mixture. The infrared spectrum in acetonitrile solution showed a broad band at 3300 (OH) and a strong band at 1768 cm^{-1} (C=O).

Anal. Calcd for $C_4H_2F_6O_3$: F, 52.40; mol wt, 212. Found: F, 51.80; mol wt, 216 (neutral equivalent).

Preparation of the Methyl Ester of Bistrifluoromethylglycolic Acid (VII).—To a cold solution of 10 g of acid V in anhydrous ethyl ether was added an alcohol-free ethereal solution of diazomethane (prepared in the usual manner)[8] in small portions until an excess of diazomethane was present. The ether was distilled off using a water bath at 70°, and the residue was taken up in 20 ml of ether. The ether solution was dried over sodium sulfate and distilled to give 6.8 g (64% yield) of the methyl ester of bistrifluoromethylglycolic acid (VII), bp 109–111°. The infrared spectrum in carbon tetrachloride solution exhibited bands at 3490 (OH) and 1768 cm^{-1} (C=O).

Anal. Calcd for $C_5H_4F_6O_3$: F, 50.47. Found: F, 50.13.

Registry No.—I, 2378-02-1; 2,2,2-trifluoroethanol, 75-89-8; 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol, 1515-14-6; 1,1,1,3,3,3-hexafluoro-2-propanol, 920-66-1; III, 7594-49-2; IV, 7594-48-1; V, 662-22-6; VII, 7594-51-6.

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The Action of Cyanide Ion on 1,2-Dichlorohexafluorocyclopentene

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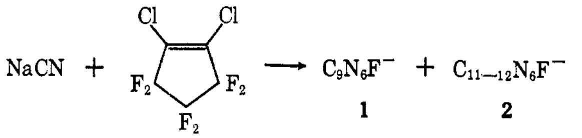
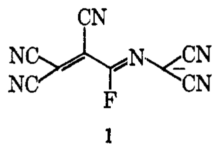
The action of sodium or potassium cyanide in polar solvents on 1,2-dichlorohexafluorocyclopentene leads to the formation of two polycyanocarbanions, red and magenta in color. The red anion ($C_9N_6F^-$) was isolated in about 30% yield after one recrystallization of its tetramethylammonium salt. The magenta anion, ($C_{11-12}N_6F^-$) was separated from the red by repeated recrystallization of the tetramethylammonium salt; its yield is very low, about 1–2%.



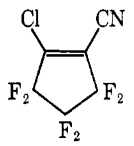
An X-ray diffraction investigation[1] on the tetraphenylarsonium salt of the red dye determined it to be 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide (1).



1

The structure of 2 remains in doubt but is probably related to that of 1 as borne out by the close similarity of its physical and spectral data to those of 1.

Although the X-ray crystallographic determination of 1 leaves little doubt about its structure, the mechanism by which it is formed is somewhat obscure. The most probable first step is the formation of a monocyano derivative (3) in which the double bond is now highly activated toward a Michael-type addition of another cyanide ion. A series of subsequent addition–elimination reactions could lead to intermediates which are progressively more reactive. Attempts to isolate intermediates by chromatography of the complex product mixture were fruitless. Furthermore, it is not certain that any component of the mixture which could be isolated and purified could then be identified as either an intermediate or a by-product. Attempts were also made, without success, to isolate volatile initial substitution products. Nor did the use of a large excess of olefin relative to sodium cyanide inhibit the formation of the dye. These phenomena are consistent with the idea that the intermediates are much more reactive toward cyanide ion than the starting material is.



3

The infrared spectra of 1 and known cyanocarbanions are similar.[2]

The tetramethylammonium salt of 1 has infrared bands at 4.5 (s), 6.7 (s), 7.2 (s), 7.7 (m), and 10.5 (m) μ. The visible absorption spectrum of 1 has a maximum at 502 mμ (ϵ 35,200); 2 has a maximum at 550 mμ (ϵ 45,800). In comparison, two closely related anions have the following values: heptacyanopentadienide,[3] at λ_{max} 528 mμ (ϵ 33,000); 1,1,2,4,5,5-hexacyano-3-azapentadienide,[4] at λ_{max} 464 mμ (ϵ 45,300) and at λ_{max} 440 mμ (ϵ 38,000).

Microanalyses of metal salts, such as cesium, sodium, magnesium, potassium, silver, and manganese were very unsatisfactory because these salts recrystallize poorly. They tend to be extremely soluble in water, ethanol, acetone, acetonitrile, etc., and very insoluble in less polar solvents. The use of cations such as tetramethylammonium, tetraphenylphosphonium, and tetraphenylarsonium enabled the salts to be purified by crystallization. It is interesting that all of the salts of 1 and 2 are quite soluble in most polar organic solvents. However, in dioxane they are almost completely insoluble. With one to two molecules of dioxane the sodium and cesium salts form complexes which are insoluble in dioxane, but soluble in other polar organic solvents. The complexes are weak and dissociate in other solvents or upon heating to 150°.

The reaction between cyanide ion and polyhalo olefins to produce colored compounds appears to be general. Several olefins were tested including tetrachloroethylene, 1,1,1-trifluorotrichloropropene, 1,1,1,-4,4,4-hexafluorodichlorobutene, 1,2-dichlorotetrafluorocyclobutene, and hexachlorocyclopentadiene. All produced colors in DMF ranging from yellow to reddish brown, but no attempt was made to isolate any products. The commercially available 1,2-dichlorohexafluorocyclopentene has about 15% trichloropentafluorocyclopentene as impurity. Pure samples of both

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materials were isolated by preparative gas chromatography. As expected, both the di- and trichloroperfluorocyclopentenes produced the same mixture of red and magenta dyes when treated with sodium cyanide in acetonitrile.

Experimental Section

3-Fluoro-1,1,4,5,5-pentacyano-2-azapentadienide Carbanion.—A mixture of 25.0 g of 1,2-dichlorohexafluorocyclopentene, 25.0 g of 100-mesh sodium cyanide, and 200 ml of ordinary acetonitrile was stirred 4 hr at room temperature. The reaction mixture became somewhat warm for about 30 min but then cooled. The mixture was then filtered through a bed of Celite with the aid of several washings with small quantities of acetonitrile. The filtrate was concentrated to dryness under vacuum with gentle warming. The greenish black, amorphous residue (13.5 g) was dissolved in 200 ml of 10% sodium chloride solution containing 10 ml of concentrated sulfuric acid. This solution was extracted with 200 ml of ether. The ether phase was then washed with another 200-ml portion of 10% sodium chloride solution before being neutralized with 10% tetramethylammonium hydroxide solution, taking care not to exceed a pH of 7. The mixture was left in the refrigerator for about 1 hr to crystallize before being filtered. The filter cake was then washed with small portions of water before being dried in the desiccator. The crude product, mp 170–190°, weighed 7.15 g. This consisted mainly of red dye with some magenta dye impurity. Several fractional recrystallizations from hot water were required to separate the components. The pure red dye melts at 216–218° without decomposition.

Anal. Calcd for $C_{13}H_{12}FN_7$: C, 54.73; H, 4.24; N, 34.37. Found: C, 55.37; H, 4.66; N, 34.46.

The molecular weight was determined ebullioscopically in acetone with tetramethylammonium pentacyanopropenide as the reference material. *Anal.* Calcd: mol wt, 285. Found: mol wt, 291.

The pure magenta dye melts at 261–263° without decomposition. *Anal.* Calcd for $C_{15}H_{12}FN_7$: C, 58.24; H, 3.91; N, 31.70. Calcd for $C_{16}H_{12}N_7F$: C, 59.81; H, 3.77; N, 30.52. Found: C, 58.30; H, 4.20; N, 31.16.

The molecular weight was determined ebullioscopically in acetone with tetramethylammonium pentacyanopropenide as the reference material. *Anal.* Calcd: mol wt, 309 or 321. Found: mol wt, 344.

The red dye may also be prepared free of magenta dye contamination by carrying out the reaction with tetrahydrofuran instead of acetonitrile. In this solvent the reaction mixture was stirred for 1 week. The work-up is otherwise identical with the above.

The tetraphenylphosphonium salts of **1** and **2** were prepared in water by exchange between the sodium or tetramethylammonium salts of **1** and **2** and tetraphenylphosphonium iodide. The precipitated tetraphenylphosphonium salts were recrystallized from a 1:1 acetone–water solution. The tetraphenylphosphonium salt of **1** melted at 169–171° without decomposition. *Anal.* Calcd for $C_{33}H_{20}FN_6P$: C, 72.59; H, 3.58; N, 14.94; P, 5.51. Found: C, 72.37; H, 3.85; N, 14.47; P, 5.40.

The pure tetraphenylphosphonium salt of **2** melted at 212–214°. *Anal.* Calcd for $C_{35}H_{20}FN_6P$: C, 73.16; H, 3.51; F, 3.31; N, 14.63; P, 5.39. Calcd for $C_{36}H_{20}FN_6P$: C, 73.72; H, 3.44; F, 3.24; N, 14.33; P, 5.28. Found: C, 74.02; H, 3.85; F (by difference), 2.89; N, 13.99; P, 5.25.

The tetraphenylarsonium salts of **1** and **2** were also prepared by metathesis in H_2O. The precipitated salts were removed by filtration, dried, and recrystallized from benzene. The pure tetraphenylarsonium salt of **1** is obtained in large, ruby needles, mp 161–163°. *Anal.* Calcd for $C_{33}H_{20}AsFN_6$: C, 66.67; H, 3.39; As, 12.60; F, 3.20; N, 14.14. Found: C, 66.84; H, 3.51; As, 13.76; F, 3.04; N, 14.28.

The tetraphenylarsonium salt of **2** prepared in the same way occurs in large needles with a metallic blue sheen, mp 208°. *Anal.* Calcd for $C_{35}H_{20}AsFN_6$: C, 67.97; H, 3.26; As, 12.11; F, 3.07; N, 13.59. Calcd for $C_{36}H_{20}AsFN_6$: C, 68.58; H, 3.20; As, 11.88; F, 3.01; N, 13.33. Found: C, 68.70; H, 3.50; As, 11.83; F, 2.87; N, 13.46.

Cesium 3-Fluoro-1,1,4,5,5-pentacyano-2-azapentadienide Dioxanate.—Eight grams of crude sodium salt of **1** was refluxed with 100 ml of dioxane for 0.5 hr and then the mixture was filtered. The filter cake when dried weighed 8.7 g and melted with evolution of dioxane at 140–150°. A solution of 7.32 g of the dioxanate in 22 ml of H_2O was added to a solution of 15.2 g of cesium fluoride in 10 ml of H_2O. A viscous syrup separated which slowly turned into crystals, which were filtered and dried, mp 163–165° (4.40 g). This was dissolved in a hot solution of 4 ml of acetonitrile and 10 ml of dioxane. On cooling, shiny, gray crystals formed which were filtered and dried under vacuum over P_2O_5, mp 175–176°. *Anal.* Calcd for $C_{13}H_8CsN_6FO_2$: C, 36.14; H, 1.87; F, 4.40; N, 19.45. Found: C, 36.79; H, 2.01; F, 4.27; N, 19.07.

Heating the salt at 130° (0.5 mm) for 22 hr removed nearly all of the dioxane.

Registry No.—1,2-Dichlorohexafluorocyclopentene, 706-79-6; tetramethylammonium salt of **1**, 7731-11-5; tetraphenylphosphonium salt of **1**, 7771-13-3; tetraphenylarsonium salt of **1**, 7731-12-6; cesium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide dioxanate, 7731-13-7.

The Reaction of 9,9-Dibromobicyclo[6.1.0]non-2-ene with Methyllithium[1]

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The reaction of *gem*-dibromocyclopropanes with methyllithium, magnesium, or sodium on alumina to give allenes has been shown to be quite general.[3] The reaction takes other courses in certain cases where the rate of allene formation is diminished owing to its strain energy.[4] We wish to describe here the reaction of 9,9-dibromobicyclo[6.1.0]non-2-ene (I) which is of the latter type.[5]

Treatment of I with a large excess of methyllithium afforded a hydrocarbon fraction which was at first thought to be homogeneous.[5] However, very careful vapor–liquid chromatography showed it to consist of two compounds in the ratio 2:1. A small amount of each has now been obtained by repeated preparative vapor–liquid chromatography and the data which follow show the components of this mixture to be tricyclo-

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(1) Sponsored by the Robert A. Welch Foundation. Work was done at the University of Texas.

(2) Department of Chemistry, University of Utah.

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(5) Mention of the product of this reaction was made earlier[6] and on the basis of ozonolysis and hydrogenation I was stated to be 1,3,6-cyclononatriene. The work of Watthey and Winstein[7] has adequately shown this is not so. A repetition in our laboratories of each experiment on which the assignment was based has failed to give the results previously reported[6] and these data should therefore be disregarded.

(6) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963); D. Devaprabhakara, Ph.D. Dissertation, University of Texas, 1962, p 32.

(7) J. W. H. Watthey and S. Winstein, *J. Am. Chem. Soc.*, **85**, 3715 (1963); D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Letters*, 377 (1965).