman, *ibid.*, **85**, 2014 (1963). The bridgehead hydrogens do not couple: W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(21) The mass spectra of the carbene–benzene adducts also show the expected cracking patterns: D. M. Gale, to be published.

spectrum of XXVI (at -58 to $+150°$) exhibited symmetrical multiplets at $+51.2$ (CF$_2$) and $+10.9$ ppm (CF$_3$).[21] The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ 293 mμ (ϵ 2300), $\lambda_{max}^{cyclohexane}$ 292 mμ (ϵ 2350), $\lambda_{max}^{acetonitrile}$ 293 mμ (ϵ 2240), which suggests an even more planar ring than for tropylidene XX; this result is in keeping with the greater steric requirement of the pentafluoroethyl groups. Conrow[18] has suggested that a value of 293 mμ would correspond to a *completely planar tropylidene*.

Experimental Section[22]

Bis(trifluoromethyl)diazomethane (I). A solution of 9 g (0.058 mole) of hexafluoroacetone hydrazone[10] in 10 ml of benzonitrile was added dropwise with stirring to a suspension of 26 g (0.058 mole) of lead tetraacetate (obtained from 30 g of commercial lead tetraacetate after removing the acetic acid by drying under reduced pressure) in 75 ml of benzonitrile. The reaction mixture was kept under an atmosphere of nitrogen and cooled in an ice bath. When the addition was completed, the reaction mixture was stirred at 25° for 1 hr. The most volatile material was distilled from the mixture at 10 mm and collected in a trap cooled to $-78°$. Distillation of the material in the trap gave 4.5 ml (about 6.8 g, 77%) of I, bp 12–13°, as a yellow liquid. The infrared spectrum contained a band at 2137 cm^{-1}. The F^{19} nmr spectrum contained a singlet at -7.09 ppm.

Anal. Calcd for C$_3$F$_6$N$_2$: F, 64.02. Found: F, 63.88, 64.07.

Bis(trifluoromethyl)diazomethane–Triphenylphosphine Adduct (IVa). A solution of 1.0 g (0.0056 mole) of I in 5 ml of methylene chloride cooled to 0° was mixed with a solution of 2.14 g (0.0056 mole) of triphenylphosphine in 7 ml of methylene chloride. The reaction mixture was allowed to remain at 0° until most of the yellow color faded and a white precipitate formed (about 10 min). The mixture was cooled to about $-30°$, and the suspended white solid was collected on a filter and washed with cold carbon tetrachloride. There was obtained 3.05 g (97%) of the phosphazine as white plates, mp 137–138°. The F^{19} nmr spectrum exhibits a multiplet centered at -3.10 ppm. The ultraviolet spectrum shows $\lambda_{max}^{ethanol}$ 280 mμ (ϵ 16,300), 273 (16,700), 268 (16,600), and 221 (27,200).

Anal. Calcd for C$_{21}$H$_{15}$F$_6$N$_2$P: C, 57.28 H, 3.44; F, 25.88; N, 6.37; P, 7.04. Found: C, 57.09; H, 3.79; F, 25.78; N, 6.68; P, 6.82.

Bis(trifluoromethyl)diazomethane–Piperidine Adduct (V). Piperidine (0.3 ml, 0.003 mole) was added to a solution of 0.5 g (about 0.003 mole) of I in 2 ml of ether cooled to $-78°$. The white precipitate that formed remained until the solution had warmed to room temperature; then it slowly dissolved. The reaction mixture was distilled through a microcolumn to give 0.5 g (65%) of the triazene, 2-(1-piperadineazo)-1,1,1,3,3,3-hexafluoropropane (V), as a light yellow oil, bp 66–68° (10 mm), n^{25}D 1.3990. The F^{19} nmr spectrum contained a doublet centered at 4.27 ppm ($J = 8$ cps). The H^1 nmr contained a septet at τ 5.87 ($J = 8$ cps) of area 1, a singlet at 6.60 of area 4, and a singlet at 8.65 of area 6.

Anal. Calcd for C$_8$H$_{11}$F$_6$N$_3$: C, 36.51; H, 4.22; F, 43.33; N, 15.97. Found: C, 37.00; H, 4.36; F, 42.87; N, 15.86.

4,5-Dimethyl-3,3-bis(trifluoromethyl)-3H-pyrazole (VII). A 4.5-ml (6.7 g) sample of I was heated with 50 g of dimethylacetylene in a 240-ml Hastelloy tube at 150° for 8 hr. The recovered light yellow liquid (55 g) was distilled to give 5.12 g (60%) of VII as a faint yellow liquid, bp 140°, n^{25}D 1.3634. The F^{19} nmr spectrum was a singlet at 1.97 ppm, and the H^1 nmr spectrum showed a broad singlet at τ 7.91 and a quartet at 7.59 ($J = 1.4$ cps) of equal area. The ultraviolet spectrum showed λ_{max} 273 mμ (ϵ 2800) and 358 mμ (ϵ 320). The mass spectrum showed a parent ion at m/e 232.

Anal. Calcd for C$_7$H$_6$F$_6$N$_2$: C, 36.21; H, 2.61; F, 49.09; N, 12.07. Found: C, 36.46; H, 2.89; F, 49.00; N, 12.18.

1,2-Dimethyl-3,3-bis(trifluoromethyl)cyclopropene (VIII). A 18.5-g sample of 4,5-dimethyl-3,3-bis(trifluoromethyl)-3H-pyrazole was pyrolyzed through a quartz tube at 400°. About 13 ml of

liquid was collected in a trap cooled by Dry Ice–acetone. Distillation gave 9.2 g (56%) of the cyclopropene as a colorless liquid, bp 38° (100 mm), n^{25}D 1.3218. The infrared spectrum showed a band at 1745 cm^{-1}. The H^1 nmr spectrum showed a singlet at τ 7.87, and the F^{19} nmr had a singlet at -2.22 ppm. The mass spectrum showed a parent ion at m/e 204.

Anal. Calcd for C$_7$H$_6$F$_6$: C, 41.19; H, 2.96; F, 55.85. Found: C, 41.24; H, 3.22; F, 55.85.

5,5-Bis(trifluoromethyl)-2-pyrazoline-3-carbonitrile (VI). A 6-g sample (4.0 ml) of I, 6 g of acrylonitrile, 100 mg of hydroquinone, and 20 ml of trichlorotrifluoroethane were heated together in a Hastelloy bomb for 16 hr at 60°. Evaporation of the solvent gave 7.9 g (quantitative yield) of the pyrazoline as a white solid, mp 32–34°. The H^1 nmr spectrum in CDCl$_3$ showed a broad peak at τ 2.55 (area 1) and a sharp peak at 6.55 (area 2). The F^{19} nmr spectrum showed a sharp singlet at 9.07 ppm. The ultraviolet spectrum had λ_{max} 264 mμ (ϵ 10,700).

Anal. Calcd for C$_6$H$_3$N$_3$F$_6$: C, 31.18; H, 1.31; N, 18.18. Found: C, 31.25; H, 1.37; N, 18.25.

Bis(perfluoroethyl)diazomethane (II). A 15-g sample of lead tetraacetate (commercial, containing about 10% acetic acid stabilizer) was place in a 250-ml flask, and the stabilizer was removed under reduced pressure. A 75-ml portion of benzonitrile was added, and the resulting solution was stirred magnetically and cooled in an ice bath while 6 g of perfluoro-3-pentanone hydrazone[10] dissolved in 5 ml of benzonitrile was added dropwise over 15 min. After stirring at room temperature for 30 min, the most volatile material was distilled at 1 mm into a trap cooled by Dry Ice–acetone. There was obtained 3.0 ml (about 4.5 g, 76%) of II, bp 56–57°. The infared spectrum contained a band at 2119 cm^{-1}. The F^{19} nmr spectrum showed a broadened signal at 17.89 (area 3) and one at 42.11 ppm (area 2).

Bis(pentafluoroethyl)diazomethane (II) was further identified by preparing an adduct (IVb) with triphenylphosphine. A 1.5-g sample of II suspended in 5 ml of methylene chloride was added at 0° to 3 g of triphenylphosphine dissolved in 10 ml of methylene chloride. The mixture was kept at 4° for 16 hr and then cooled in a Dry Ice–acetone bath to induce crystallization of a white solid. The phosphazine (IVb, 3 g, quantitative), mp 118–120°, was collected on a filter and washed with cold carbon tetrachloride. The infrared spectrum showed strong absorption in the CF region. The F^{19} nmr showed multiplets at 13.00 (area 3), 13.25 (area 3), 39.52 (area 2), and 46.19 (area 2) ppm. The ultraviolet spectrum was λ_{max} 284 mμ (ϵ 16,700), 273 (16,300), 268 (15,300), and 223 (ϵ 25,000). The H^1 nmr spectrum had a multiplet at τ 2.4.

Anal. Calcd for C$_{23}$H$_{15}$N$_2$F$_{10}$P: C, 51.12; H, 2.80; N, 5.19; P, 5.72. Found: C, 51.06; H, 2.81; N, 5.40; P, 5.83.

2-Aminohexafluoroisopropyl Azide. Concentrated sulfuric acid (50 g, 0.5 mole) was added dropwise to a mechanically stirred suspension of 65 g (1 mole) of sodium azide in 500 ml of dimethylformamide cooled to 0°. Hexafluoroisopropylidenimine (150 g, 0.91 mole) was distilled into the stirred suspension over a period of 1 hr, keeping the temperature between 0 and 10°. The reaction mixture was then poured into water, and the lower organic layer was separated, washed with water, and dried over magnesium sulfate. Distillation gave 106.2 g (56% yield) of 2-aminohexafluoroisopropyl azide as a colorless liquid, bp 84–85° (lit.[10] bp 84–85°).

3,3-Bis(trifluoromethyl)diaziridine. 2-Aminohexafluoroisopropyl azide (20.8 g, 0.1 mole) was heated at reflux for 7 days. Periodically the white solid that formed in the water-cooled condenser was removed. Only a small amount of charred residue was left in the flask at the end of this time. The white solid was sublimed at 50° (760 mm) to give 12.1 g (67% yield) of 3,3-bis(trifluoromethyl)-diaziridine as large, transparent crystals, mp 79–80° (sealed capillary) (lit.[10] mp 80° (sealed capillary)).

3,3-Bis(trifluoromethyl)diazirine (III). A solution of 47.7 g (0.265 mole) of bis(trifluoromethyl)diaziridine[10] in 200 ml of benzonitrile was added dropwise over a period of 1 hr to a stirred suspension of 200 g of 90% lead tetraacetate–10% acetic acid in 565 ml of benzonitrile. The reaction temperature rose to 35°. The gases evolved during the reaction were condensed in a trap cooled by Dry Ice–acetone. After the addition was completed, the remainder of the gas dissolved in the reaction mixture was distilled into the trap by heating the mixture to 60° and reducing the pressure to 50 mm. Distillation of the condensate gave 41.0 g (87%) of a colorless liquid (III), bp -13 to $-12°$. The F^{19} nmr spectrum of a neat sample showed a singlet at $+0.32$ ppm. The infrared spectrum showed no major absorption bands at shorter wavelength than 7 μ. The mass spectrum showed the most abundant ion at m/e 69

(22) Melting points and boiling points are uncorrected. F^{19} nmr data were taken on a Varian HR-56.4 or Varian A-56/60 instrument and are reported in parts per million from 1,2-difluorotetrachloroethane (higher field taken as positive). H^1 nmr spectra were measured on a Varian A-60 or A60T spectrometer. Coupling constants (J) are given in cycles per second. Gas chromatographic data were obtained on homemade or Nester-Faust Anakro 1A instruments. Mass spectra were run on a CEC 21-103C instrument equipped with an inlet system at 150°.

(CF_3^+, 100), the parent ion at m/e 178 (17), and other major ions at m/e 131 (81), and 100 (53).

Anal. Calcd for $C_3F_6N_2$: F, 64.04. Found: F, 63.85.

VIII from III and Methylacetylene. A mixture of 10 g of dimethylacetylene and 10 g of bis(trifluoromethyl)diazirine was heated at 150° for 8 hr in a 80-ml stainless steel bomb. The bomb was cooled and vented, and the residual liquid was distilled to give 5.05 g (45%) of 1,2-dimethyl-3,3-bis(trifluoromethyl)cyclopropane as a colorless liquid, bp 88–88.5°, n^{25}D 1.3218.

Pyrolysis of I. A. In a Helium Flow System. Samples of gaseous I (1 cc) were injected into a 1.27 × 30 cm "Inconel"-alloy pyrolysis tube filled with 30-mesh quartz beads connected to a 3.7-m 20% "Kel-F Ester" column on 40–60 mesh firebrick maintained at 35°. The pyrolyses were carried out at 150 to 300° with a 50-cc/min helium flow maintained throughout; the contact time was 0.2–0.3 min. At 150° pyrolysis had just begun and at 300° no starting material could be detected. The major products (*ca.* 80% total yield) were collected and identified as hexafluoropropene[23] and tetrakis(trifluoromethyl)ethylene[24] by direct infrared and mass spectrometric comparisons with authentic samples. The ratio of the products formed was sensitive to pyrolysis conditions, but no quantitative data were obtained.

B. Under Reduced Pressure.[25] A 1.167-g sample of bis(trifluoromethyl)diazomethane was bled into an evacuated quartz pyrolysis tube (24 mm o.d., packed for a length of 30 cm with 4 × 6 mm quartz rings) heated at 423° over 60.0 min (pressure before addition was 0.005 mm; during the run the pressure was 0.35 mm). The product (0.901 g, 92%) was trapped with a liquid-nitrogen cold finger and shown by mass spectrometric analysis to be 99.8 mole % hexafluoropropene[23] and 0.2 mole % tetrakis(trifluoromethyl)ethylene.[24]

Pyrolysis of III. The diazirine was pyrolyzed in a helium flow system similar to that described for the pyrolysis of I. At 150° pyrolysis had just begun and at 350° no starting material could be detected. The major products (*ca.* 65% total yield) were collected and identified as hexafluoropropene[23] and hexafluoroacetone azine[10] by direct infrared and mass spectrometric comparisons with authentic samples. No evidence was obtained for the formation of tetrakis(trifluoromethyl)ethylene or for the isomerization of the diazirine to the diazo compound.

2-Methyl-2-(1-methylvinyl)-1,1-bis(trifluoromethyl)cyclopropane (XIX). A mixture of 25 g of 2,3-dimethylbutadiene and 15.4 g of III was heated at 150° for 16 hr in a 80-ml stainless steel bomb. The bomb was cooled and vented, and the contents was distilled. The fraction boiling at 120–122° was further purified by preparative gas chromatography on a 1,2,3-tris(2-cyanoethoxy)propane column at 100° to give 2.1 g (11%) of 2-methyl-2-(1-methylvinyl)-1,1-bis(trifluoromethyl)cyclopropane. The F^{19} nmr spectrum showed two quartets (J = 9.5 cps) centered at +9.8 and +12.64 ppm. The H^1 nmr showed a broad singlet centered at τ 5.12 (2 H), a doublet (J = 1.2 cps) split to a doublet (J = 1.0 cps) at 8.17 (3 H), and a complex multiplet centered at 8.55 (5 H). The infrared spectrum showed a band at 1656 cm^{-1} for >C=C<.

Anal. Calcd for $C_9H_{10}F_6$: C, 46.56; H, 4.32; F, 49.10. Found: C, 46.69; H, 4.53; F, 49.19.

9,9-Bis(trifluoromethyl)bicyclo[6.1.0]non-4-ene (IX). A 4.0-g sample of I was heated in an autoclave with 50 ml of *cis,cis*-1,5-cyclooctadiene and 1.0 g of hydroquinone at 150° for 8 hr. Spinning-band distillation led to 2.1 g (36%) of IX, bp 98° (45 mm), n^{25}D 1.4145. The infrared spectrum (neat) showed 1635 cm^{-1} (>C=C<), strong CF absorption. The H^1 nmr spectrum (neat) had a multiple at τ 4.28 (area 2, vinyl H), a complex multiplet at 7.2–8.1 (area 8), and a multiplet at 8.32 (area 2, cyclopropane H). The F^{19} nmr spectrum (neat) showed a pair of quartets (J = 10.5 cps) at −11.3 and −8.75 ppm. The mass spectrum indicated a molecule weight of 258.

Anal. Calcd for $C_{11}H_{12}F_6$: C, 51.17; H, 4.30; F, 44.15. Found: C, 51.50; H, 4.81; F, 44.37.

trans-1,2-Dimethyl-3,3-bis(trifluoromethyl)cyclopropane (Xa). A 10-g sample of I and 25 g of 99% pure *trans*-2-butene (Matheson, CP) were heated in a 80-ml autoclave for 8 hr at 150°. The bomb was vented at room temperature, and the recovered residue (7.5 g; considerable mechanical loss due to high volatility) was distilled

through a spinning-band column, giving 6.2 g (53.5%) of Xa, bp 87° (see text for nmr data).

Anal. Calcd for $C_7H_8F_6$: C, 40.79; H, 3.91; F, 55.30. Found: C, 40.71; H, 3.81; F, 55.26.

Reaction of I with *cis*-2-Butene. A 25-g sample of 99% pure *cis*-2-butene was heated with 9 g of I in an 80-ml autoclave for 8 hr at 150°. The vent gases (17 g) were collected and shown by gas chromatographic analysis to be be nitrogen and *cis*-2-butene. The amount of *trans*-2-butene in the olefin fraction was less than 1.5%. The recovered liquid (8.5 g) was 29% dissolved *cis*-2-butene and 71% higher boiling products. The higher boiling fraction contained two major and numerous minor products. The major product and one of the minor products were collected by preparative gas chromatography. The minor component (8%) was shown to be Xa by comparison with an authentic sample. One of the major products (39%) was identified as Xb, n^{25}D 1.3337, bp 95.5°, on the basis of its nmr (see text) and infrared spectra (no olefinic absorption).

Anal. Calcd for C_7H_8F: C, 40.79; H, 3.91; F, 55.30. Found: C, 41.41; H, 4.55; F, 54.93.

The other major product (49%) was shown to be XI, n^{25}D 1.3408, bp 103.5°. The H^1 nmr spectra showed a triplet at τ 8.81 (J = 7.0 cps) for CH_2CH_3, a quartet at 7.54 (J = 7.0 cps; split further) for CH_2CH_3, and a multiplet at 7.89 for the allylic methyl group split by the fluorine atoms. The F^{19} nmr spectrum exhibited a multiplet at −10.1 ppm (neat) due to an A_3B_3 pattern perturbed by proton interactions.

Anal. Calcd for C_7H_8F: C, 40.79; H, 3.91; F, 55.30. Found: C, 40.97, 41.09; H, 3.90, 4.16; F, 54.93.

Reaction of III with Cyclohexene. A mixture of 10.0 g of III and 25 g of cyclohexene was heated at 165° for 12 hr in a 145-ml autoclave. The autoclave was cooled and vented, and the contents was distilled to give 9.0 g of a colorless liquid, bp 115–150°. Both F^{19} nmr and gas chromatography indicated the liquid contained two major and one minor product. These products were collected by preparative gas chromatography.

7,7-Bis(trifluoromethyl)norcarane (XII), bp 150°, n^{25}D 1.3768, was present as 47.4% of the original mixture. The F^{19} nmr showed a pair of quartets (J = 8.7 cps) centered at −10.42 (broad) and +1.24 ppm (sharp). The H^1 nmr spectrum showed broad multiplets centered at τ 8.23 (6 H) and 8.57 (4 H).

Anal. Calcd for $C_9H_{10}F_6$: C, 46.56; H, 4.34; F, 49.10. Found: C, 47.02; H, 4.39; F, 49.24.

3-(2,2,2-Trifluoro-1-trifluoromethylethyl)-1-cyclohexene (XIII), bp 138°, n^{25}D 1.3768, was presented as 43.8% of the original mixture. The F^{19} nmr spectrum showed a complex multiplet (A_3B_3) from −4.26 to −2.57 ppm. The H^1 nmr spectrum showed multiplets at τ 4.3 (2 =CH), 7.15 (CHC(CF$_3$)$_2$H), and 8.0 (6 H). The infrared spectrum showed a band at 1658 cm^{-1} for C=C.

Anal. Calcd for $C_9H_{10}F_6$: C, 46.56; H, 4.34; F, 49.10. Found: C, 46.77; H, 4.48; F, 49.05.

2-(2,2,2-Trifluoro-1-trifluoromethylethyl)-1-cyclohexene (XIV) was present as 8.8% of the original mixture. The F^{19} nmr spectrum showed a doublet (J = 8.6 cps) at −1.44 ppm. The H^1 nmr spectrum showed a multiplet at τ 4.06 (=CH), 6.69 (1 H), 7.85 (4 H), and 8.33 (4 H). The infrared spectrum showed a band at 1661 cm^{-1} for C=C.

Anal. Calcd for $C_9H_{10}F_6$: C, 46.56; H, 4.34; F, 49.10. Found: C, 46.69; H, 4.51; F, 49.00.

Reaction of III with *cis*-2-Butene. A 10-g sample of III and 25 g of 99% pure *cis*-2-butene were heated in an 80-ml autoclave for 8 hr at 165°. The autoclave was cooled and vented, and the contents was distilled to give 8.05 g of colorless liquid, bp 85–90°. Both gas chromatography and the F^{19} nmr spectrum of this sample showed it was a mixture of five components. These products were collected by preparative gas chromatography. The major component (54.9%) was shown to be Xb by comparison of its nmr and infrared spectrum with those of an authentic sample. Two other components, Xa (7.8%) and XI (2.5%), were identified similarly.

A component present at 26.5% in the original mixture was identified as *cis*-6,6,6-trifluoro-5-trifluoromethyl-2-hexene (XVII) by spectral and analytical data. The F^{19} nmr spectrum showed a doublet (J = 7.8 cps) at +0.84 ppm. The H^1 nmr spectrum showed a multiplet at τ 4.44 (2 =CH), a multiplet at 7.33 (CH$_2$ + (CF$_3$)$_2$-CH), and a doublet (J = 5.5 cps) at 8.34 (CH$_3$). The infrared spectrum showed a band at 1639 cm^{-1} for C=C.

Anal. Calcd for $C_7H_8F_6$: C, 40.79; H, 3.91; F, 55.30. Found: C, 40.59; H, 4.01; F, 55.39.

A component present at 8.3% in the original mixture was identified as *trans*-5,5,5-trifluoro-4-trifluoromethyl-3-methyl-2-pentene

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(23) R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 3607 (1953).

(24) W. J. Middleton, U. S. Patent 3,136,781 (1964). See below for experimental details.

(25) This experiment was carried out in collaboration with Dr. W. J. Linn.

(XVIII) by spectral data only. The F^{19} nmr spectrum showed a doublet ($J = 8.5$ cps) at -0.53 ppm. The H^1 nmr spectrum showed a quartet ($J = 6$ cps) at τ 4.40 ($=$CH), a septet ($J = 8.5$ cps) at 6.72 (($CF_3)_2$CH), a singlet at 8.32 (CH_2), and a doublet ($J = 6$ cps) at 8.38 (CH_3).

Reaction of III with *trans*-2-Butene. A 10.0-g sample of III and 25 g of 99% pure *trans*-2-butene were heated in an 80-ml autoclave for 8 hr at 165°. The autoclave was cooled and vented, and the contents was distilled to give 9.32 g of colorless liquid, bp 85-90°. Both gas chromatography and the F^{19} nmr spectrum of this material indicated that it contained three products. These products were collected by preparative gas chromatography. The major component (57%) was shown to be Xa by comparison of its nmr and infrared spectra with those of an authentic sample.

The second component (39%) was shown to be *trans*-6,6,6-trifluoro-5-trifluoromethyl-2-hexene (XV), n^{25}D 1.3282, by analytical and spectral data. The F^{19} nmr spectrum showed a doublet ($J = 7.7$ cps) at $+1.24$ ppm. The H^1 nmr spectrum showed a multiplet at τ 4.5 (2 $=$CH), a multiplet at 7.5 ($CH_2 + C(CF_3)_2$H), and a doublet ($J = 5$ cps) at 8.37 (CH_3). The infrared spectrum showed a weak band at 1669 cm^{-1} for C$=$C.

Anal. Calcd for $C_7H_8F_6$: C, 40.79; H, 3.91; F, 55.30. Found: C, 40.90; H, 4.04; F, 55.23.

The third component (4%) was shown to be *cis*-5,5,5-trifluoro-4-trifluoromethyl-3-methyl-2-pentene (XVI) by analytical and spectral data. The F^{19} nmr spectrum showed a doublet ($J = 8.5$ cps) at -1.33 ppm. The H^1 nmr spectrum showed a quartet ($J = 7$ cps) at τ 4.18 ($=$CH), a septet ($J = 8.5$ cps) at 6.00 (C$(CF_3)_2$H), a singlet at 8.12 (CH_3), and a doublet ($J = 7$ cps) at 8.32 (CH_3).

Anal. Calcd for $C_7H_8F_6$: C, 40.79; H, 3.91; F, 55.30. Found: C, 40.57; H, 4.00; F, 55.00.

Thermolysis of I in Benzene. A 6.5-g sample of I was heated with 50 ml (44 g) of dry benzene at 200° for 8 hr in an autoclave. The recovered colorless solution (46 g) was shown to contain (in addition to benzene) two products (88:12) by gas chromatographic analysis (silicone grease column at 67°). Spinning-band distillation gave 6.05 g (70%) of material boiling at 132-141°. The minor product was shown to be hexafluoroisopropylbenzene[16] (XXI, bp 137.5°) by infrared and ultraviolet comparisons with an authentic sample. The major product (which also could be obtained essentially pure by fractionation) was assigned structure XX, bp 141°, nD^{25} 1.4062. The Raman spectrum (CCl$_4$) showed bands at 3050 (36), 2985 (8), 1620 (25), 1565 (100), 1450 (8), 1280 (5), 1225 (19), 965 (16), 740 (9), 580 (7), 475 (6), 430 (11) cm^{-1}. See text for other spectral data.

Anal. Calcd for $C_9H_6F_6$: C, 47.39; H, 2.65; F, 49.98. Found: C, 47.77, 47.69; H, 2.92, 3.01; F, 49.90.

1,1-Bis(trifluoromethyl)cycloheptane.[26] Catalytic hydrogenation of a solution of 430 mg of XX (96.5% pure) in 6 ml of tetrahydrofuran with 65 mg of palladium-on-charcoal catalyst resulted in the uptake of 126 ml of hydrogen at 25° (2.83 equiv). Gas chromato-

graphic analysis of the product solution (XF-1150 column at 55°) showed three peaks. The major "peak" (95%) was isolated by preparative gas chromatography. Ultraviolet spectroscopy showed only end absorption. H^1 nmr showed only bands in the τ 8.0-9.2 region. F^{19} nmr (neat) showed a broad singlet (half-band width $=$ 8 cps) at $+6.94$ ppm.

Anal. Calcd for $C_9H_{12}F_6$: C, 46.15; H, 5.17; F, 48.68. Found: C, 46.48; H, 5.35; F, 49.08.

Photolysis of I in Benzene. A 5.6-g sample of I was photolyzed for 40 hr with a G.E. H85A3 lamp through Pyrex glass in the presence of 40 ml (35 g) of dry benzene (water-cooled apparatus). Gas chromatographic analysis (silicone grease at 60°) showed three major peaks in addition to benzene (as eluted, 55:5:40). The products (2 g, 28%) were isolated by preparative gas chromatography after distillation. The 5% "peak" was XXI and the 40% "peak" was XX. The major product, bp 139°, was assigned the diene structure XXIV (see text).

Anal. Calcd for $C_9H_6F_6$: C, 47.39; H, 2.65; F, 49.98. Found: C, 47.77; H, 2.92; F, 50.66.

Interconversion of XX and XXIV. Diene XXIV gave 70% conversion to XX when heated in a sealed tube at 225° for 5 hr (and 89% conversion at 225° for 12 hr). Tropylidene XX gave 10% conversion in 16 hr and 97% conversion in 72 hr to XXIV when irradiated in a sealed tube (Pyrex) with a G.E. H85A3 lamp. The products (essentially quantitative yields) were identified by gas chromatographic retention volumes and by infrared analysis.

Pyrolysis of XX. Tropylidene XX was pyrolyzed over 20-mesh quartz chips at temperatures from 300 to 850° (gas chromatography-pyrolysis setup; 100-cc/min helium flow; 15-sec contact time). At 500°, the major product (>95%) was collected (silicone grease column at 100°) and shown by infrared analysis to be a 3:2 mixture of XXI and XXV, respectively.

7,7-Bis(pentafluoroethyl)-1,3,5-cycloheptatriene (XXVI). A 4.7-g sample of II was heated at 150° for 8 hr in the presence of 45 ml (39.5 g) of benzene. Distillation (spinning band) afforded 1.3 g (22%) of XXVI, bp 42° (5 mm), n^{25}D 1.3886 (see text for spectral data).

Anal. Calcd for $C_{11}H_6F_{10}$: C, 40.25; H, 1.83; F, 57.90. Found: C, 39.87; H, 2.09; F, 57.83.

Tetrakis(trifluoromethyl)ethylene. A mixture of 45 g (0.135 mole) of 2,2,3,3-tetrakis(trifluoromethyl)thiirane[27] and 10 ml of quinoline was heated at total reflux in a spinning-band still for 10 min and then the fraction boiling at 54° was collected to give 37.6 g (93%) of tetrakis(trifluoromethyl)ethylene as a colorless liquid, n^{25}D <1.3, d_4^{25} 1.6802. The F^{19} nmr spectrum showed a singlet at -5.50 ppm. The two strongest bands in the infrared spectrum of a liquid sample were at 1215 and 1245 cm^{-1}; no band was observed for C$=$C.

Anal. Calcd for C_6F_{12}: C, 24.02; F, 75.98. Found: C, 24.45; F, 76.05.

(26) We are indebted to Dr. E. Ciganek for this experiment.

(27) W. J. Middleton, U. S. Patent 3,136,781 (1964).