

100 g. of phosphorous pentoxide in a 500-ml. flask. The mixture was warmed at 50-mm. pressure to distil volatile material into a trap cooled at -80° . Fractionation of the material in the trap gave 18.3 g. (39%) of starting imine and 8.1 g. (27% yield) of product, b.p. 122° , n_D^{25} 1.3211. The infrared spectrum showed a doublet for NH_2 at 2.7 and 2.9 μ , an intense band at 6.2 μ ascribed to NH_2 deformation, and a weaker band at 6.1 μ ascribed to $\text{C}=\text{N}$. The proton n.m.r. showed a broad peak at +12.8 p.p.m., and the F^{19} n.m.r. showed multiplets at +15.7 (area 3), +17.5 (area 3), +43.3 (area 2), and +50.1 (area 2) p.p.m.

Anal. Calcd. for $\text{C}_5\text{H}_2\text{F}_{10}\text{N}_2$: C, 21.44; H, 0.72; F, 67.84; N, 10.01. Found: C, 21.88; H, 0.86; F, 67.95; N, 10.19.

2-H-Hexafluoroisopropylamine.—Hexafluoroisopropylideneimine, 25 g. (15.5 ml. at -10° , 0.15 mole), was slowly distilled into a stirred suspension of 5.0 g. (0.13 mole) of lithium aluminum hydride in 125 ml. of diethylene glycol dimethyl ether cooled in an ice bath. After the addition, the reaction mixture was stirred at room temperature for 1 hr., and then a solution of 15 ml. of water in 30 ml. of diethylene glycol dimethyl ether was cautiously added. The reaction mixture was warmed to 35° under reduced pressure (ca. 1 mm.), and the volatile fraction that distilled was condensed in a cold trap. Redistillation gave 14.4 g. (57%) of product as a colorless liquid, b.p. $58-59^{\circ}$, $n_D^{25} < 1.3$. The F^{19} n.m.r. contained a doublet ($J = 7$ c.p.s.) centered at +9.22 p.p.m. The proton n.m.r. showed two broad peaks at +3.83 and +2.08 p.p.m. with an area ratio of 1:2. The infrared spectrum showed bands at 2.93, 2.99, and 6.12 μ for NH_2 and 3.37 μ for saturated CH.

Anal. Calcd. for $\text{C}_3\text{H}_3\text{F}_6\text{N}$: C, 21.57; H, 1.81; F, 68.23; N, 8.38. Found: C, 21.64; H, 1.93; F, 68.00; N, 8.69.

2-H-Hexafluoroisopropylamine Hydrochloride.—Dry hydrogen chloride gas was passed into a solution of 10 g. (0.06 mole) of 2-H-hexafluoroisopropylamine in 200 ml. of dry ether. When no further precipitation occurred, the addition was stopped and the

precipitate was collected on a filter, washed with ether, and then recrystallized from dioxane. There was obtained 10.1 g. (83%) of the hydrochloride as white crystals, m.p. $125-130^{\circ}$ (with sublimation). The F^{19} n.m.r. spectrum in alcohol showed a doublet ($J = 8$ c.p.s.) centered at -3.50 p.p.m.

Anal. Calcd. for $\text{C}_3\text{H}_4\text{ClF}_6\text{N}$: C, 17.72; H, 1.98; Cl, 17.42. Found: C, 17.36; H, 2.16; Cl, 17.44.

Heptafluoroisopropylamine.—Hexafluoroisopropylideneimine, 1.65 g. (0.01 mole), was mixed with 0.2 g. (0.01 mole) of anhydrous hydrogen fluoride in a polyethylene bottle cooled in an ice bath. An exothermic reaction occurred. The F^{19} n.m.r. spectrum of this product showed a doublet in the CF_3 region and a septet at higher field. Further identification and purification was not attempted since this amine reacts rapidly with glass.

2,2-Bis(trifluoromethyl)-4,5-dimethyl-1,2,3,6-tetrahydropyridine (VI).—A mixture of 5.0 g. (0.03 mole) of hexafluoroisopropylideneimine and 5 ml. of 2,3-dimethylbutadiene was sealed in a Carius tube and heated at 100° for 18 hr. The tube was cooled and opened, and the contents were distilled to give 5.4 g. (74%) of VI as a colorless liquid, b.p. 44° (5 mm.), n_D^{25} 1.3911. The F^{19} n.m.r. showed a singlet at +9.58 p.p.m. The proton n.m.r. contained broad peaks at +1.66 (area 6), +2.33 (area 3), and +3.35 p.p.m. (area 2).

Anal. Calcd. for $\text{C}_9\text{H}_{11}\text{F}_6\text{N}$: F, 46.12; N, 5.67. Found: F, 46.19; N, 5.38.

3,3-Bis(trifluoromethyl)-2-azabicyclo[2.2.1]hept-5-ene.—A mixture of 8.25 g. (0.05 mole) of hexafluoroisopropylideneimine and 10 ml. of cyclopentadiene was stirred at room temperature overnight. Distillation gave 7.4 g. (64%) of product as a colorless oil, b.p. $44-45^{\circ}$ (10 mm.), n_D^{25} 1.3988. The F^{19} n.m.r. spectrum contained two quartets ($J = 11$ c.p.s.) centered at -3.51 and $+4.52$ p.p.m.

Anal. Calcd. for $\text{C}_8\text{H}_7\text{F}_6\text{N}$: C, 41.57; H, 3.06; F, 49.32; N, 6.07. Found: C, 41.50; H, 3.45; F, 49.06; N, 6.34.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene¹

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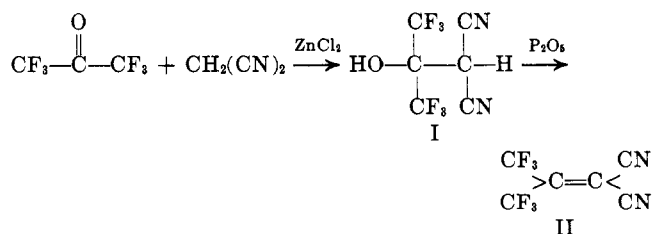
Received December 28, 1964

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene has been prepared from hexafluoroacetone and malononitrile. Reactions of this ethylene are of particular interest for it is both electron poor and highly polarizable. Adducts with dienes, electron-rich olefins, olefins with allylic hydrogens, and nucleophiles are discussed.

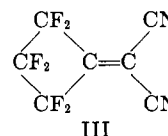
Perfluoro² and percyano olefins³ have received an extensive amount of study. These electron-poor olefins are very active in addition reactions with monoolefins and dienes and are very susceptible to nucleophilic attack. Reactions of olefins that contain both cyano and perfluoroalkyl groups, however, do not appear to have been studied to any great extent. Reactions of unsymmetrically substituted olefins such as 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) would be of particular interest. Like the perfluoro and the percyano olefins, the ethylene would be electron deficient owing to the four electronegative groups attached to the ethylenic carbons. Unlike the perfluoro and percyano olefins, however, II would be highly polarizable, for the geminal cyano groups could stabilize a negative charge at only one end of the double bond in any transition state involving charge separation.

We have discovered a facile synthesis for 1,1-dicyano-2,2-bis(perfluoroalkyl)ethylenes based on the conden-

sation of fluoro ketones with malononitrile. Hexafluoroacetone condenses with malononitrile in the presence of zinc chloride to yield the unstable alcohol I.



Dehydration of this adduct with phosphorus pentoxide gives 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 50% over-all yield. Dicyanomethylenehexafluorocyclobutane (III) was prepared in a similar manner from malononitrile and hexafluorocyclobutanone.



(1) Portions of this paper were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962.

(3) T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).

π -Complexes.—The cyanofluoro olefins II and III both form intensely colored solutions when mixed with aromatic compounds and other π -bases. These colors are due to the formation of π -complexes that are characterized by an intense electronic absorption in the visible or near-ultraviolet that is attributed to neither component of the complex alone, but to a new molecular species, the complex itself. Several complexes are listed in Table I, along with their wave length

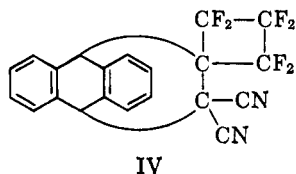
TABLE I

π -Base	$(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$			$\text{C}_4\text{F}_6=\text{C}(\text{CN})_2$		
	λ_{max} , m μ	ϵ	K^a	λ_{max} , m μ	ϵ	K^a
Pyrene	500	3670	5.6	580	1930	7.7
Durene	386	2520	4.1	423	2430	1.1
Hexamethyl- benzene	445	1060	5.6	497	1040	3.2
Benzene	316	1950	0.85	334	2170	0.51
Toluene	327	1720	1.1	358	1720	0.68

^a Solvent, CH_2Cl_2 ; temperature, 24°.

of maximum absorption, extinction coefficients, and the calculated association constant, K .⁴ These complexes bear a close resemblance to those formed from tetracyanoethylene (TCNE) and aromatic compounds,⁵ although the association constants are somewhat lower. The strength of these complexes appears to be very sensitive to the steric requirements of the rather bulky fluoroalkyl groups. For example, II forms a stronger complex with pyrene than it does with hexamethylbenzene, although hexamethylbenzene is a stronger π -base. This reverse relationship is not noted with TCNE, which has a less critical steric requirement.⁵

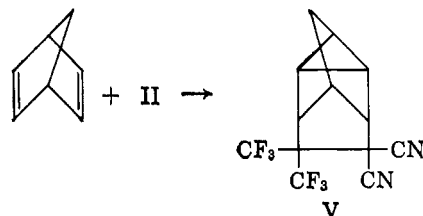
Diels-Alder Reactions.—Both II and III are active dienophiles in the Diels-Alder reaction. Cyclopentadiene and 2,3-dimethylbutadiene react at room temperature and anthracene reacts at 100° with II to give adducts in a few minutes. III is even a more active dienophile than is II, for it will react with anthracene in benzene solution at room temperature to give a quantitative yield of adduct IV in only 3 min. Using



IV

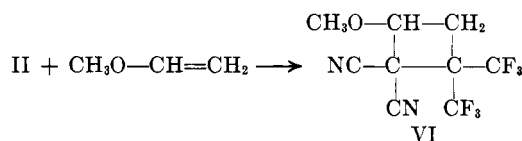
the reaction with anthracene as a comparison, it appears that II is a less active dienophile than TCNE,⁶ and III is roughly equivalent in activity with TCNE.

In a related reaction, II reacts with norbornadiene in pentane solution at room temperature to give the adduct V. Since the reaction requires only 3 hr., it is much faster than the reaction of TCNE with norbornadiene, which is reported to take 3–4 days at room temperature.⁷ This difference in rate is surprising, since TCNE is generally a more active dienophile



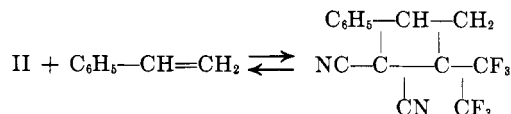
than II. However, the reactions with norbornadiene probably involve more ionic character than normal Diels-Alder reactions. We believe that II reacts faster with norbornadiene because it is more easily polarized than TCNE and can form a charge-separated intermediate or transition state easier than TCNE can.

Cycloaddition Reactions with Olefins.—The dicyano olefins II and III combine with electron-rich olefins in a remarkably facile reaction to form cyclobutanes. Adducts were formed from II with styrene, α -methylstyrene, *p*-methoxystyrene, methylvinyl ether, and *t*-butyl vinyl sulfide, and from III with α -methylstyrene and *t*-butyl vinyl sulfide. All of these reactions occur



rapidly at 0°, even in nonpolar solvents such as pentane and carbon tetrachloride. As with other active enophiles, such as TCNE⁸ and 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene,⁹ the course of the reaction can be followed visually by the disappearance of the color due to the π -complex formed between the reactants. A comparison of the reaction rates of II and TCNE with methyl vinyl ether indicate that II is vastly more reactive than TCNE in this reaction. II reacts almost instantaneously with methyl vinyl ether, even at -78°, whereas TCNE requires 1.5 hr. at room temperature. A comparison of the reactivity of II and TCNE with styrene is also striking. II reacts rapidly with styrene in pentane at room temperature, but TCNE does not react at all with styrene under these conditions.⁸ The cyanofluoro olefin III is even more reactive than II in these cycloaddition reactions.

The cycloaddition reactions of II with styrene and α -methylstyrene are easily reversed. The adducts that result from these reactions will partially dissociate when dissolved in benzene, and in these solutions



the cyanobutane is actually in equilibrium with the reactants. Adducts of *p*-methoxystyrene and the vinyl ether and sulfide adducts are more stable, for they do not show this behavior.

Cycloaddition reactions of this type have been shown to possess a large amount of ionic character, for their rates are markedly dependent on solvent polarity.⁹ We believe that II is a more active enophile than TCNE and the isomeric *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene, because it is more polarizable

(4) The association constants were calculated by the method of R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950).

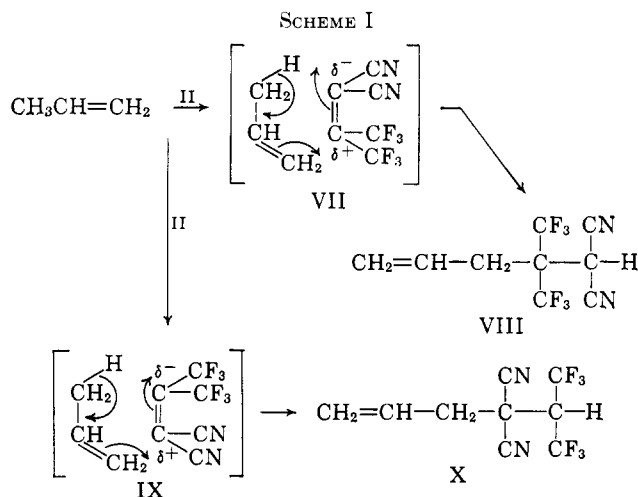
(5) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2779 (1958).

(6) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

(7) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

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

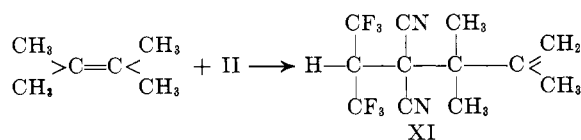
(9) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **85**, 2341 (1963).



and can form polar intermediates or transition states more readily than can TCNE or its more symmetrical isomers.

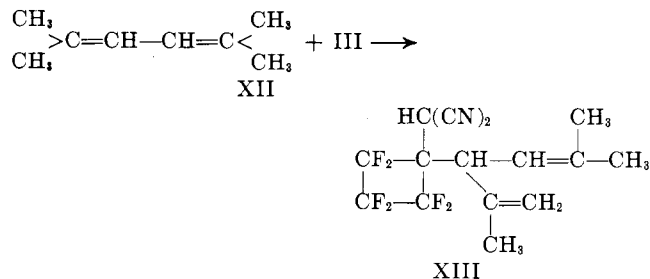
The direction of addition of II and III with electron-rich olefins was not conclusively established. However, the adducts were assigned the 1,1-dicyano-2-substituted 4,4-bis(perfluoroalkyl)cycloalkyl)cyclobutane structure from a consideration of the normal polarity of the reactants. More direct evidence was obtained for the methyl vinyl ether adduct of II. This adduct was assigned the structure VI on the basis of its mass spectrum, which showed a major ion at 108 mass units, which corresponds to $[\text{C}(\text{CN})_2\text{CHOCH}_3]^+$.

Reactions with Olefins Possessing Allylic Hydrogens.—Nonactivated olefins that contain allylic hydrogens also react with II and III. For example, II reacts with propylene at 150° to give the two isomeric adducts, VIII and X. The most abundant isomer, VIII, is the product that would be expected from electronic considerations, as is illustrated in Scheme I. It is surprising that X is formed at all, for this product would be formed by a mechanism (IX) in which a positive charge would accumulate on the dicyanomethylene carbon. We propose that a consideration of steric factors can explain the formation of this isomer. Because the CF_3 groups are relatively bulky in comparison with the CN groups, the transition state in intermediate IX would be sterically favored over that in VII. Support for this theory was obtained from the reaction of the hindered olefin, tetramethylethylene, with II. This reaction occurred at room temperature to give XI as the only isolated product. Thus, steric factors must have completely overcome the electronic effects in this reaction.

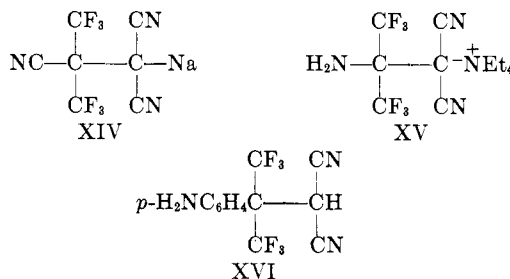


The cyanofluoro olefin III also reacts with allylic hydrogen olefins. Reaction of III with 1,1,4,4-tetramethylbutadiene (XII) at room temperature gave the adduct XIII instead of the expected Diels-Alder adduct.

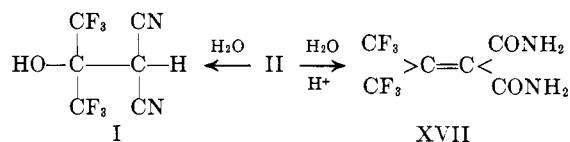
Addition of Nucleophiles.—As would be expected from the electrophilic nature of II, nucleophiles add easily to give stable adducts. Sodium cyanide reacts



with II in acetonitrile to give an adduct (XIV) that does not decompose even at 300° . Ammonia adds to II to give an amphoteric amine, which was isolated as the tetraethylammonium salt XV. Aniline gives the carbon-alkylated product XVI.

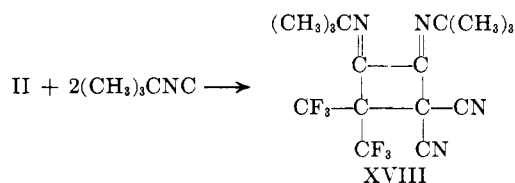


Water adds uncatalyzed to II to regenerate the alcohol precursor to II (I). In strongly acidic media, however, II can be hydrolyzed to the diamide XVII. Alcohols add to II in a reversible reaction to give ad-



ducts unstable to distillation that exist in equilibrium mixtures with their reactants. Steric requirements are important in establishing the position of the equilibrium. With methyl and ethyl alcohol, the equilibrium lies far on the side of the products; with *t*-butyl alcohol, the equilibrium is far on the side of the reactants; and, with isopropyl alcohol, approximately equal amounts of products and reactants exist at equilibrium.

Reaction with *t*-Butyl Isocyanide.—A white crystalline 1:2 adduct formed when II was mixed with *t*-butyl isocyanide at ice-bath temperature. This adduct showed two singlets in its proton n.m.r. spectrum, and a single resonance in its F^{19} n.m.r. spectrum. Unfortunately, the adduct is quite unstable, for it decomposes in a few hours at room temperature. We propose the structure XVIII for this adduct.



Experimental¹⁰

Hydroxybis(trifluoromethyl)methylmalononitrile.—A mixture of 75 g. (1.14 moles) of malononitrile, 4 g. (0.03 mole) of anhydrous zinc chloride, and 150 g. (0.9 mole) of hexafluoroacetone was heated in a 240-ml. pressure vessel at 80° for 8 hr. An off-white, crystalline solid, 211 g., was obtained. A sample of the solid was recrystallized from methylene chloride to give the product as hygroscopic white needles, m.p. 59–70°.

Anal. Calcd. for C₈H₂F₆N₂O: C, 31.05; H, 0.87; F, 49.12. Found: C, 31.46; H, 1.00; F, 50.15.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene.—A mixture of 211 g. (0.9 mole) of crude hydroxybis(trifluoromethyl)methylmalononitrile and 454 g. (3.2 moles) of phosphorus pentoxide was heated strongly in a 5-l. flask connected to a simple still until no further distillate was collected. The distillate was filtered and redistilled to give 97 g. (50%) of product, b.p. 107°, *n*_D²⁵ 1.3526, *d*₄²⁵ 1.479. The F¹⁹ n.m.r. spectrum contained a single unsplit resonance band at -3.81 p.p.m. The infrared spectrum contained bands at 4.45 (CN) and 6.1 μ (C=C).

Anal. Calcd. for C₆F₈N₂: C, 33.66; F, 53.25; N, 13.09. Found: C, 34.01; F, 53.48; N, 12.80.

Dicyanomethylenehexafluorocyclobutane.—A mixture of malononitrile, 14.4 g. (0.2 mole), 1 g. (0.007 mole) of zinc chloride, and 36 g. (0.2 mole) of hexafluorocyclobutanone¹¹ was sealed in a 130-ml. Carius tube and heated to 50° for 2 hr. The tube was cooled, opened, and vented. The reaction mixture was a fluid semisolid that was not further characterized.

All but a small portion of this product was mixed with 100 g. (0.7 mole) of phosphorus pentoxide and heated strongly in a simple still. The distillate that collected was redistilled through a fractionating column to give 15.8 g. of product as a colorless liquid, b.p. 117.5°, *n*_D²⁵ 1.3730. The infrared spectrum contained bands at 4.47 (CN) and 5.98 μ (C=C). The F¹⁹ n.m.r. spectrum showed singlets at 51.7 (relative area 2) and 63.2 p.p.m. (relative area 1).

Anal. Calcd. for C₇H₆N₂: C, 37.18; F, 50.52. Found: C, 37.18; F, 50.28.

The small portion of the reaction mixture of malononitrile and hexafluorocyclobutanone that was not dehydrated was recrystallized from benzene. A low yield of a 2:1 adduct of hexafluorocyclobutanone with malononitrile, as colorless prisms, m.p. 90–95°, was obtained.

Anal. Calcd. for C₁₁H₂F₁₂N₂O₂: C, 31.30; H, 0.48; N, 6.63. Found: C, 31.61; H, 0.73; N, 6.69.

4,4-Dicyano-1,2-dimethyl-5,5-bis(trifluoromethyl)-1-cyclohexene.—2,3-Dimethylbutadiene, 2.05 g. (0.025 mole), was added dropwise to 5.35 g. (0.025 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene cooled by an ice bath. A solid formed immediately. Recrystallization from pentane gave the product as colorless prisms, m.p. 57–58°.

Anal. Calcd. for C₁₂H₁₀F₆N₂: C, 46.65; H, 3.41; F, 38.49; N, 9.46. Found: C, 46.56; H, 3.40; F, 38.74; N, 9.67.

2,2-Dicyano-3,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-4-ene.—A solution of 4.5 g. (0.021 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 5 ml. of pentane was added dropwise to a stirred solution of 3 ml. of cyclopentadiene in 10 ml. of pentane cooled in an ice bath. The bright yellow color that first formed faded rapidly and a white precipitate formed. The precipitate was collected on a filter, washed with pentane, and recrystallized from carbon tetrachloride to give 4.9 g. (83%) of product as colorless prisms, m.p. 182–183°. The F¹⁹ n.m.r. spectrum showed two quartets.

Anal. Calcd. for C₁₁H₆F₆N₂: C, 47.16; H, 2.16; F, 40.69; N, 10.00. Found: C, 46.83; H, 2.45; F, 40.73; N, 10.00.

11,11-Dicyano-12,12-bis(trifluoromethyl)-9,10-ethanoanthracene.—A mixture of 80 mg. of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, 50 mg. of anthracene, and 2 ml. of benzene was heated in a test tube in a steam bath for 15 min. The deep purple solution became colorless. The solid that precipitated

upon cooling was collected on a filter. Recrystallization from benzene gave 75 mg. of product as colorless needles m.p. 185°.

Anal. Calcd. for C₂₀H₁₀F₆N₂: C, 61.24; H, 2.57; F, 29.06; N, 7.04. Found: C, 61.14; H, 2.56; F, 28.79; N, 7.29.

11,11-Dicyano-12,12-hexafluorotrimethylene-9,10-ethanoanthracene.—A solution of 2.26 g. (0.01 mole) of dicyanomethylenehexafluorocyclobutane in 5 ml. of benzene was added rapidly to a stirred suspension of 1.78 g. (0.01 mole) of anthracene in 10 ml. of benzene. The initial green color faded in about 3 min. The precipitate was collected on a filter and recrystallized from benzene to give 3.79 g. of product as colorless prisms, m.p. 160–161°.

Anal. Calcd. for C₂₁H₁₀F₆N₂: C, 62.38; H, 2.50; F, 28.20; N, 6.93. Found: C, 62.35; H, 2.67; F, 27.77; N, 6.86.

Norbomadiene-1,1-dicyano-2,2-bis(trifluoromethyl)ethylene Adduct.—A solution of 10.7 g. (0.05 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene and 9.2 g. (0.1 mole) of norbornadiene in 50 ml. of pentane was allowed to stand at room temperature for 2 hr. The orange color of the π-complex faded, and the crystals that precipitated were collected on a filter and recrystallized from benzene. There was obtained 14.0 g. of 8,8-dicyano-9,9-bis(trifluoromethyl)tetracyclo[2.2.1.0^{2,3}.1.2^{3,6}]nonane as colorless needles, m.p. 132–133°. The F¹⁹ n.m.r. spectrum in CDCl₃ showed two quartets (*J* = 13 c.p.s.) of equal intensity centered at -7.45 and -2.93 p.p.m. The proton n.m.r. and infrared spectra showed no evidence of unsaturation.

Anal. Calcd. for C₁₃H₈F₆N₂: C, 50.99; H, 2.64; F, 37.22; N, 9.15. Found: C, 50.52; H, 2.59; F, 37.26; N, 8.78.

1,1-Dicyano-2,2-bis(trifluoromethyl)-4-methoxycyclobutane.—Methyl vinyl ether (10 ml.) was condensed into a calibrated receiver cooled to -78°, and 18.6 g. (0.2 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene was added dropwise over 30 min. with cooling. Reaction occurred almost instantaneously. The reaction mixture was distilled to give 20.6 g. (87%) of product as a colorless liquid, b.p. 47–48° (0.1 mm.), that solidified upon cooling to a colorless solid, m.p. 31–31.5°. The F¹⁹ n.m.r. showed two quartets (*J* = 10 c.p.s.) centered at +1.52 and +2.79 p.p.m. The proton n.m.r. showed a singlet (area 3) at 3.63 p.p.m., a doublet (*J* = 8 c.p.s.) (area 2) at 2.94 p.p.m., and a triplet (*J* = 8 c.p.s.) (area 1) at 4.66 p.p.m. The mass spectrum contained a major peak at 108 mass units.

Anal. Calcd. for C₉H₈F₆N₂O: C, 39.72; H, 2.23; F, 41.89; N, 10.29. Found: C, 39.64; H, 2.40; F, 41.84; N, 10.31.

1,1-Dicyano-2-phenyl-4,4-bis(trifluoromethyl)cyclobutane.—A solution of 2.08 g. (0.02 mole) of styrene in 5 ml. of pentane was added to a solution of 4.28 g. (0.02 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 5 ml. of pentane cooled to 0°. The deep yellow color that first formed faded rapidly, and the white crystalline precipitate that formed was collected on a filter and washed with pentane. Recrystallization from pentane gave 5.55 g. (88%) of product as colorless prisms, m.p. 77–78° (yellow melt). The product formed a yellow solution in benzene. F¹⁹ n.m.r. of this solution showed a pair of quartets due to the cyclobutane and a singlet due to the cyano olefin that is formed on reversal.

Anal. Calcd. for C₁₄H₈F₆N₂: C, 55.82; H, 3.80. Found: F, 35.22; N, 8.44.

Other Cyclobutanes.—The following cyclobutanes were prepared by a similar procedure.

1,1-Dicyano-2-methyl-2-phenyl-4,4-bis(trifluoromethyl)cyclobutane was isolated as colorless prisms, m.p. 83–84°, 80% yield, from α-methylstyrene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene.

Anal. Calcd. for C₁₅H₁₀F₆N₂: C, 54.22; H, 3.03; F, 34.31; N, 8.42. Found: C, 54.51; H, 3.31; F, 34.33; N, 8.62.

1,1-Dicyano-2-*p*-methoxyphenyl-4,4-bis(trifluoromethyl)cyclobutane was isolated as colorless plates, m.p. 103–104°, 85% yield, from *p*-methoxystyrene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. F¹⁹ n.m.r. in CDCl₂ showed two quartets (*J* = 10 c.p.s.) centered at +0.64 and +2.30 p.p.m. The proton n.m.r. showed an A₂B₂ pattern typical of a *para*-substituted aromatic ring centered at 7.16 p.p.m., a singlet for OCH₃ at 3.81 p.p.m., and an ABC pattern with components centered at 4.5 and 3.0 p.p.m.

Anal. Calcd. for C₁₅H₁₀F₆N₂O: C, 51.73; H, 2.90; F, 32.74; N, 8.05. Found: C, 51.83; H, 3.01; F, 33.49; N, 8.12.

1,1-Dicyano-2-*t*-butylthio-4,4-bis(trifluoromethyl)cyclobutane was isolated as colorless plates, m.p. 75–77°, 82% yield, from *t*-butyl vinyl sulfide and 1,1-dicyano-2,2-bis(trifluoromethyl)-

(10) Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of higher field displacement in parts per million (p.p.m.) from the F¹⁹ resonance of 1,2-difluorotetrachloroethane used as an external reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in parts per million from the proton resonance of tetramethylsilane used as an internal reference. All melting points and boiling points are uncorrected.

(11) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

ethylene. F^{19} n.m.r. in $CDCl_3$ showed two quartets ($J = 10$ c.p.s.) centered at +0.76 and +2.29 p.p.m. The proton n.m.r. showed a singlet at 1.45 p.p.m. for $C(CH_3)_2$ and a ABC pattern with components centered at 2.85 and 4.40 p.p.m.

Anal. Calcd. for $C_{12}H_{12}F_6N_2S$: F, 34.51; N, 8.48; S, 9.72. Found: F, 34.56; N, 8.83; S, 9.83.

1,1-Dicyano-2-methyl-2-phenyl-5,5,6,6,7,7-hexafluorospiro[3.3]heptane was isolated as colorless prisms, m.p. 82–84°, 80% yield, from α -methylstyrene and dicyanomethylenehexafluorocyclobutane.

Anal. Calcd. for $C_{15}H_{10}F_6N_2$: C, 55.82; H, 2.93; F, 33.11; N, 8.13. Found: C, 56.03; H, 3.11; F, 32.92; N, 8.30.

1,1-Dicyano-2-*t*-butylthio-5,5,6,6,7,7-hexafluorospiro[3.3]heptane was isolated as colorless crystals, m.p. 142°, 85% yield, from *t*-butyl vinyl sulfide and dicyanomethylenehexafluorocyclobutane.

Anal. Calcd. for $C_{13}H_{12}F_6N_2S$: C, 45.61; H, 3.54; F, 33.30; N, 8.20; S, 9.37. Found: C, 46.05; H, 3.86; F, 32.95; N, 8.40; S, 9.51.

Addition of Water.—One drop of water was added to a solution of 0.1 g. of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 1 ml. of methylene chloride. The white solid that formed upon standing overnight was collected on a filter and dried under nitrogen. The melting point, 68–70°, and fluorine n.m.r. spectrum were identical with those of a previously prepared sample of hydroxy(bis(trifluoromethyl)methylmalononitrile).

Addition of Alcohols.—1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene reacts exothermically with equimolar amounts of methyl, ethyl, and isopropyl alcohol, but not with *t*-butyl alcohol. The F^{19} n.m.r. spectra of all of these reaction mixtures indicated an equilibrium mixture of products and reactants. In the case of methyl and ethyl alcohol, the equilibrium was mainly on the side of the products, and, with *t*-butyl alcohol, the equilibrium was mainly on the side of the reactants. With isopropyl alcohol, the reaction mixture was almost evenly divided between reactants and products.

Sodium 1,1,2-Tricyano-2,2-bis(trifluoromethyl)ethanide.—1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene, 6.4 g. (0.03 mole), was added dropwise to a stirred suspension of 1.5 g. (0.03 mole) of sodium cyanide in 75 ml. of acetonitrile. The mixture became deep orange immediately. When all of the olefin was added (about 5 min.), the color faded to light yellow and all of the solid dissolved. The solution was evaporated to dryness under reduced pressure, and the solid residue was recrystallized from dioxane to give 8.7 g. of colorless plates. The colorless plates lost weight rapidly when dried in a vacuum oven to give 5.50 g. (62%) of product as a white powder, m.p. >300°. The F^{19} spectrum in acetone showed a singlet at 3.65 p.p.m. The infrared spectrum contained bands at 4.53 and 4.65 μ for CN.

Anal. Calcd. for $C_7F_6N_3Na$: C, 31.96; F, 43.33; N, 15.97. Found: C, 31.87; F, 43.50; N, 15.96.

Tetramethylammonium 2-Amino-1,1-dicyano-2,2-bis(trifluoromethyl)ethanide.—1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene, 21.4 g. (0.1 mole), was added dropwise to 25 ml. of concentrated ammonium hydroxide stirred and cooled in an ice bath. A solution of 12 g. of tetramethylammonium chloride in 25 ml. of water was then added, and the precipitate that formed was collected on a filter and washed with water. Recrystallization from alcohol gave 22.0 g. (74%) of product as colorless needles, m.p. 189–190°. The infrared spectrum contained bands at 3.00, 3.11, and 6.11 μ for NH_2 and at 4.58 and 4.63 μ for CN. The F^{19} n.m.r. spectrum in acetone showed a singlet at +9.92 p.p.m.

Anal. Calcd. for $C_{10}H_{14}F_6N_4$: F, 37.47; N, 18.42. Found: F, 37.32; N, 18.24.

***p*-[β , β -Dicyano- α , α -bis(trifluoromethyl)ethyl]aniline.**—A solution of 0.93 g. (0.01 g. mole) of aniline in 5 ml. of ether was added dropwise to a stirred and cooled solution of 2.14 g. (0.01 g. mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 10 ml. of ether. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The solid residue was recrystallized from hexane to give 1.58 g. (52%) of product as colorless needles, m.p. 107°. The product was insoluble in water but soluble in dilute hydrochloric acid and sodium hydroxide. The infrared spectrum showed bands at 2.82 and 2.89 μ for NH_2 and at 12.12 μ for *para*-substituted aromatic ring. The F^{19} n.m.r. spectrum in $CDCl_3$ showed a singlet at +2.98 p.p.m. The proton spectrum showed bands at 4.95 p.p.m. for $C(CN)_2H$, 3.92 p.p.m. for NH_2 , and an A_2B_2 pattern centered at 7.0 p.p.m. for the aromatic protons.

Anal. Calcd. for $C_{12}H_7F_6N_3$: C, 46.92; H, 2.30; F, 37.1; N, 13.68. Found: C, 46.60; H, 2.85; F, 38.0; N, 14.06.

The hydrochloride was prepared in and recrystallized from water, m.p. 145–148°.

Anal. Calcd. for $C_{12}H_9ClF_6N_3$: Cl, 10.32. Found: Cl, 10.26.

Reaction of 1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene with Propylene.—A mixture of 21 g. (0.5 mole) of propylene and 42.8 g. (0.2 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene was heated in a 145-ml. Hastelloy bomb at 150° and autogenous pressure for 12 hr. The bomb was cooled and vented, and the residue was distilled to give 34.1 g. (67%) of a colorless oil, b.p. 70° (3.8 mm.).

Twenty grams of this product was shaken with 200 ml. of 5% aqueous potassium hydroxide. Most of the organic layer dissolved. The aqueous layer was separated from the undissolved organic layer, washed with 10 ml. of methylene chloride, and acidified with concentrated hydrochloric acid. The organic layer that formed upon acidification was separated, dried over anhydrous magnesium sulfate, and distilled. There was obtained 14.8 g. of 5,5-dicyano-4,4-bis(trifluoromethyl)pentane as a colorless liquid, b.p. 69° (3 mm.), n_D^{25} 1.3817. The infrared spectrum had bands at 4.40 for CN and 6.05 μ for $C=C$. The F^{19} n.m.r. spectrum showed a singlet at +0.39 p.p.m. The proton n.m.r. spectrum showed a doublet ($J = 5$ c.p.s.) at 2.88 p.p.m. for CH_2 , a singlet at 4.54 p.p.m. for $C(CN)_2H$, and a multiplet centered at 5.54 p.p.m. for $CH=CH_2$.

Anal. Calcd. for $C_9H_6F_6N_2$: C, 42.16; H, 2.37; F, 44.32; N, 10.94. Found: C, 42.31; H, 2.58; F, 44.25; N, 10.64.

The portion of the original sample that did not dissolve in the aqueous potassium hydroxide was dissolved in 10 ml. of methylene chloride, washed with water, and dried over anhydrous magnesium sulfate. Distillation gave 1.1 g. of 4,4-dicyano-5,5-bis(trifluoromethyl)-1-pentene as a colorless liquid, b.p. 61° (2.3 mm.), n_D^{25} 1.3817. The infrared spectrum showed bands at 4.42 for CN and 6.04 μ for $C=C$. The F^{19} n.m.r. spectrum contained a doublet ($J = 8$ c.p.s.) at +4.83 p.p.m. The proton n.m.r. showed a doublet ($J = 6$ c.p.s.) at 2.95 p.p.m. for CH_2 , a septet ($J = 8$ c.p.s.) at 3.95 p.p.m. for $C(CF_3)_2H$, and a multiplet centered at 5.65 p.p.m. for $CH=CH_2$.

Anal. Calcd. for $C_9H_6F_6N_2$: C, 42.16; H, 2.37; F, 44.32; N, 10.94. Found: C, 42.58; H, 2.29; F, 44.25; N, 11.02.

4,4-Dicyano-6,6,6-trifluoro-5-trifluoromethyl-2,3,3-trimethyl-1-hexene.—A mixture of 21.4 g. (0.1 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene and 16.8 g. (0.2 mole) of 2,3-dimethyl-2-butene was allowed to remain overnight at room temperature. The deep orange color faded to light yellow, and the reaction mixture became filled with crystals. These crystals were collected on a filter, washed with ether, and recrystallized from pentane. There was obtained 21.4 g. (72%) of product as colorless prisms, m.p. 69°. The infrared spectrum contained a band at 6.12 μ . The F^{19} n.m.r. spectrum contained a doublet. The proton spectrum showed a septet for the $C(CF_3)_2H$ group.

Anal. Calcd. for $C_{12}H_{12}F_6N_2$: C, 48.32; H, 4.07; F, 38.22; N, 9.40. Found: C, 48.17; H, 4.28; F, 38.27; N, 9.46.

1-Dicyanomethyl-1-[3-methyl-1-(1-methylvinyl)-2-butenyl]-2,2,3,3,4,4-hexafluorocyclobutane.—Dicyanomethylenehexafluorocyclobutane, 1.13 g. (0.005 mole), was added to a solution of 0.55 g. of 2,5-dimethyl-2,4-hexadiene in 2 ml. of pentane. The deep purple color of the π -complex faded after 2 hr., and a white solid separated. The solid was collected on a filter and recrystallized from pentane to give 1.60 g. (85%) of colorless crystals, m.p. 69–70°. The infrared spectrum contained bands at 5.99 and 6.10 μ for $C=C$, and a band at 4.47 μ for CN. The F^{19} n.m.r. spectrum, showing 26 lines, was consistent with that expected for a compound having six different fluorines (requiring attachment of the cyclobutane ring to an asymmetric carbon). Integration of the proton n.m.r. showed 9/14 of the total protons to be between 1.7 and 2.0 p.p.m., with the remainder occurring below 3.4 p.p.m.

Anal. Calcd. for $C_{15}H_{14}F_6N_2$: C, 53.57; H, 4.20; F, 33.90; N, 8.33. Found: C, 53.23; H, 4.08; F, 33.91; N, 7.98.

Bis(trifluoromethyl)methylenemalonamide.—A mixture of 10.7 g. (0.05 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 50 ml. of concentrated sulfuric acid was stirred and heated with a steam bath. After 1 hr., the two-phase reaction mixture became homogeneous. The mixture was cooled and poured over 300 ml. of ice, and the white solid that formed was collected on a filter, washed with water, and dried. Recrystal-

lization from alcohol gave 7.9 g. (63%) of product as colorless matting needles, m.p. 299–300°. The infrared spectrum contained bands for amide groups.

Anal. Calcd. for $C_6H_4F_6N_2O_2$: C, 28.81; H, 1.61; F, 45.58; N, 11.21. Found: C, 28.69; H, 1.66; F, 45.03; N, 11.09.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene-*t*-Butyl Isocyanide Adduct.—A solution of 10.7 g. (0.05 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 10 ml. of ether was added dropwise to a stirred solution of 4.5 g. of *t*-butyl isocyanide in 50 ml. of ether cooled in an ice-methanol bath. The reaction mix-

ture was then cooled to -78° , and the crystalline solid (9.2 g.) that precipitated was collected on a filter. Recrystallization from ether gave 5.7 g. of a white, crystalline 1:2 adduct, m.p. 68–71°. The adduct was not stable when stored at room temperature. The proton n.m.r. spectrum in nitromethane showed two singlets of equal area at 1.42 and 1.60 p.p.m. The F^{19} n.m.r. spectrum showed a singlet in a fresh sample but upon standing other peaks developed.

Anal. Calcd. for $C_{16}H_{18}N_4F_6$: F, 29.97; N, 14.74. Found: F, 29.82; N, 14.67.

Reactions of Enamines. VI. The Protonation of Enamino Ketones¹

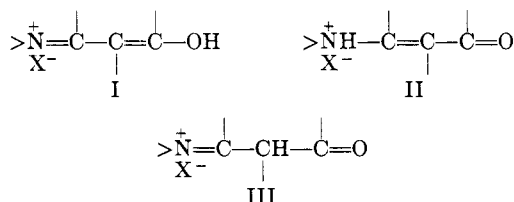
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Received October 23, 1964

Ultraviolet spectra are shown to be a convenient tool for distinguishing the sites of protonation in enamino ketones. The enamino ketones examined [4-*N*-pyrrolidyl-3-penten-2-one (IV), 5,5-dimethyl-3-*N*-pyrrolidylcyclohex-2-en-1-one (VI), 5,5-dimethyl-3-*N*-morpholinylcyclohex-2-en-1-one (VII), and 5,5-dimethyl-3-cyclohexylaminocyclohex-2-en-1-one (VIII)] were all shown to protonate on oxygen.

Enamino ketones, which may be regarded as vinylogous amides, form stable salts with strong acids. Protonation of these salts can take place on O, N, or C to give I, II, and III, respectively. Leonard and Adamcik² on the basis of infrared spectral evidence³ concluded that these salts were O-protonated. Recently, Kramer



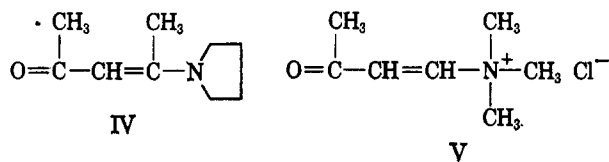
and Gompper⁴ arrived at the same conclusion by nuclear magnetic resonance (n.m.r.) studies⁵ of the perchlorate of 4-dimethylamino-3-penten-2-one. Although ultraviolet spectra have been reported for enamino ketones, their potential as a tool for distinguishing the sites of protonation in enamino ketones has not been fully recognized.⁶ Our work is now presented to illustrate the use of ultraviolet spectra for determining the site of protonation in enamino ketones.

Examination of structures I and II indicates that I should show "diene"-, while II should show "enone"-type absorption. Since the chromophores are no longer in conjugation, III should show only low intensity carbonyl and end absorption. In addition, it would be expected that the O-protonated salts, I, would exhibit absorption maxima in the same range as the unprotonated enamino ketones and their O-alkylated salts.

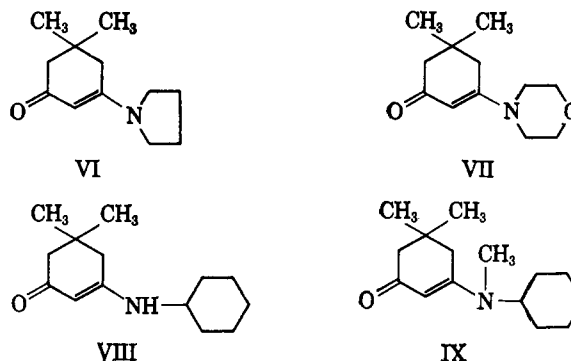
Both have essentially the same chromophoric system and would thus be good models for O-protonation.

The N-protonated salts, II, would be expected to absorb at much lower wave lengths and with lower intensities, as the electrons on nitrogen are not available for participation in the chromophoric system. The absorption of II would therefore be expected to be close to that of simple α,β -unsaturated ketones or of the N-alkylated salts, which should serve as good models for N-protonation.

Table I shows the ultraviolet spectra of some enamino ketones and their salts, together with those of model compounds for O- and N-protonation. 4-*N*-Pyrrolidyl-3-penten-2-one (IV) did not form a crystalline hydro-



chloride but the perchlorate had $\lambda_{\text{max}}^{\text{EtOH}}$ 302 μ (ϵ 24,000). The models for O-protonation, *i.e.*, the free enamino ketone and the O-alkylated salt, have $\lambda_{\text{max}}^{\text{EtOH}}$ 312 μ (ϵ 32,000) and 302 μ (ϵ 24,600), respectively, while the models for N-protonation, β -acetylvinyltrimethylammonium chloride (V) and mesityl oxide, have $\lambda_{\text{max}}^{\text{EtOH}}$ 206.5 μ (ϵ 7300) and 239 μ (ϵ 10,000), respectively. As C-protonation is excluded *a priori*, the perchlorate of IV is clearly O-protonated.



(1) Part V: G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 798 (1964).

(2) N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

(3) D. Cook [*Can. J. Chem.*, **40**, 2362 (1962)] has recently used infrared spectra to show that amides protonate on the oxygen of the carbonyl group. C. L. Bell, J. Shoffner, and L. Bauer [*Chem. Ind. (London)*, 1435 (1963)] have used a similar technique to show that the salts of 2- and 4-pyridones are protonated on oxygen [see also S. F. Mason, *J. Chem. Soc.*, 4874 (1957)].

(4) H. E. A. Kramer and R. Gompper, *Tetrahedron Letters*, 969 (1963).

(5) Nuclear magnetic resonance studies on the site of protonation in amides and 2- and 4-pyridones have been previously reported by A. R. Katritzky and R. A. Jones [*Chem. Ind. (London)*, 722 (1961); *Proc. Chem. Soc.*, 313 (1960)] and A. R. Katritzky and R. E. Reavill [*J. Chem. Soc.*, 753 (1963)] who showed that protonation occurs on oxygen.

(6) S. F. Mason in his studies of the tautomerism of *N*-heteroaromatic hydroxy compounds adumbrated the use of ultraviolet spectra for this purpose [*J. Chem. Soc.*, 5010 (1957)]. See also H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).