to estimate the concentration of isocyanate in the reaction system. Iodine was not consumed in the reaction (visible absorption band was of constant intensity when checked on a Cary Model 14.) Thus the data were treated in a conventional manner using a pseudo-second-order treatment.

Each run was accurately pseudo second order. A typical run was complete in approximately 10 min. Trinitrobenzene had no effect on the reaction, nor did small amounts of AIBN.

Reaction of Isopropylisonitrile with Bromine and Pyridine N-Oxide.—A solution of isopropylisonitrile (0.69 g, 0.01 mole) and pyridine N-oxide (0.95 g, 0.01 mole) in 100 ml of chloroform was treated with an equmolar amount of bromine in chloroform. A colorless precipitate appeared, 2.40 g (75%), mp 95–96° dec; the material darkened rapidly at room temperature, but appeared to be stable at 0°. The precipitate II was soluble in water and methanol, slightly soluble in acetonitrile, and insoluble in ether, tetrahydrofuran, carbon disulfide, chloroform, and petroleum ether (bp 30–60°). II gave an immediate precipitate with silver nitrate solution.

Anal. Calcd for $C_9H_{12}Br_2N_2O$: C, 33.36; H, 3.73; N, 8.65; Br, 49.32. Found: C, 33.30; H, 3.76; N, 8.58; Br, 48.16 (after 24 hr of standing at room temperature: Br, 46.19).

Infrared maxima were 3.30 (m), 3.42 (m), 3.51 (m), 5.88 (s), 6.25 (m), 6.79 (s), 6.86 (s), 7.28 (w), 7.35 (w), 7.46 (w), 7.81 (w), 8.15 (w), 8.40 (w), 8.51 (w), 8.80 (w), 8.88 (w), 9.12 (w), 9.75 (w), 10.04 (m), 10.25 (vs), 11.42 (w), 12.0 (w), 12.78 (s), 14.00 (w) (in KBr Pellet). In Nujol some prominent peaks were 5.85 (s), 6.25 (m), 10.25 (vs); no peaks were in the 4.0–5.7-μ region.

Treatment of II with water gave a precipitate of *sym*-diisopropylurea, mp 193–194° after sublimation.[7] Its infrared spectrum was identical with that of an authentic sample, and the melting point was not depressed on admixture. Reaction with *sec*-butylamine in methanol gave 1-isopropyl-3-*sec*-butylurea, mp and mmp 135–136°.[8] Infrared spectra of material from an unknown and an authentic sample were superimposable. Heating the unknown under high vacuum gave a complex mixture; volatiles had pyridine (vpc and infrared spectrum), isopropylisonitrile (vpc and mass spectrum), and isopropyl isocyanate (vpc mass spectrum, and infrared spectrum) present. Some pyridine N-oxide was also formed and indications of isopropylisonitrile dibromide (infrared spectrum) were also found. Treatment of the unknown with isopropylisonitrile gave isopropyl isocyanate and isopropylisonitrile dibromide (infrared spectrum). Reduction of 0.25 g of unknown with 3 g of lithium aluminum hydride in ether gave a mixture of pyridine and methylisopropylamine (vpc and infrared spectra).

Reaction of Isopropylisonitrile with Chlorine and Pyridine N-Oxide.—Chlorine gas was bubbled into a solution of pyridine N-oxide and isopropylisonitrile (0.01 M in each) in chloroform. After about 5 min, a colorless precipitate formed which was removed by filtration. The material was crystallized from ethanol to yield pyridine N-oxide hydrochloride, mp 179–180, whose infrared and nmr spectra were identical with those of an authentic sample prepared by bubbling anhydrous hydrogen chloride through a chloroform solution of pyridine N-oxide. It was possible to recover 85% of the pyridine N-oxide as solid hydrochloride by allowing the solution to stand for about 1 hr at room temperature.

In a separate experiment chlorine was bubbled through a solution of isopropylisonitrile (0.50 g) in chloroform (25 ml) for 3–5 min. The solvent was removed using a vacuum pump, and the residue was pumped until no more material seemed to be removed. The residue was dissolved in chloroform and an equimolar amount of pyridine N-oxide was added. No reaction occurred immediately; after standing for about 24 hr approximately 25% of the isonitrile dichloride had been converted to the isocyanate as shown by infrared spectra.

In a third experiment a solution of chlorine in chloroform was prepared which gave an optical density of 1.0 in a 1-cm cell at the visible maximum. This solution was divided into two parts; one part was diluted with an equal volume of chloroform; the other was diluted with 0.1 M pyridine N-oxide in chloroform. The time for the reduction in optical density by 0.2 and 0.4 unit was identical for the two solutions.

Reaction of Isopropylisonitrile with Miscellaneous Materials.—A solution of isopropylisonitrile (10%) in chloroform was allowed to react with mercuric oxide at reflux for 1 hr; infrared spectra showed that complete conversion to the isocyanate occurred during this time. A second portion of the isonitrile was allowed to react with pyridine N-oxide in chloroform in the absence of added halogen. No reaction had occurred after 3 hr.

Solutions of the isonitrile in chloroform (10%) were allowed to react with dimethyl sulfone, benzoyl peroxide, and triphenylphosphine oxide (approximately equimolar proportions) in the presence of small amounts of bromine. Infrared spectra were recorded after a 1-hr reaction. In all instances the isocyanate had formed. In the absence of bromine, no isocyanate formed, except in the case of benzoyl peroxide. With benzoyl peroxide a small amount of isocyanate formed after several days of refluxing.

Registry No.—II, 10349-37-8; pyridine N-oxide, 694-59-7; phenylisonitrile, 931-54-4; *p*-anisylisonitrile, 10349-38-9; isopropylisonitrile, 598-45-8.

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[7] A. W. Hofmann [*Ber.*, **15**, 756 (1882)] reports mp 192°.

[8] Urban, *Arch. Pharm.*, **242**, 70 (1892).

Trifluoromethylmalononitrile. The Reaction of 1,1-Dichloro-2,2-dicyanoethylene with Argentous Fluoride[1]

A. D. Josey, C. L. Dickinson, K. C. Dewhirst, and B. C. McKusick

Contribution No. 1113 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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Reaction of 1,1-dichloro-2,2-dicyanoethylene with 4 equiv of argentous fluoride provides the silver salt of trifluoromethylmalononitrile, which can be converted to trifluoromethylmalononitrile by treatment with hydrogen chloride. Under the same conditions, reaction of the chloro cyano olefin with 2 equiv of argentous fluoride provides solutions from which the yellow dye 1-fluoro-1-(4-dimethylaminophenyl)-2,2-dicyanoethylene can be isolated by treatment with N,N-dimethylaniline.

Monoperfluoroalkyl derivatives of malononitrile have not previously been reported.[2] We discovered the parent member of the series, trifluoromethylmalononitrile (IV), during an attempt to convert 1,1-dichloro-2,2-dicyanoethylene (I) to 1,1-difluoro-2,2-dicyanoethylene (II) by treatment with an excess (4 molar equiv) of argentous fluoride. None of the difluoro compound was obtained. Instead, we isolated the silver salt of trifluoromethylmalononitrile (III), which was readily converted to trifluoromethylmalononitrile (IV) by reaction with hydrogen chloride.

As the equations of Scheme I indicate, we believe that 1,1-difluoro-2,2-dicyanoethylene (II) is an intermediate in the reaction. This remarkable addition of

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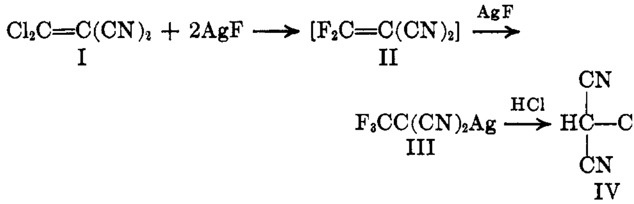
[1] Presented at the First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1966.

[2] S. Proskow (U. S. Patent 3,170,949) describes bis(trifluoromethyl)-malononitrile.

SCHEME I



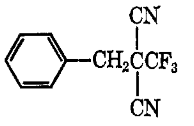
$$\underset{I}{Cl_2C{=}C(CN)_2} + 2AgF \longrightarrow \underset{II}{[F_2C{=}C(CN)_2]} \xrightarrow{AgF} \underset{III}{F_3CC(CN)_2Ag} \xrightarrow{HCl} \underset{IV}{HC(CN)_2{-}CF_3}$$

argentous fluoride to II is presumably a consequence of the exceptionally strong electrophilic character of the double bond. It is reasonable that II should be strongly electrophilic in view of its relationship to tetrafluoroethylene and tetracyanoethylene, both of which are strongly electrophilic.[3,4]

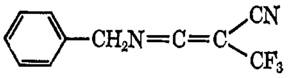
Trifluoromethylmalononitrile is a colorless, mobile liquid that has good stability when pure. It is strongly acidic, but since alkali metal hydroxides, amines, and even fluoride ion promote decomposition, salts are difficult to prepare, and only the silver salt has been isolated and characterized. On hydrolysis trifluoromethylmalononitrile gave the known 3,3,3-trifluoropropanoic acid, isolated as the anilide.[5a]

Trifluoromethylmalononitrile resembles cyanoform in its strong acidity[5b] but is much more stable and undergoes C-alkylation more readily. Thus, whereas salts of cyanoform are C-alkylated in yields of only about 10%,[6] treatment of the silver salt of trifluoromethylmalononitrile with benzyl bromide gave benzyltrifluoromethylmalononitrile (Va) in 42% yield.

The infrared spectrum of Va was free of any bands in the 5–6-μ region where absorption due to the $N{=}C{=}C<$ chromophore may be expected to appear. Therefore, the possibility that the product is Vb, the result of N-alkylation, can be eliminated.



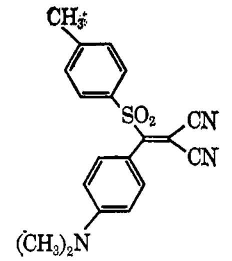
Va



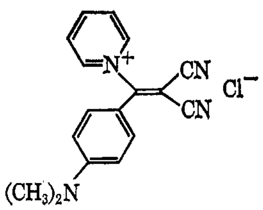
Vb

Treatment of 1,1-dichloro-2,2-dicyanoethylene (I) with 2 molar equiv of argentous fluoride gave a solution thought to contain 1,1-difluoro-2,2-dicyanoethylene (II), the presumed intermediate in the formation of trifluoromethylmalononitrile. Attempts to isolate II were unsuccessful, but its presence was strongly indicated by the formation of 1-fluoro-1-(4-dimethylaminophenyl)-2,2-dicyanoethylene (VII) in good yield when the solution was treated with N,N-dimethylaniline. The method used to prove the structure of VII, an intensely yellow substance, is outlined in Scheme II.

It is of interest that the chlorine atom of VI can be replaced in good yield by a variety of nucleophilic groups. For example, reaction with sodium *p*-toluenesulfinate gave 1-(4-dimethylaminophenyl)-1-(*p*-toluenesulfonyl)-2,2-dicyanoethylene (IX, 70%). Pyridine reacts readily with VI to give the quaternary salt N-[1-(4-dimethylaminophenyl)-2,2-dicyanovinyl]pyridinium chloride (X, 76%). This compound reverted to the chloro derivative VI during crystallization from ethanol unless small amounts of pyridine were added.



IX



X

The 1,1-dichloro-2,2-dicyanoethylene used in this work was prepared by a somewhat more convenient method (Scheme III) than that used previously.[7] Like the chlorination of tricyanoethylene[8a] and tetracyanoethylene,[8b] the chlorination of 1-chloro-2,2-dicyanoethylene (XI) is strongly catalyzed by tetramethylammonium chloride or triethylamine. It is probable here, as in the former cases, that chlorination of the strong π acid proceeds by initial attack of the nucleophilic catalyst (chloride ion or amine) on the double bond. The chlorination product XII gave 1,1-difluoro-2-chloro-2,2-dicyanoethane (XIII) when treated with argentous fluoride.

Experimental Section

1-Chloro-2,2-dicyanoethylene (XI).[7]—A solution of potassium ethoxide was prepared by dissolving 80 g (2 g-atoms) of potassium metal in 1500 ml of absolute ethanol. To this warm solution there were added successively 132 g (2 moles) of malononitrile, 300 g (4.05 moles) of ethyl formate, and 300 ml of absolute ethanol. The mixture was stirred at reflux for 1.5 hr and cooled, and the precipitated potassium salt of hydroxymethylenemalononitrile[9a] was collected by filtration, washed thoroughly with ether, and dried in a vacuum desiccator. The yield was 202 g (76%).

A slurry of 100 g (0.76 mole) of the dry potassium salt in 400 ml of methylene chloride was treated with 158 g (0.76 mole) of phosphorus pentachloride in one portion. The mixture was stirred under reflux for 4 hr, cooled, and filtered. The solids were washed on the filter with fresh methylene chloride, and the combined filtrate was concentrated by distillation at reduced pressure. The dark residue was distilled through a 20-cm Vigreux column to provide 51 g (62%) of 1-chloro-2,2-dicyanoethylene, bp 73° (10 mm), n^{25}_{D} 1.4930.

1,1,2-Trichloro-2,2-dicyanoethane (XII).[7]—Chlorine gas was slowly bubbled through a solution of 50 g (0.445 mole) of 1-chloro-2,2-dicyanoethylene in 70 ml of methylene chloride until the solution was saturated. Triethylamine (2 drops) was added, and the temperature rose quickly to 50°. The slow addition of chlorine was continued for 8 hr. The solvent was removed at the water pump, and the product was distilled to yield 75 g (92%) of 1,1,2-trichloro-2,2-dicyanoethane, bp 76–76.5° (15 mm). On standing, the distillate crystallized. Three crystallizations from pentane provided white needles, mp 46–47°.

1,1-Dichloro-2,2-dicyanoethylene (1).[7]—A solution of 40 g (0.21 mole) of 1,1,2-trichloro-2,2-dicyanoethane in 250 ml of anhydrous ether was cooled in an ice bath and vigorously stirred

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(3) D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, *J. Am. Chem. Soc.*, **82**, 5116 (1960).

(4) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, Edith G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *ibid.*, **80**, 2775 (1958).

(5) (a) A. Henne, R. Pelley, and R. Alm, *ibid.*, **72**, 3370 (1950); (b) S. Trofimenko, *J. Org. Chem.*, **28**, 217 (1963); R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

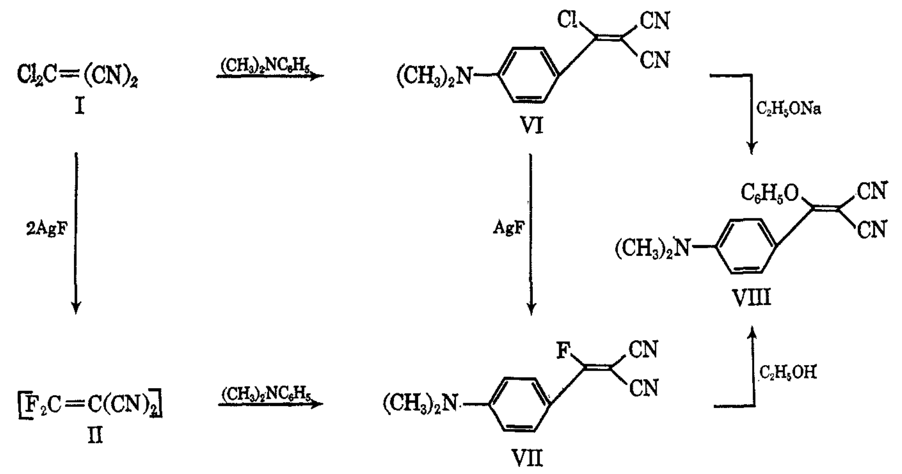
(6) A. Hantzsch and G. Oswald, *Ber.*, **32**, 648 (1899).

(7) A. E. Ardis, U. S. Patent 2,774,783 (1956).

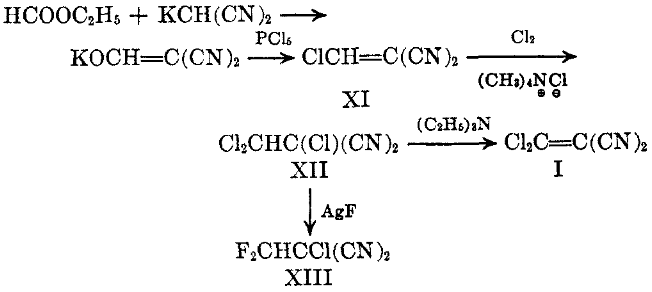
(8) (a) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960); (b) C. L. Dickinson and B. C. McKusick, *J. Org. Chem.*, **29**, 3087 (1964).

(9) (a) R. Schenk and H. Finken, *Ann.*, **462**, 158 (1928). (b) The ^{1}H nmr spectrum was observed with a Varian A-60 spectrometer using an internal tetramethylsilane reference.

Scheme II



Scheme III



$$
\begin{array}{l}
HCOOC_2H_5 + KCH(CN)_2 \longrightarrow \\
KOCH{=}C(CN)_2 \xrightarrow{PCl_5} \underset{\text{XI}}{ClCH{=}C(CN)_2} \xrightarrow[(CH_3)_4\underset{\oplus}{N}\underset{\ominus}{Cl}]{Cl_2} \\
\underset{\text{XII}}{Cl_2CHC(Cl)(CN)_2} \xrightarrow{(C_2H_5)_3N} \underset{\text{I}}{Cl_2C{=}C(CN)_2} \\
\quad\Big\downarrow AgF \\
\underset{\text{XIII}}{F_2CHCCl(CN)_2}
\end{array}
$$

while a solution of 21 g (0.21 mole) of triethylamine in 50 ml of anhydrous ether was added dropwise. When the addition was complete, the mixture was stirred 10 min, then filtered. The ether was removed by distillation, and the dark, semicrystalline residue was sublimed at 70° (10 mm) to provide 27 g (84%) of 1,1-dichloro-2,2-dicyanoethylene, mp 60–62°. A second sublimation together with four crystallizations from hexane gave white prisms, mp 61.5–62°, lit.[5b] mp 63–64°.

Trifluoromethylmalononitrile (1,1,1-Trifluoro-2,2-dicyanoethane) (IV).—A suspension of 51.1 g (0.402 mole) of anhydrous powdered argentous fluoride on 150 ml of acetonitrile (freshly distilled from phosphorus pentoxide) was stirred vigorously while a solution of 14.8 g (0.101 mole) of 1,1-dichloro-2,2-dicyanoethylene in 60 ml of acetonitrile was added dropwise over a period of 15–20 min. Moderate cooling with a cool-water bath dissipated the heat developed in the mixture. When the addition of the dichloro compound was complete, stirring was continued for 2 hr at room temperature. The resultant slurry was filtered through a sintered-glass funnel to remove silver chloride and any unchanged silver fluoride, and the filter cake was washed with acetonitrile. The orange-yellow filtrate was evaporated to dryness. The residue, consisting largely of the silver salt of trifluoromethylmalononitrile, was a pasty orange solid.

Without further purification, the pasty solid was suspended in 250 ml of anhydrous ether and rapidly stirred, while hydrogen chloride was bubbled in. The flow of gas was stopped when the orange solution failed to yield additional silver chloride. Solids were removed by filtration, the ether was removed by careful distillation through a semimicro spinning-band column, and the residue was fractionally distilled to yield 9.0 g (67%) of trifluoromethylmalononitrile as a mobile, colorless liquid of pungent odor, bp 77–78° (100 mm), $n^{25}D$ 1.3347.

Anal. Calcd for $C_4HF_3N_2$: C, 35.9; H, 0.75; F, 42.5; N, 20.9. Found: C, 36.3; H, 0.96; F, 42.6; N, 20.4.

Trifluoromethylmalononitrile was hydrolyzed to 3,3,3-trifluoropropanoic acid as follows. A mixture of 0.7 ml of the nitrile and 10 ml of 12 *N* hydrochloric acid was heated at 100–120° for 6 hr, cooled, and treated with 15 ml of saturated sodium chloride solution, and the hydrolysate was extracted with ether. The ether solution was dried over magnesium sulfate and concentrated to yield 0.78 g of straw-colored liquid. The infrared spectrum showed λ_{max} 3.85 (OH), 5.76 (C=O), and strong absorption in the region 7.7–9.1 μ (CF) in accord with the expected structure, CF_3CH_2COOH.[10] The ^1H nmr spectrum[9b] of the neat liquid showed a quartet of resonances centered at τ 6.72 from coupling of CH_2 with the CF_3 group (J = 10 cps). In addition, a single sharp resonance was observed for the carboxyl proton at τ −1.05. The anilide, prepared by a standard method,[10] had mp 121–122°, lit.[5a] 117–118°).

Reaction of Trifluoromethylmalononitrile with Alcoholic Silver Nitrate.—A solution of 0.5 ml of trifluoromethylmalononitrile in chilled ethanol was treated with excess 5% alcoholic silver nitrate. A white precipitate of the silver salt formed immediately. The product was removed by filtration, thoroughly washed with ethanol and ether, and dried.

Anal. Calcd for $C_4N_2AgF_3$: N, 11.6. Found: N, 11.8.

Benzyltrifluoromethylmalononitrile (Va).—Crude silver trifluoromethylmalononitrile (*ca.* 0.06 mole, 14 g) was suspended in 100 ml of anhydrous ether, and a solution of 10.25 g (0.06 mole) of benzyl bromide in 25 ml of ether was added in one portion. Moderate evolution of heat occurred, and a light yellow color developed. The suspension was stirred at room temperature overnight, heated at reflux 1 hr, cooled, and filtered.

The ether was removed by careful distillation to give a red-brown residue that solidified. The product was rubbed on filter paper to absorb residual oil, and the resulting yellow powder was sublimed at 60° (93 mm). The sublimate (5.5 g, 42%) collected as a white, crystalline solid, mp 73–74°. Two crystallizations from pentane gave 1,1,1-trifluoro-2,2-dicyano-3-phenylpropane, mp 72–73°. The infrared spectrum contained only aromatic bands in the 5–6.5-μ region and showed no absorption attributable to the ketimine chromophore, thus eliminating Vb as the structure of the product.

Anal. Calcd for $C_{11}H_7F_3N_2$: C, 59.0; H, 3.2. Found: C, 59.3; H, 3.3.

1-Fluoro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene (VII). A. From 1,1-Dichloro-2,2-dicyanoethylene, Argentous Fluoride, and N,N-Dimethylaniline.—A solution of 5.0 g (0.034 mole) of 1,1-dichloro-2,2-dicyanoethylene in 20 ml of anhydrous acetonitrile was cooled in a cool water bath. While the solution was rapidly stirred, 8.64 g (0.068 mole) of argentous fluoride was slowly added over 0.5 hr. After the addition was completed, the mixture was stirred an additional 15 min, then filtered. The solids were washed with a little acetonitrile, and this was added to the filtrate. Approximately one-half of the filtrate (theoretically containing 0.017 mole of 1,1-difluoro-2,2-dicyanoethylene) was treated with 2 molar equiv (4.3 ml) of dimethylaniline. The color of the solution darkened, and a precipitate formed. The mixture was allowed to stand at room temperature for 5 hr; then it was evaporated *in vacuo* to give a dark crystalline mass. Recrystallization from chloroform–methylcyclohexane, using Norit decolorizing carbon, afforded fine, orange needles, mp 161–164°; $\lambda_{max}^{CH_3CN}$ 424 (ϵ 51,500), 315 (1360), 263 (1700), and 240 mμ sh (5380).

Anal. Calcd for $C_{12}H_{10}FN_3$: F, 8.83. Found: F, 8.90.

A small portion of the product was dissolved in absolute ethanol, and the solution was boiled for several minutes. Addition

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(10) R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 200.

of a few drops of water and cooling afforded stubby, yellow prisms. The product had mp 87.5–88.5° and did not depress the melting point of authentic 1-ethoxy-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene, mp 90°.

B. From 1-Chloro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene and Argentous Fluoride.—A solution of 3.84 g (0.017 mole) of 1-chloro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene in 100 ml of anhydrous acetonitrile in a cold water bath was rapidly stirred while 2.55 g (0.017 mole) of argentous fluoride was added over 0.5 hr. The reaction mixture was stirred 65 hr, filtered, and the filtrate was concentrated to obtain 2.75 g (77%) of crude 1-fluoro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene. A sample was crystallized twice from chloroform–methylcyclohexane and had mp and mmp 162–164°.

1-Chloro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene (VI).—A solution of 9.68 g (0.08 mole) of N,N-dimethylaniline in 20 ml of anhydrous ether was added dropwise to a stirred solution of 5.88 g (0.04 mole) of 1,1-dichloro-2,2-dicyanoethylene in 25 ml of anhydrous ether. After 2 hr, the ether was removed by distillation, and the residue was washed with water. Recrystallization of the crude material yielded 7.05 g (76%) of orange product, mp 132–134°; $\lambda_{\max}^{\mathrm{EtOH}}$ 245 (ϵ 7625), 273 (7850), 317 (2400), 320 (1350), and 445 mμ (44,000).

Anal. Calcd for $C_{12}H_{10}ClN_3$: C, 62.2; H, 4.3; Cl, 15.3; N, 18.1. Found: C, 61.9; H, 4.5; Cl, 14.8; N, 18.1.

1-Ethoxy-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene (VIII).—A solution of sodium ethoxide was prepared by dissolving 0.100 g of freshly trimmed sodium metal in 15 ml of absolute ethanol. There was added in one portion a warm (50°) solution of 1.0 g (0.0043 mole) of 1-chloro-1-[4-dimethylaminophenyl]-2,2-dicyanoethylene in 20 ml of absolute ethanol. The orange solution quickly became yellow. After 15 min the mixture was filtered to remove the solid which had collected. The filtrate was diluted with 100 ml of water, and the turbid yellow mixture was extracted with three 50-ml portions of ether. The extracts were dried over magnesium sulfate, filtered, and evaporated to provide a yellow-orange crystalline residue. Four crystallizations from methanol–water provided an analytical sample, mp 90°; $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (ϵ 20,000).

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.7; H, 6.26; N, 17.4. Found: C, 69.8; H, 6.33; N, 17.6.

Compound IX.[11]—To a solution of 0.232 g of 1-chloro-1-(4-dimethylaminophenyl)-2,2-dicyanoethylene in 3 ml of dimethylformamide was added 0.178 g of sodium *p*-toluenesulfinate in small portions. The mixture was stirred 5 min and diluted with water, and the crystalline precipitate was collected. The product was recrystallized from a methylene chloride–ether mixture to give 0.25 g (70%) of the sulfone, mp 155–157°, $\lambda_{\max}^{\mathrm{EtOH}}$ 518 mμ ($\epsilon_{\max}$ 17,900).

Anal. Calcd for $C_{19}H_{17}N_3O_2S$: C, 64.9; H, 4.5; N, 12.0. Found: C, 64.5; H, 5.2; N, 11.7.

N-[1-(4-Dimethylaminophenyl)-2,2-dicyanovinyl]pyridinium Chloride (X).—Pyridine (4 ml) was added to a solution of 2.31 g (0.01 mole) of 1-chloro-1(4-dimethylaminophenyl)-2,2-dicyanoethylene (VI) in 50 ml of ethanol. The solution became bright orange, and after 4 hr the orange precipitate was collected. The yield of pyridinium salt (mp 144–146°) was 2.43 g (76%). After the compound was recrystallized from ethanol once, the melting point was lower, and after several crystallizations the starting material VI was obtained. The recrystallization was repeated using ethanol containing about 2% pyridine. Several crystallizations gave material melting at 147–148°.

Anal. Calcd for $C_{17}H_{16}ClN_4$: C, 65.8; H, 4.8; Cl, 11.2; N, 18.1. Found: C, 65.9; H, 5.0; Cl, 11.3; N, 17.9.

The visible spectrum showed a pronounced change with a change in solvent, for in water $\lambda_{\max}$ 499 mμ ($\epsilon_{\max}$ 43,800) while in acetone $\lambda_{\max}$ 449 mμ ($\epsilon_{\max}$ 37,800).

1,1-Difluoro-2-chloro-2,2-dicyanoethane (XIII).—Argentous fluoride (150 g, 1.2 moles) was slowly added to an ice-cold, stirred solution of 90 g (0.49 mole) of 1,1,2-trichloro-2,2-dicyanoethane in 150 ml of anhydrous acetonitrile. When the addition was complete, the mixture was stirred an additional 15 min at room temperature and filtered. The filtrate was distilled through a 35-cm column packed with glass helices, and after removal of solvent there was obtained 35 g (48%) of 1,1-difluoro-2-chloro-2,2-dicyanoethane, bp 77–79° (200 mm), d^{27} 1.34.

Anal. Calcd for $C_4HClF_2N_2$: C, 31.9; H, 0.82; F, 25.2. Found: C, 32.3; H, 1.06; F, 25.6.

Registry No.—I, 10472-00-1; III, 10472-01-2; IV, 10472-02-3; Va, 10472-03-4; VI, 10472-04-5; VII, 10472-05-6; VIII, 10472-06-7; IX, 10472-07-8; X, 10472-08-9; XI, 10472-09-0; XII, 10472-12-5; XIII, 10487-73-7; argentous fluoride, 7775-41-9; 3,3,3-trifluoropropionic acid, 2516-99-6.

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[11] This experiment was performed by Dr. E. L. Martin.

Organic Fluoronitrogens.[1] VI. Reduction of Difluoramino Compounds with Iodide

ROBERT L. REBERTUS, JOHN J. MCBRADY, AND JOHN G. GAGNON

Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota

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The oxidation–reduction reactions of iodide ion with some hydrolytically stable difluoramino compounds have been surveyed. Generally, complete four-electron reductions of the nitrogen atoms in the difluoramino groups do not occur, and nonintegral electron changes result from the formation of mixtures of nitrogen-containing products. Nitrogen gas and nitrogen(3−) species are formed in water, but interesting intermediates including substituted diazirines and fluorimines result from the partial reductions which occur in some other solvent systems.

The oxidation number of the nitrogen atom in the difluoramino group NF_2 is 1+, while that in the monofluoramino (>NF) or the fluorimino group (=NF) is 1−. Both inorganic and organic molecules containing these groups are capable of oxidizing iodide ion. This general reaction constitutes an important qualitative test.[2–5] However, the products of iodide reductions have been reported for only a few fluoronitrogens. Among the inorganic materials, difluoramine undergoes a quantitative, four-electron reduction to ammonium ion,[6] whereas difluorodiazine is reduced only to nitrogen gas.[7] The reported iodometric reactions of organic fluoronitrogens are limited to the four-electron reduction of N,N-difluorourea,[8] which readily hydrolyzes to difluoramine, and to the two-electron reductions of some cyclic compounds containing the monofluoramino group.[2,9]

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