

# The Addition of Trifluoromethanesulfonyl Chloride to Tetracyanoethylene

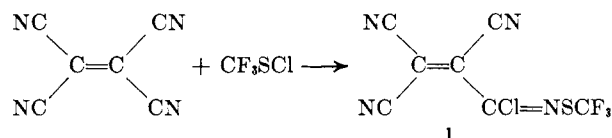
H. D. HARTZLER

Contribution No. 896 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

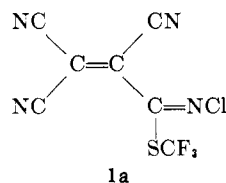
Received December 9, 1963

Trifluoromethanesulfonyl chloride adds to a nitrile of tetracyanoethylene in a chloride ion-catalyzed reaction to give 2-chloro-1-trifluoromethylthio-3,4,4-tricyano-1-aza-1,3-butadiene (**1**). Compound **1** is a weak  $\pi$ -acid as is shown by the formation of charge transfer complexes with aromatic hydrocarbons. Dienes add rapidly to **1** to give the expected substituted cyclohexenes. Electron-deficient olefins react rapidly at the carbon-nitrogen double bond of **1** to give substituted azetidines.

A large number of addition reactions of tetracyanoethylene (TCNE) have been reported.<sup>1-3</sup> The overwhelming majority of these reactions are nucleophilic additions to the carbon-carbon double bond<sup>1-3</sup> or cycloadditions to the carbon-carbon double bond.<sup>4,5</sup> Additions to a nitrile of TCNE have been few but are found with ethyl diazoacetate<sup>6</sup> and benzonitrile oxide.<sup>7</sup> This paper reports the addition of trifluoromethanesulfonyl chloride to TCNE to give 2-chloro-1-trifluoromethylthio-3,4,4-tricyano-1-aza-1,3-butadiene (**1**) and describes the unusual behavior of **1** in cycloaddition reactions.



**Formation of 1.**—A 1:1 adduct of TCNE and trifluoromethanesulfonyl chloride is formed in about 50% yield when an equimolar mixture of the reactants is held for thirty hours in acetonitrile at room temperature. Since the adduct, recrystallized from hexane,<sup>8</sup> is yellow [ $\lambda_{\text{max}}$  335 m $\mu$  ( $\epsilon$  8700)], addition to the carbon-carbon double bond is excluded. The infrared spectrum of the adduct showed absorption due to conjugated nitrile (4.48  $\mu$ ), tricyanovinyl double bond (6.35  $\mu$ ), carbon-nitrogen double bond (6.55  $\mu$ ), and carbon-fluorine (8  $\mu$ ). The spectral evidence is in agreement with structure **1** or its isomer **1a**. Evidence



in support of **1** is given below in the reactions of azetidines obtained from cycloaddition reactions of **1** where the NSCF<sub>3</sub> group is converted to NH.

Pure TCNE and trifluoromethanesulfonyl chloride react very slowly in methylene chloride at room temperature. A 77% yield of **1** is obtained after five days,

(1) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(2) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

(3) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *ibid.*, **80**, 2806 (1958).

(4) J. K. Williams, *ibid.*, **81**, 4013 (1959).

(5) J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962).

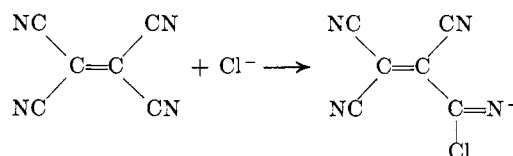
(6) R. M. Scribner, G. N. Sausen, and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

(7) Unpublished work of Dr. C. L. Dickinson and Dr. C. D. Weis.

(8) The trifluoromethylthio substituent has a tremendous solubilizing effect on polycyano compounds.

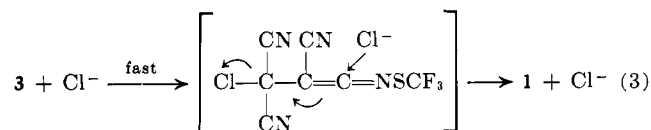
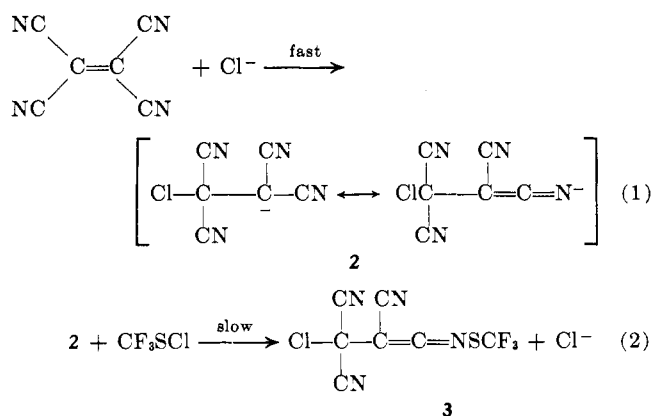
however, if anhydrous tetraethylammonium chloride is added to the system. TCNE is recovered in 90% yield after five days, if the salt is not present. Chloride ion catalysis has been observed previously in the chlorination of tricyanoethylene<sup>9</sup> and TCNE.<sup>10</sup> In these cases, chlorination occurs in acetonitrile solution without added chloride ion, but chloride ion is readily produced from reaction of chlorine with solvent.

It seems unlikely that chloride ion adds directly to a nitrile carbon of TCNE. The resultant anion would



not be expected to have any resonance stabilization. Moreover, under conditions similar to the addition to TCNE we have been unable to detect addition of trifluoromethanesulfonyl chloride to other negatively substituted nitriles, such as cyanogen chloride, trifluoroacetonitrile, tricyanovinylbenzene, and **1**.

The following reaction sequence is suggested as a preferable alternative to direct attack on the nitrile.



Step 1 is known to occur rapidly in the chlorination of TCNE. Step 2 has ample precedent in the addition of alcohol and amines to cyanoforn ion to form 1,1-dicyanoethylene derivatives, probably by way of keten-

(9) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).

(10) Unpublished work of Dr. C. L. Dickinson of this laboratory.

imines.<sup>11,12</sup> Step 3 looks eminently feasible thermodynamically, for a cumulative double bond system is being isomerized to a highly conjugated system.

Since we have been unable to obtain any spectral evidence for **3**, we must conclude that step 3 occurs much more rapidly than does 2 or that the entire reaction scheme is untenable. The former explanation is preferred.

**Chemical Reactivity of 1.**—Compound **1** gives many of the reactions expected of a negatively substituted unsaturated system. Polarographic reduction of **1** in acetonitrile solution occurs at +0.1 v. *vs.* s.c.e. as compared with the reduction of TCNE at +0.15 v. under these conditions. The reduction of **1**, however, is irreversible and appears to involve more than one electron.

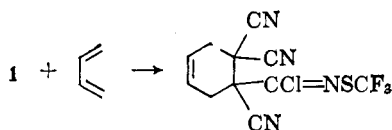
Weak  $\pi$ -complexes are formed with **1** and aromatic hydrocarbons. Wave lengths of maximum absorption, extinction coefficients, and association constants for some of these complexes are given in Table I. The

TABLE I  
 $\pi$ -COMPLEXES BETWEEN **1** AND AROMATIC HYDROCARBONS IN METHYLENE CHLORIDE AT 25°

Base	$\lambda_{\max}$ , m $\mu$	$\epsilon$	K
<i>p</i> -Xylene	460	2600	4
Durene	500	2600	15
Hexamethylbenzene	537	5000	33
Pyrene	470, 670	1600, 1750	11, 12

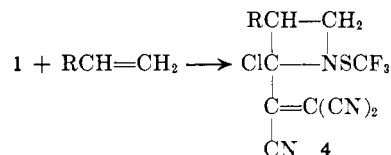
association constants for complex formation were calculated by the method of Keefer and Andrews.<sup>13</sup> Although **1** is reduced polarographically almost as readily as is TCNE, the association constants of **1** with aromatic hydrocarbons are much smaller than those of TCNE.<sup>14</sup> Interaction of **1** with benzene and toluene was too weak to measure spectroscopically.

As a dienophile, **1** is nearly as reactive as is TCNE. Aliphatic dienes, such as butadiene and 2,3-dimethylbutadiene, react exothermically with ethereal solutions of **1** at room temperature. With anthracene, a  $\pi$ -complex is obtained at room temperature which is converted to the adduct by warming to 60°. These addi-



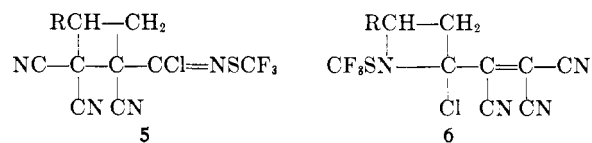
tions occur across the tricyanovinyl double bond of **1** as is evidenced by the infrared spectra of the adducts. The spectra show the absorptions of nonconjugated nitrile, carbon-nitrogen double bond (6.15 to 6.2  $\mu$ ), and nonconjugated carbon-carbon double bond (in the adducts from butadiene and 2,3-dimethylbutadiene).

While TCNE reacts with electron-rich olefins to give tetracyanocyclobutanes, **1** reacts with vinyl ethers and styrenes at the carbon-nitrogen double bond to give substituted azetidines **4**. These reactions occur even more rapidly than do the reactions of TCNE with the

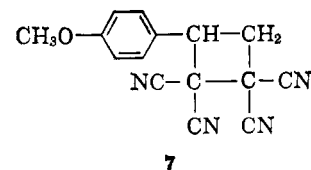


corresponding olefin. The reactions are usually exothermic upon mixing ethereal solutions of the reactants at room temperature. A list of the azetidines of structure **4** which have been prepared is given in Table II.

The structural assignments of the adducts **4** are based primarily on spectral evidence. The presence of a tricyanovinyl group is clearly indicated by infrared absorptions near 4.5 (conjugated nitrile) and 6.3  $\mu$  (tricyanovinyl double bond), and ultraviolet absorption at 260 to 268 m $\mu$  with molar extinction coefficient around 16,000. The isomeric cyclobutane structures **5** are clearly excluded. Structures **6** are discarded in favor of **4** on the basis of the ultraviolet absorption spectrum of the adduct of **1** with *p*-methoxystyrene (**4**,



R = *p*-methoxyphenyl). The absorptions of the tricyanovinyl group [ $\lambda_{\max}$  268 m $\mu$  ( $\epsilon$  18,300)] and the *p*-methoxyphenyl group [ $\lambda_{\max}$  230 m $\mu$  ( $\epsilon$  15,000)] are more intense than would be expected for the isolated chromophores. The extinction coefficient of the tricyanovinyl group is typically  $\sim$ 16,000 for the azetidines **4**, and compound **7** has  $\lambda_{\max}$  238  $\mu$  ( $\epsilon$  13,000).<sup>5</sup> The most reasonable explanation for the increased in-



tensity of absorption is spatial proximity of the two groups. Thus, not only is **4** the preferred structure, but when R = *p*-methoxyphenyl, it is probably *cis* to the tricyanovinyl group.

The n.m.r. spectra of the azetidines **4** are in good agreement with the proposed structures. The ring hydrogens give an ABX pattern common to all the azetidines. Thus, **4** with R = CH<sub>3</sub>O has a proton spectrum with the methoxy hydrogens at  $\tau$  6.50, the methine hydrogen as four peaks centered at  $\tau$  4.80, and the methylene hydrogens as a weak, strong, strong, weak pattern with each split into doublets and centered at  $\tau$  7.25.

The rate of formation of tetracyanocyclobutanes, such as **7**, from TCNE and an electron-rich olefin is markedly dependent upon solvent polarity.<sup>5</sup> The rates of adduct formation are larger in solvents of high dielectric constant. The rates of formation of the azetidines **4** are likewise markedly solvent dependent, although not to the extent of the TCNE reactions. When cycloadditions of **1** and vinyl ethers were run in polar solvents such as acetonitrile, the course of addition was not changed. There was still no addition to the tricyanovinyl double bond. The rate dependence on solvent suggests that there is appreciable charge


(11) A. Hantzsch and G. Oswald, *Ber.*, **32**, 641 (1899).

(12) S. Trofimenko, E. L. Little, Jr., and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962).

(13) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950); L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951).

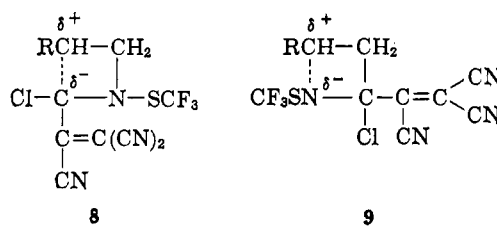
(14) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

TABLE II  
2-CHLORO-2-TRICYANOVINYL-1-TRIFLUOROMETHYLTHIOAZETIDINES

R	Empirical formula <sup>a</sup>	M.p., °C.	Recrystallization solvent	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %		Fluorine, %		Chlorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH <sub>3</sub> CH <sub>2</sub> O	C <sub>11</sub> H <sub>10</sub> ON <sub>4</sub> F <sub>3</sub> ClS	112-112.4	Heptane	76	39.2	38.9	2.40	2.45	16.6	16.2	16.9	17.0	10.6	11.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O	C <sub>13</sub> H <sub>12</sub> ON <sub>4</sub> F <sub>3</sub> ClS	106-106.6	Hexane	89	42.8	42.9	3.31	3.46	15.4	15.5	..	..	..	..
CH <sub>3</sub> O	C <sub>10</sub> H <sub>8</sub> ON <sub>4</sub> F <sub>3</sub> ClS	139-140	Hexane-benzene	82	37.2	37.1	1.87	2.29	17.4	17.2	..	..	11.0	11.2
CH <sub>2</sub> =CHO	C <sub>11</sub> H <sub>6</sub> ON <sub>4</sub> F <sub>3</sub> ClS	132.8-134	Hexane-benzene	74	39.5	39.9	1.81	2.11	16.7	16.7	..	..	10.6	10.5
C <sub>6</sub> H <sub>5</sub>	C <sub>15</sub> H <sub>8</sub> ON <sub>4</sub> F <sub>3</sub> ClS	115-117	Hexane	91	48.8	48.4	2.20	2.19	15.2	15.5	..	..	..	..
CH <sub>3</sub> O- 	C <sub>16</sub> H <sub>10</sub> ON <sub>4</sub> F <sub>3</sub> ClS	132.8-133.6	Hexane-benzene	87	48.2	48.1	2.54	2.65	14.0	13.7	14.3	14.3	8.89	8.90

<sup>a</sup> These compounds may merit consideration as unknowns in organic qualitative elemental analysis.

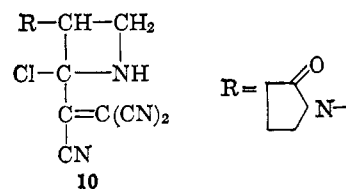
separation in the transition state. On this basis the transition state leading to **4** appears much more reasonable than one leading to the isomeric **6**. Thus, **8** allows a greater delocalization of charge than does **9**. The



transition state **8** leading to **4** has a charge distribution of the azomethine double bond which is opposite that of simpler azomethines in their cycloaddition reactions with ketenes.<sup>15</sup> The reversal in polarity is a consequence of the ability of the adjacent tricyanovinyl group to stabilize a negative charge.

The addition of styrene to **1** is a reversible reaction. When the resultant azetidine is dissolved in benzene, the red color of the  $\pi$ -complex of **1** and styrene develops. This indicates the ease of dissociation of the azetidine into its components. The reversal of the cycloaddition reaction gives additional support to the thesis that there is considerable charge separation in the transition states of these cycloadditions. There is no reason to expect homolytic fission of the carbon-carbon bond in question in **8**. Starting materials were recovered from the attempted addition of **1** to 2,3-dimethyl-2-butene.

The reaction of **1** with N-vinylpyrrolidone gave a compound without a trifluoromethylthio group. Spectral evidence similar to that cited above showed the presence of the tricyanovinyl group. In addition, N-H absorption was apparent in the infrared spectrum. The product has been assigned structure **10**. Conver-



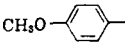
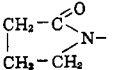
sion of the trifluoromethylthioazetidines **4** to the azetidines **10** has been found to be a general reaction conveniently effected by nucleophilic reagents, such as alcohols or pyridine. The properties of the azetidines **10** are given in Table III.

Although the conversion of **4**  $\rightarrow$  **10** generally required heating **4** with an alcohol for several hours, the reaction is not a thermal fission of the nitrogen-sulfur bond. The azetidines **4** may be quantitatively recovered from solutions in refluxing dimethoxyethane after several days. The reaction probably proceeds by way of nucleophilic attack on sulfur. No attempt was made to isolate the thiaperoxides which are presumed to have been formed.

The azetidine **10** with R = *p*-methoxyphenyl also shows the increased intensities of the *p*-methoxyphenyl [ $\lambda_{\max}$  230  $m\mu$  ( $\epsilon$  15,500)] and the tricyanovinyl [ $\lambda_{\max}$  269  $m\mu$  ( $\epsilon$  19,400)] absorptions, indicating an adjacent *cis* relationship of the two groups.

(15) H. Staudinger, *Ber.*, **40**, 1145 (1907); *Ann.*, **356**, 93 (1907).

TABLE III  
 2-CHLORO-2-TRICYANOVINYLAZETIDINES

R	Empirical formula	M.p., °C.	Recrystallization solvent	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	C <sub>15</sub> H <sub>11</sub> N <sub>4</sub> OCl	262-263.5	Ethylene chloride	73	60.3	60.3	3.71	3.99	18.7	18.4	11.9	12.1
CH <sub>3</sub> O-	C <sub>9</sub> H <sub>7</sub> N <sub>4</sub> OCl	166-167.4	Methanol	64	48.6	48.8	3.17	3.27	25.2	25.3	15.9	15.9
CH <sub>2</sub> CH <sub>2</sub> O-	C <sub>10</sub> H <sub>9</sub> N <sub>4</sub> OCl	154-155.5	Ethylene chloride	60	50.8	51.4	3.83	3.97	23.7	24.0	15.0	14.9
	C <sub>12</sub> H <sub>10</sub> N <sub>5</sub> OCl	222-223	<i>a</i>	70	52.3	52.3	3.66	3.52	25.4	25.8	12.9	12.8

<sup>a</sup> Recrystallization was not effected. Purification was by rinsing with dimethoxyethane.

The conversion of 4 → 10 provides the evidence mentioned previously for the selection of structure 1 rather than 1a for the adduct of TCNE and trifluoromethanesulfonyl chloride.

### Experimental<sup>16</sup>

**2-Chloro-1-trifluoromethylthio-3,4,4-tricyano-1-aza-1,3-butadiene (I).**—A slurry of 64 g. of TCNE, 75 g. of trifluoromethanesulfonyl chloride, and about 2 g. of tetraethylammonium chloride in 500 ml. of methylene chloride was stirred under nitrogen at room temperature for 5 days. The mixture was then filtered and the filtrate was evaporated to dryness. The residue was crystallized from hexane to give 1 as yellow plates, m.p. 86-87°, 103 g. (77%).

*Anal.* Calcd. for C<sub>7</sub>ClF<sub>3</sub>N<sub>4</sub>S: C, 31.8; Cl, 13.4; F, 21.5; N, 21.2; S, 12.1. Found: C, 32.5; Cl, 13.5; F, 21.2; N, 21.1; S, 12.0.

The infrared spectrum of 1 showed the absorption of conjugated nitrile at 4.48 μ, conjugated carbon-carbon and carbon-nitrogen double bonds at 6.35 and 6.55 μ, and carbon-fluorine at 8 μ. The ultraviolet spectrum of 1 in acetonitrile showed absorption at 355 mμ (ε 8700), 258 (7430), and 223 (7400).

**1 with Trifluoromethanesulfonyl Chloride.**—Compound 1 was recovered in 90% yield after standing for 1 day with excess trifluoromethanesulfonyl chloride in acetonitrile solution at room temperature.

**1 with 2,3-Dimethylbutadiene.** 1,1,2-Tricyano-2-[chloro(trifluoromethylthioimino)methyl]-4,5-dimethyl-4-cyclohexene.—A solution of 1.0 g. of the diene in 5 ml. of ether was added to a solution of 2.66 g. of 1 in 30 ml. of ether. The temperature rose to 30°. After stirring overnight, the solvent evaporated, and the residue was crystallized from hexane-benzene (1:3) to give 2.51 g. (73%) of adduct, m.p. 110-115°. Another recrystallization gave pure adduct, m.p. 115-116°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>10</sub>ClF<sub>3</sub>N<sub>4</sub>S: C, 45.0; H, 2.92; Cl, 10.2; F, 16.4; N, 16.2; S, 9.25. Found: C, 45.4; H, 3.36; Cl, 10.7; F, 16.4; N, 16.0; S, 8.85.

The infrared spectrum is consistent with the Diels-Alder adduct structure. There is weak absorption at 4.46 μ attributable to the nonconjugated nitrile, at 6.10 and 6.15 μ for the carbon-carbon and carbon-nitrogen double bonds, and strong absorption at 8 to 9 μ of the carbon-fluorine.

**1 with Butadiene.**—A mixture of 13.5 g. of 1, 4 g. of butadiene, and 100 ml. of ether was stirred at room temperature for 2 hr. The ether was evaporated, and pentane (50 ml.) was added. The adduct crystallized and was filtered to give 10.7 g. (66%) of crude product, m.p. ~90°. Recrystallization from dibutyl ether raised the melting point to 104-104.6°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>6</sub>ClF<sub>3</sub>N<sub>4</sub>S: C, 41.5; H, 1.90; Cl, 11.1; N, 17.6; S, 10.1. Found: C, 41.7; H, 2.19; Cl, 11.3; N, 17.7; S, 9.95.

The infrared spectrum of the adduct was very similar to that of the adduct with 2,3-dimethylbutadiene.

**1 with Anthracene.**—A solution of 2.70 g. of 1, 1.8 g. of anthracene, and 50 ml. of benzene was heated at 60° for 18 hr. The green color of the π-complex which had formed on mixing the reactants disappeared. The mixture was cooled in ice, filtered, and the white solid was rinsed with ether to give 1.16 g. of crude adduct, m.p. 111-117°. A second crop of 2.0 g. was obtained from the filtrate. Attempts to recrystallize or sublime the crude adduct were unsuccessful. Purification was achieved by rinsing the adduct with ether. The purified adduct melted at 143-147°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>10</sub>ClF<sub>3</sub>N<sub>4</sub>S: C, 57.0; H, 2.28; N, 12.7. Found: C, 57.0; H, 2.17; N, 12.8.

The infrared spectrum of the adduct exhibited absorptions of carbon-carbon and carbon-nitrogen double bonds at 6.1 and 6.2 μ, carbon-fluoride at 8 to 9 μ, and very weak nitrile absorption at 4.5 μ. The infrared spectrum was completely consistent with the assigned structure.

**1 with Vinyl Ethers and Styrenes.**—The products which have been obtained are given in Table II. The general procedure is illustrated by the reaction of 1 with styrene.

A solution of 2.70 g. of 1, 2.10 g. of styrene, and 25 ml. of ether was stirred at room temperature. The red color of the π-complex between 1 and styrene formed upon mixing. The mixture was warmed overnight at 40°. The mixture was cooled, and the solvent was removed under nitrogen. Addition of 20 ml. of pentane caused the residue to crystallize. Filtration gave a light tan solid (3.56 g.); crystallization from hexane gave the azetidine, m.p. 115-117°, 3.35 g. (91%).

The infrared spectrum of the adduct showed the intense tricyanovinyl absorption at 6.34 μ and conjugated nitrile absorption at 4.5 μ. The spectrum was completely consistent with the azetidine structure. The ultraviolet spectrum of the adduct in acetonitrile solution showed the presence of the tricyanovinyl group, λ<sub>max</sub> 268 mμ (ε 16,400). When the adduct is dissolved in benzene solution, the red color of the π-complex of I and styrene develops.

**2-Chloro-2-tricyanovinylazetidines.**—These products are given in Table III. The general procedure is illustrated with the preparation of 2-chloro-3-methoxy-2-tricyanovinylazetidine. A solution of 16.2 g. of 2-chloro-3-methoxy-2-tricyanovinyl-1-trifluoromethylthioazetidine and 4.6 g. of ethanol in 50 ml. of glyme was heated at reflux for 2 days. The solvent was evaporated. The residue was triturated with ether and filtered to give 8.3 g. of azetidine, m.p. 159-161°. Recrystallization from methanol gave the pure product (7.09 g., 64%), m.p. 166-167.4°.

The ultraviolet spectrum of the product in acetonitrile solution shows the tricyanovinyl absorption at 261 mμ (ε 16,100). The infrared spectrum shows the absorptions of NH at 3.04 μ, conjugated nitrile at 4.53 μ, tricyanovinyl double bond at 6.27 μ, and carbon-oxygen single bond at 9 μ.

**1 with N-Vinylpyrrolidone.**—A slurry of 10.8 g. (0.04 mole) of 1 in 50 ml. of ether was stirred at room temperature while N-vinylpyrrolidone (4.5 g.) was added dropwise. The temperature rose to reflux. A reddish solution formed, and a tan solid was deposited. The mixture was cooled to room temperature and filtered to give 6.72 g. of crude adduct, m.p. 220-225°.

(16) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 21, ultraviolet and visible spectra on a Cary Model 14, and n.m.r. spectra on a Varian A60 spectrometer.

Recrystallization of the adduct was not successful. Purification was achieved by rinsing the adduct with glyme. This gave material of m.p. 222–223° dec.

*Anal.* Calcd. for  $C_{12}H_{10}ClN_2O$ : C, 52.3; H, 3.66; Cl, 12.9; N, 25.4. Found: C, 52.3; H, 3.52; Cl, 12.8; N, 25.8.

The infrared spectrum of the azetidine confirms the fact that the  $CF_3S$  group has been removed during the reaction. There was absorption of the conjugated nitrile and the tricyanovinyl

double bond as in the other azetidines.  $CF$  and  $SCF_3$  absorptions were absent. Additional absorption due to  $NH$  and  $C=O$  was apparent. The ultraviolet absorption of the adduct in acetonitrile solution showed the presence of the tricyanovinyl group,  $\lambda_{max}$  265  $m\mu$  ( $\epsilon$  15,300).

**Acknowledgment.**—The author is greatly indebted to Dr. H. E. Simmons for advice and suggestions.

## Free-Radical Additions Involving Fluorine Compounds. VII.<sup>1</sup> The Addition of Perhaloalkanes to Vinyl Ethyl Ether and Vinyl 2,2,2-Trifluoroethyl Ether

PAUL TARRANT AND EUGENE C. STUMP, JR.<sup>2</sup>

*The Department of Chemistry, University of Florida, Gainesville, Florida*

*Received August 23, 1963*

The addition of perhaloalkanes to some vinyl and allyl ethers were carried out satisfactorily in the presence of ultraviolet irradiation. Adducts obtained from vinyl trifluoroethyl ether showed a marked increase in thermal and hydrolytic stabilities over the vinyl ethyl ether adducts. The products,  $\alpha$ -bromo ethers, were converted into a variety of fluorine-containing compounds.

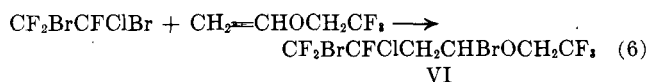
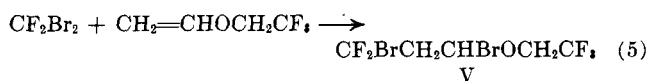
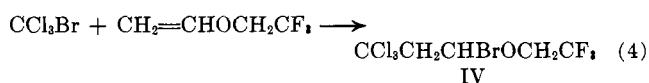
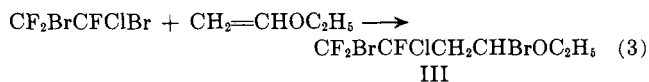
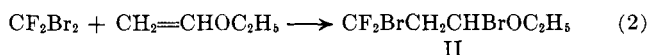
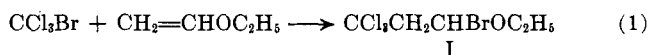
As part of a program designed to prepare new fluorine-containing monomers, the synthesis of some unsaturated fluoro ethers has been investigated. Earlier work<sup>1</sup> had shown that free-radical addition of perhaloalkanes such as bromotrichloromethane, dibromodifluoromethane, and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to allyl ethers could be accomplished easily to give adducts capable of transformation to both olefinic and dienic ethers. Consequently, this reaction was extended to include addition of  $CCl_3Br$ ,  $CF_2Br_2$ , and  $CF_2BrCFClBr$  to some vinyl ethers. Vinyl ethyl ether and vinyl 2,2,2-trifluoroethyl ether were chosen because of their availability and also in order to compare the effect of the  $\beta$ -fluorine atoms on the properties of the adducts.

A number of investigators have shown the high reactivity of vinyl ethers in free-radical additions. Glickman<sup>3</sup> added carbon tetrachloride, carbon tetrabromide, and dibromodichloromethane to a number of vinyl ethers using peroxides or ultraviolet irradiation to give high yields of 1-halo-3-trihalopropyl ethers. Similar additions have been reported by Levas<sup>4</sup> and Shostakovskii.<sup>5</sup>

Initial attempts to carry out radical additions to vinyl ethyl ether in an autoclave using benzoyl peroxide initiator at 75° resulted, in every case, in decomposition of product as evidenced by heavy fuming and formation of black, spongy polymer. This thermal instability, characteristic of most  $\alpha$ -haloalkyl ethers,<sup>6</sup> necessitated the adoption of a procedure in which materials could react at temperatures lower than the decomposition temperature of the products. Such a method was found in the use of ultraviolet irradiation as a free-radical initiator. An additional advantage of this procedure is the absence of contaminants resulting from the de-

composition of the peroxide. It was subsequently found that ultraviolet-catalyzed additions to allyl ethers could be carried out in conversions comparable to those from peroxide-catalyzed reactions.<sup>1</sup>

The following free-radical addition reactions were carried out using ultraviolet initiation.



Adducts from vinyl ethyl ether (I, II, III) fumed heavily on exposure to moist air and decomposed rapidly with evolution of hydrogen halide between 70–85° during distillation. Consequently, only II could be satisfactorily fractionated owing to its lower boiling point, although apparent boiling points for the  $CCl_3Br$  and  $CF_2BrCFClBr$  adducts (I, III) are reported (see Table I for properties of the compounds prepared). These adducts, although not isolated could be treated to give stable derivatives which will be described later. Satisfactory analysis of the  $\alpha$ -bromoalkyl ethyl ethers was not accomplished owing to their rapid decomposition. Compounds I, II, and III were also found to be extremely reactive hydrolytically. Upon basic hydrolysis, I was found to give appreciable quantities of a highly lachrymatory material identified as dichloroacrolein,  $CCl_2=CHCHO$ . Hydrolysis of the  $CF_2Br_2$  and  $CF_2BrCFClBr$  adducts (II and III) resulted in vigorous reactions leading to the formation of extremely lachrymatory compounds which were not

(1) Preceding paper in this series: P. Tarrant and E. C. Stump, Jr., *J. Org. Chem.*, **26**, 4646 (1961).

(2) To whom requests for reprints should be sent at Peninsular Chem. Research, Inc., P. O. Box 14318, Gainesville, Fla.

(3) S. A. Glickman, U. S. Patent 2,560,219 (1951).

(4) M. Levas, *Ann. chim. (Paris)*, **7**, 697 (1952); *Chem. Abstr.*, **48**, 1243d (1954).

(5) M. F. Shostakovskii, A. V. Bogdanova, M. M. Zverov, and G. I. Plotnikova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1236 (1956); *Chem. Abstr.*, **51**, 5730e (1957).

(6) L. Summers, *Chem. Rev.*, **55**, 337 (1955).