same salt of phenol-4-sulfonic acid. It thus appears that no reaction occurred since a nearly quantitative recovery (95%) of starting material was realized.

Run 2.—The fusion reactor was charged with 85 g (2.1 moles) of sodium hydroxide and heated to 425°. Over a period of 90 min, 34.8 g (0.177 mole) of sodium phenol-4-sulfonate was added while the reaction temperature was held at 400–440°. After the addition was complete, the mixture was held at 420–440° for 5 min. The cooled reaction mixture was dissolved in water and added to 190 ml (2.3 moles) of concentrated hydrochloric acid, then extracted with ether. The ether extract was distilled at reduced pressure (final conditions 25° (0.1 mm)) yielding 15.3 g. Sublimation of this material at 0.1 mm yielded sublimate 1, 2.0 g. by heating to 170°; sublimate 2, 2.6 g by heating to 250°; and residue, 6.9 g. Analyses of the above products showed that the reaction produced at most 0.5 g of phenol (3% conversion) and demonstrated the absence of detectable amounts of hydroquinone, resorcinol, and catechol. With the exception of phenol, infrared spectra indicated the above products to be a mixture of complex phenolic compounds.

The aqueous phase, which was distilled to dryness then extracted with methanol as in the preceding experiments, failed to yield any salts of the phenolsulfonic acids.

Reaction of Benzene-1,3-disulfonate with Sodium Hydroxide.—The fusion reactor, charged with 28 g (0.7 mole) of sodium hydroxide and 5 ml of water, was heated to 180° where a melt was obtained. Sodium benzene-1,3-disulfonate (50 g, 0.18 mole) was added over 6 min at 180–195°. An additional 57 g (2.1 moles total) of sodium hydroxide was added after the mixture had been held at 195–220° for 20 min. The mixture was heated to 350° over 45 min (heating rate limited by foamy nature of reaction) and held at 350–360° for 10 min. The diluted product was neutralized to pH 7 with about 140 ml (1.7 moles) of concentrated hydrochloric acid, and the resulting solution (about 750 ml) was extracted with ether (one 50-ml portion, three 75-ml portions, two 100-ml portions). The ether extract was distilled (final conditions, 40° (0.1 mm)) yielding 16.44 g (83.4% conversion) of resorcinol (mp 102–107° found, lit.[16] mp 110°) which contained some phenol but no detectable amount of catechol or hydroquinone.

Reaction of Sodium Benzene-1,2-disulfonate with Sodium Hydroxide.—A 50-g (0.18 mole) sample of sodium benzene-1,2-disulfonate was added to 85 g (2.1 moles) of molten sodium hydroxde at 340–360°. The addition was completed in 35 min after which the reaction mixture was held at 350–370° for 30 min. The cooled product was diluted with water to a volume of about 300 ml, strongly acidified with excess hydrochloric acid, and extracted with ether (five 200-ml portions). The ether extract was distilled yielding 8.61 g of residue which was identified as catechol containing some phenol but no detectable amount of resorcinol or hydroquinone. The aqueous phase was distilled to dryness at reduced pressure and the solids extracted with hot methanol (six 200-ml portions). The methanol solution was distilled to dryness yielding 24.2 g of a mixture of phenol-2-sulfonic acid and its sodium salt contaminated with sodium chloride. This mixture was found to be free of detectable amounts of the other isomeric phenolsulfonic acids or their sodium salts.

Acknowledgment.—The author is indebted to J. E. Graham and R. W. Mainier, of the Analytical Section of Koppers Co., Inc., for the infrared analyses and to T. S. Croft for the preparation of analytical standards. The author is particularly indebted to Dr. G. G. Ecke for consultation throughout this investigation.

Oxidative Coupling of 3,3,3-Trifluoropropyne

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Cupric chloride and the zinc derivative of 1,1,1-trifluoropropyne in dimethylformamide give 1,1,1,6,6,6-hexafluorohexa-2,4-diyne (III), along with various amounts of 1-chloro-3,3,3-trifluoropropyne (IV), *cis-* and *trans-*2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne, and 2-chloro-3(3,3,3-trifluoropropynyl)-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VI). Chlorination of III by cupric chloride in the reaction mixture leads to *trans*-2,3-dichloro-1,1,1,6,6,6-hexafluoro-2-ene-4-yne, and addition of a chloro group and a 3,3,3-trifluoropropynyl group (*via* the cupric salts) to III gives VI. 1,1,1,6,6,6-Hexafluorohexa-2,4-diyne is a low-boiling liquid (33°) which polymerizes at 25° but is stable at −78°. It reacts with 2 moles of organic azide to give bitriazolyl derivatives.

In this paper we wish to report our work on the oxidative coupling of the 3,3,3-trifluoropropyne derivative, $CF_3C\equiv CZnX$ (I,[1] where X = Cl or $CF_3C\equiv C$).

An initial attempt to couple 3,3,3-trifluoropropyne through oxidation of its cuprous salt with oxygen in aqueous solution gave no 1,1,1,6,6,6-hexafluorohexa-2,4-diyne (III). The diyne (III) was synthesized successfully by treating I with cupric chloride in dimethylformamide at reduced pressure.[2] This method is particularly convenient since I is prepared with dimethylformamide as solvent.[1] In addition to III there is produced 1-chloro-3,3,3-trifluoropropyne (IV), 2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne, 2-chloro-3-(3,3,3-trifluoropropynyl)-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VI), and a compound which is probably 2- or 3-chloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (VII).

The composition and yield of the product mixture are strongly dependent upon the reaction conditions. It is necessary to run the reaction under reduced pressure in order to remove the products as quickly as possible. Most of them are consumed by undetermined processes if left in contact with the reaction mixture. Another important factor is the manner of mixing the solutions of I and cupric chloride. When I is added to an excess of cupric chloride in dimethylformamide the recovery of fluorinated products is low and consists chiefly of *cis-* and *trans-*2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne (V) with lesser amounts of III, IV, VI, and VII. When the order of addition is reversed the total yield of products is even lower but now the major component is III and no VI or VII is detected. Simultaneous mixing of approximately equimolar solutions of I and of cupric chloride in a simple flow reactor gives the best yield of III. Using this method III can be prepared in 46% yield along with lesser amounts of IV, V, and VI.

The first step (1) in the reaction must be the formation of the cupric derivative, II. The details of step

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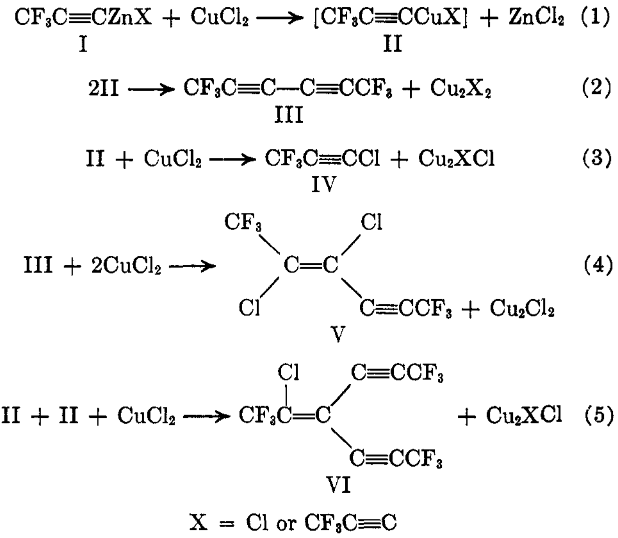
[1] W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

[2] Alkynylmagnesium halides and cupric halides in ether give coupled products: (a) J. P. Danehy and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 1609 (1936); (b) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2014 (1952); (c) H. H. Schlubach and V. Franzen, *Ann.*, **572**, 116 (1951). In one case (ref a) a 1-bromoalkyne also was isolated.



$$\underset{\text{I}}{CF_3C{\equiv}CZnX} + CuCl_2 \longrightarrow \underset{\text{II}}{[CF_3C{\equiv}CCuX]} + ZnCl_2 \quad (1)$$

$$2\text{II} \longrightarrow \underset{\text{III}}{CF_3C{\equiv}C{-}C{\equiv}CCF_3} + Cu_2X_2 \quad (2)$$

$$\text{II} + CuCl_2 \longrightarrow \underset{\text{IV}}{CF_3C{\equiv}CCl} + Cu_2XCl \quad (3)$$

(4) V

(5) VI

X = Cl or $CF_3C{\equiv}C$

2 are not known, but the work of Bohlmann and coworkers[3] suggests that this type of reaction cannot be considered simply as a coupling of two free alkynyl radicals. In addition, the intermediacy of free radicals seems improbable when one considers that the coupling reactions of acetylenes are sometimes carried out with the aid of oxygen,[4] the latter being well known for its reactivity toward free radicals, and cupric halides, which are extremely reactive toward free radicals.[5] It will be noted that reactions 2 to 5 each involves the reduction of two cupric ions to cuprous ions. All probably involve intermediate complexes of copper ions and various amounts of chloride, acetylide, and π-bonded acetylene units which give rise to the various products. Reaction 3 is analogous to (2) in which a chloride and an acetylide, rather than two acetylides, give up electrons to cupric ions.

1,1,1,6,6,6-Hexafluorohexa-2,4-diyne (III) is a low-boiling liquid[6] which spontaneously polymerizes to an insoluble, infusible polymer at 25°. The polymer sometimes contains visible amounts of crystalline material, which has not been isolated and characterized as yet. The low-pressure, gas phase infrared absorption spectrum of III shows a moderately strong band at 4.55 (triple bond), very strong bands at 8.15, 8.30, and 8.50 μ (associated with trifluoromethyl), and little else. Its F^{19} nmr spectrum exhibits a single peak at 52.0 ppm upfield from chlorotrifluoromethane. The mass spectrum of III has a base and parent peak at *m/e* 186 which corresponds to the calculated molecular weight. The ultraviolet spectrum (Table I) shows the diyne triplet plus an additional peak at 214 (shoulder) in cyclohexane and at 212 mμ in the gas phase. This is another example of the relative insensitivity of the absorption frequency and amplitude of the diyne triplet to variations in the substituents on the diyne function.[7] The spectrum of the hydrogen analog, hexa-2,4-diyne, is included for comparison.

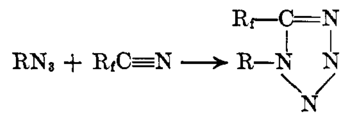
TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF III AND ITS HYDROGEN ANALOG

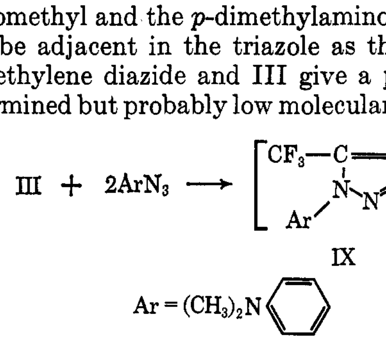
Compound	λ_{max}, mμ (ε)	λ_{max}, mμ (ε)	λ_{max}, mμ (ε)	λ_{max}, mμ (ε)
$(CF_3C{\equiv}C)_2$ (gas phase)[a,b]	212	222	234	248
$(CF_3C{\equiv}C)_2$ (cyclohexane[a] solution)	214[c] (200)	227 (210)	239 (230)	253 (160)
$(CH_3C{\equiv}C)_2$ (hexane)[d]	218 (300)	226 (360)	236 (330)	250 (160)

[a] The spectrum was obtained on a Cary Model 11 spectrophotometer. [b] The pressure was not measured. [c] Shoulder. [d] See ref 7.

1,1,1,6,6,6-Hexafluorohexa-2,4-diyne (III) reacts very readily with 2 moles of *p*-dimethylaminophenyl azide to give a high yield of the expected bistriazole (IX). The H^1 nmr spectrum shows a single sharp line at 3.0 ppm for the dimethylamino group and a quartet at 6.7 ppm for the *p*-phenylene (both downfield with respect to tetramethylsilane). This suggests a symmetrical structure and IX represents the least hindered of the two possible symmetrical forms. Also, it is known that organic azides condense with perfluoronitriles to give only 1-substituted tetrazoles.[8] By analogy the



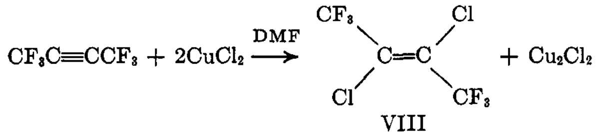
trifluoromethyl and the *p*-dimethylaminophenyl groups should be adjacent in the triazole as they are in IX. Hexamethylene diazide and III give a polytriazole of undetermined but probably low molecular weight.



IX

Other components separated by glpc were IV, V, VI, and VII. 1-Chloro-3,3,3-trifluoropropyne (IV), a previously reported compound,[9] was identified on the basis of its infrared spectrum (–C≡C– at 4.40 μ) and the parent peaks in its mass spectrum at *m/e* 128 and 130 in a 3:1 ratio.

trans chlorination of III in reaction 4 to give V is assumed since 1,1,1,4,4,4-hexafluorobutyne-2 gives *trans*-2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2 (VIII) when treated with cupric chloride in dimethylformamide. The *trans* relationship of the CF_3 groups in VIII was determined from the coupling constant for



VIII

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[3] F. Bohlmann, H. Schönowsky, E. Inhoffen, and G. Grau, *Ber.*, **97**, 794 (1964).

[4] C. Glaser, *ibid.*, **2**, 422 (1869); A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962); G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); F. Sondheimer and Y. Amiel, *J. Am. Chem. Soc.*, **79**, 5817 (1957).

[5] H. E. De La Mare, J. K. Kochi, and F. F. Rust, *ibid.*, **85**, 1437 (1963).

[6] A comparison of the boiling points of III and its hydrogen analog, hexa-2,4-diyne, discloses a great disparity. Hexa-2,4-diyne is notable for its unusually high boiling point of 129° [J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 44 (1951)] while III may be notable for its low boiling point of 33°. Both benzene and hexafluorobenzene, corresponding isomers of the diynes, boil at 80°.

[7] J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones, and M. C. Whiting, *ibid.*. 1998 (1952).

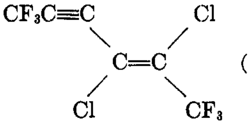
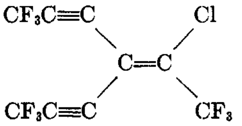
[8] W. Carpenter, *J. Org. Chem.*, **27**, 2085 (1962).

[9] A. M. Shchekotikhin, V. S. Blagoveshchenskii, V. V. Sidorenko, and O. K. Denisov, *Zh. Vses. Khim. Obshchestva im D. I. Mendeleeva*, **7**, 580 (1962); *Chem. Abstr.*, **58**, 6680*b* (1963). A. I. Shchekotikhin and O. K Denisov, U.S.S.R. Patent 169,522 (1965); *Chem. Abstr.*, **63**, 2897*d* (1965).

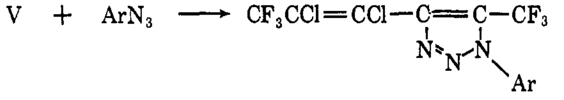
the C^{13} satellite peaks in the F^{19} nmr spectrum.[10] In one instance (see the Experimental Section) a mixture of V and its *cis* isomer was obtained. The infrared spectrum of the mixture was quite similar to that of V (–C≡C– at 4.44 μ and >C=C< at 6.32 μ) with no differences from 2.5 μ to past 7 μ. The F^{19} nmr spectra (Table II) show slight differences between the two isomers. The isomers were separated by glpc and their mass spectra were obtained. Each shows parent peaks at *m/e* 256, 258, and 260 in approximately 9:6:1 ratios, indicating two chlorine atoms. (The parent peaks correspond to the molecular weights calculated for V using the three possible combinations of the two chlorine isotopes.) *p*-Dimethylaminophenyl azide and V react to give the triazole, X.

TABLE II

F^{19} NMR SPECTRA OF PRODUCTS[a]

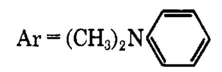
Compound	$CF_3C{\equiv}C$	$\overset{\text{Cl}}{\overset{\vert}{CF_3C}}{=}C$
$CF_3C{\equiv}C{-}C{\equiv}CCF_3$	52.0	. . .
 (*trans*)	52.7	62.5
$CF_3{-}C{\equiv}C{-}CCl{=}CClCF_3$ (mixture of *cis* and *trans*)	52.6 52.7	62.8 63.7
	52.4, 52.5	64.4

[a] Parts per million upfield from trichlorofluoromethane.



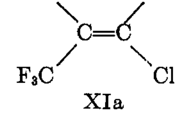
$$V + ArN_3 \longrightarrow CF_3CCl{=}CCl{-}C{=}C{-}CF_3$$

X

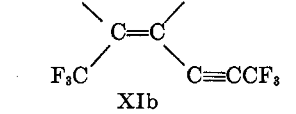


Ar = $(CH_3)_2N$–

Compound VI is an enediyne with triple-bond absorption at 4.44 and a double-bond absorption at 6.35 μ in the infrared. The mass spectrum gives parent peaks at *m/e* 314 and 316 in a 3:1 ratio indicating the presence of one chlorine and a molecular weight in agreement with formula VI. The F^{19} nmr spectrum (Table II) shows three peaks of equal size: two for CF_3 groups attached to triple bonds and one for CF_3 attached to a double bond. Structures XIa or XIb are logical alternatives to VI. There is one point, however, which argues against XIa or XIb. The 0.1-ppm difference between the peaks of the two $CF_3C{\equiv}C$ groups in the nmr spectrum of VI is precisely the same as the difference between the nmr peaks for the CF_3 groups on acetylene in *cis*- and *trans*-2,3-dichloro-1,1,1,6,6,6-hexafluorohexa-2-ene-4-yne where, in one isomer, $CF_3C{\equiv}C$ is *cis* to CF_3 and *trans* to Cl, and in the other isomer, the converse is true.[11] These are the same relationships that exist for the two $CF_3C{\equiv}C$ groups in VI. There are no model compounds available corresponding to XIa and XIb but it seems that the differences in $CF_3C{\equiv}C$ environments here are much greater than in VI and the peak separation should be considerably more than the 0.1 ppm observed. Therefore, structure VI is considered to be in the best agreement with experimental data. One possible route to VI is shown in reaction 5. Halogenation of multiple bonds by cupric halides is well known[12] and it is possible that II plus $CuCl_2$ could add trifluoropropynyl and chlorine to III to give VI. Another route to VI would be displacement of a chloro group from V by trifluoromethylacetylide from I. This latter route is probably not operative since I and $CF_3CCl{=}CCl_2$ (one of the starting materials for I) give no evidence of interacting under much longer periods of contact and much higher temperature.



XIa



XIb

Compound VII has infrared absorption bands at 3.31, 4.47, and at 6.16 μ and parent peaks at *m/e* 222 and 224 in a 3:1 ratio in its mass spectrum indicating the presence of one chlorine. These data are consistent with a compound of formula $CF_3C(H){=}C(Cl)C{\equiv}CCF_3$ or $CF_3C(Cl){=}C(H)C{\equiv}CCF_3$. The compound was not investigated further.

Experimental Section[13]

Addition of $CF_3C{\equiv}CZnX$ (I) to Cupric Chloride.—A solution containing 0.38 mole of I[14] in 250 ml of dry DMF[15] was prepared and 75 ml of liquid was distilled off at 20 mm to remove unreacted starting material and possible reduction products. The reaction mixture was then filtered, under nitrogen, through a layer of Celite to remove unreacted zinc. This solution was added, over a 20-min period, to a stirred solution (some suspended material) of 0.5 mole (67 g) of dried cupric chloride in 200 ml of dry DMF. (Cooling is required when cupric chloride is added to DMF.) The system was maintained at 45 mm and the volatile products (12 g) were collected in a Dry Ice–acetone trap. The contents from the trap were separated by glpc.[16] The five major fractions (excluding a little 1,1,1-trifluoropropyne) in the order of their elution from the column are listed in Table III. The compounds were identified on the basis of their spectral properties as given in the text.

Addition of Cupric Chloride Solution to I.—Solutions of I and of cupric chloride were prepared in the same quantities and in the same manner as in the previous experiment. The cupric chloride solution was added to the stirred solution of I over a 20-min period with the system maintained at 45 mm. The volatile products (5.0 g of liquid) were trapped in a Dry Ice–acetone trap. Glpc analysis[16] gave III as the major component (40% of isolated product) of the mixture alone with lesser

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(10) G. V. D. Tiers, *J. Chem. Phys.*, **35**, 2263 (1961).

(11) The 0.1-ppm difference between isomers is real because it was taken from the spectrum of a mixture of the isomers and not from two different spectra.

(12) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **30**, 587 (1965).

(13) The infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer. The F^{19} nmr spectra were run on a Varian DP-60 spectrometer operating at a frequency of 54.6 mHertz and the H^1 nmr spectra were run on a Varian A-60 spectrometer by Donald W. Moore of this laboratory. The mass spectra were determined on a Consolidated Electrodynamics mass spectrometer, Model 21-103C, by Joseph H. Johnson of this laboratory.

(14) The solution of I was prepared from 0.50 mole of $CF_3CCl{=}CCl_2$ according to the method in ref 1. The yield of I is assumed to be 75% on the basis of 1,1,1-trifluoropropyne recovery after addition of water to an identical preparation.

(15) Dimethylformamide was dried by stirring for 4 hr with calcium hydride and distilling at 10 mm. Dimethylacetamide dried in the same way is an equally good solvent.

(16) The instrument used was the Wilkins A 700 Autoprep with a $^3/_8$ in. × 20 ft aluminum column packed with 20% Apiezon oil on Chromasorb W. Column temperature was 65° and helium flow rate was 120 ml/min.

TABLE III

GLPC PRODUCT ANALYSIS

Component	Isolated product, %[a]
$CF_3C\equiv CCl$ (IV)	3
$(CF_3C\equiv C—)_2$ (III)	18
VII	3
$CF_3CCl=C(C\equiv CCF_3)_2$ (VI)	9
$CF_3CCl=CClC\equiv CCF_3$ (*cis* and *trans*)	51

[a] The relative abundance of each substance was estimated from its glpc peak area assuming equivalent responses for all the components.

amounts of IV and V and small amounts of unidentified substances. There was no VI or VII detected.

Simultaneous Mixing of I and Cupric Chloride.—A solution of I in 500 ml of dry DMF was prepared from 110 g (0.55 mole) of $CF_3CCl=CCl_2$ and 65 g (1.0 mole) of zinc.[1] The volume was reduced to 500 ml by distillation under reduced pressure. In another vessel 67 g (0.50 mole) of cupric chloride (dried at 120° (20 mm)) was added with stirring and cooling to 475 ml of dry dimethylacetamide.[15] The two solutions were placed in 500-ml addition funnels which were inserted in a 100-ml, three-necked, round-bottomed flask. The latter was provided with an overflow port in its side at such a height so as to restrict the volume of liquid in the flask to about 20 ml. The overflow port was connected to a 1.5 cm diameter × 100 cm long glass tube formed into a three-turn close spiral. The bottom of the spiral was connected to a 2-l., round-bottomed flask and this was connected to a Dry Ice–acetone trap and then to a liquid nitrogen trap. The entire system was evacuated to 14 mm. Contents of the two addition funnels were added simultaneously and equivalently over a 2-hr period to the little reactor flask. A magnetic stirring bar in the reactor flask provided efficient mixing of the reactants. As the reagents mixed, the temperature rose to about 40° and there was vigorous bubbling in the flask and part way down the overflow spiral. The spent reagents which collected in the large flask at the bottom of the spiral were very dark brown in color and were not examined further. The Dry Ice–acetone trap contained 25 g of a two-phase system. The smaller upper layer was chiefly dimethylformamide and was bright green in color.[17] Warming changed the color to brown. The lower layer was separated by distillation at 10^{-2} mm and trapping in a liquid nitrogen trap to give 20 g of material. Analysis by glpc[18] indicated that the product composition was IV, 2%; III, 80%; V, 10%; plus small amounts of VI, $CF_3CCl=CCl_2$, and some unidentified substances. This represents a 46% yield of III assuming 0.38 mole of starting material, I.

The 20 g of product was distilled at atmospheric pressure to give 15 g of material, bp 32–36°, which was about 96% III, bp 32–33° (709 mm). III and possibly V polymerize at this temperature to leave a dark brown residue in the still pot. However, if the distillation is conducted quickly loss of III is small.

Polymerization of III.—Seven grams of III was transferred in a vacuum system into an ampoule and sealed under vacuum. After storage at 5° for 24 hr, a brown gel had formed; after 20 days it was quite rigid. The sample was heated to 100° for 1 hr and then opened. The polymer was a brittle, reddish brown solid. Examination under the microscope showed crystalline inclusions. The polymer was broken up in a mortar and an infrared spectrum (KBr disk) was run on some of the powder. The spectrum showed broad bands at 6.6 and 7.9–8.8 μ.

Anal. Calcd for $(C_6F_6)_n$: C, 38.73; F, 61.27. Found: C, 37.49; F, 61.78.

Reaction of III with *p*-Dimethylaminophenyl Azide.—Two-tenths of a gram of III and 1.0 g of *p*-dimethylaminophenyl azide were dissolved in 10 ml of Freon 11. A slightly exothermic reaction followed. The reaction mixture was kept at 25° (stoppered flask) for 2 hr and then chilled to −10° for 12 hr. The product (0.22 g) was filtered off and recrystallized from 3:1 carbon tetrachloride–hexane solvent to give the bitriazolyl (IX), mp 170–171°.

Anal. Calcd for $C_{22}H_{20}F_6N_8$: C, 51.76; H, 3.95; F, 22.33; N, 21.96. Found: C, 51.46; H, 3.90; F, 22.53; N, 22.03.

Reaction of III with Hexamethylene Diazide.—A solution of 0.507 g (0.00273 mole) of III and 0.459 g (0.00273 mole) of hexamethylene diazide in 3 ml of methylene chloride was sealed in an ampoule and heated first at 50° for 3 hr and then at 100° for 1 hr. The ampoule was opened and the solvent was evaporated to give a slightly yellow, noncrystalline, brittle solid.

Anal. Calcd for $C_{12}H_{12}F_6N_6$: C, 40.68; H, 3.42; F, 32.18; N, 23.72. Found: C, 40.43; H, 3.25; F, 32.51; N, 23.16.

The analysis agrees with a 1:1 ratio of the reactants. The material is presumably a chain consisting of bitriazolyl groups, with CF_3 groups in the 4 position, hooked together with hexamethylene units.

Reaction of V with *p*-Dimethylaminophenyl Azide.—A hexane solution (5 ml) of 0.59 g of V and 0.37 g of *p*-dimethylaminophenyl azide was kept at 5° for 3 weeks to give 0.28 g of X, mp 95–97°. Recrystallization from hexane did not change the melting point.

Anal. Calcd for $C_{14}H_{10}Cl_2F_6N_4$: C, 40.11; H, 2.40; Cl, 16.92; F, 27.20; N, 13.37. Found: C, 40.18; H, 1.86; Cl, 16.82; F, 27.57; N, 13.47.

Chlorination of 1,1,1,4,4,4-Hexafluorobutyne-2 with Cupric Chloride.—Cupric chloride (13.4 g, 0.10 mole) was dissolved in 100 ml of dry DMF and the acetylene (8.1 g, 0.05 mole) was passed into the stirred solution maintained at 45–55°. A Dry Ice condenser prevented loss of the low-boiling hexafluorobutyne. The product and some DMF were removed under reduced pressure. Water was added to the distillate and 6.0 g of clear, dense liquid separated. Glpc analysis[18] showed two components in a 5:1 ratio, with *trans*-1,1,1,4,4,4-hexafluoro-2,3-dichlorobutene (VIII) as the major component. The lesser component contains a proton and is probably the hydrogen chloride addition product to hexafluorobutyne. Its H^1 nmr spectrum has a quartet at 6.6 ppm downfield from TMS. The major peak (VIII) appears homogeneous and nmr shows only one component with the F^{19} peak (CF_3) at 63.8 ppm (Tiers[10] reported 63.7 ppm) upfield from trichlorofluoromethane. The satellite peaks, due to the spin coupling (J = 275 cps) introduced by the naturally occurring isotope (C^{13}) in one CF_3, show a coupling constant of about 1 cps for F,F′ interaction, in agreement with the Tiers value of 1.4 cps for *trans*-1,1,1,4,4,4-hexafluoro-2,3-dichlorobutene-2.

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[17] The color may be due to a volatile trifluoropropynylcopper compound. It was observed that when an excess of the solution of I was accidentally added to the small reactor flask during the reaction a transient green color appeared in the otherwise brown reaction mixture. C_2H_5Cu and C_6H_5Cu form green solutions in ether: H. Gilman and J. M. Straley, *Rec. Trav. Chim.*, **55**, 821 (1936).

[18] The column was 3/8 in. × 15 ft aluminum tubing packed with 10% Kel F oil on Chromasorb P. The helium flow rate was 140 ml/min and the temperature was 50°.