TABLE II

Multiplicity	τ	Rel. intensity	Separation, c.p.s.
5	5.72	1	6
2	7.43	2	7
broad	8.11	4	...
broad	8.53		...
broad shoulder	8.98	5	...
1	9.07		...

The n.m.r. spectrum of this material is shown in Table II. This spectrum (Table II) is consistent only with structure III.

Anal. Calcd. for $C_{15}H_{24}N_2Br_2$: C, 45.92; H, 6.12; N, 7.14; Br, 40.82; mol. wt., 392. Found: C, 45.67; H, 6.31; N, 7.05; Br, 40.66; mol. wt. (ebull. benzene), 407.

The hexane extracts from the isolation of the high-melting isomer were combined and evaporated to dryness to give 20.8 g. (53%) of the low-melting isomer, m.p. 68–71°. The compound could be crystallized from hexane, alcohol, or petroleum ether, and melted at 76–77° after crystallization. It gave no reaction with sodium iodide in acetone on heating, nor did it react with alcoholic silver nitrate. The n.m.r. spectrum of the low-melting isomer was the same as that of the high-melting isomer except that the methylene doublet occurred at τ 7.37. Actually the lower-melting, more soluble isomer could not be entirely freed of the high-melting isomer, and the spectrum showed both doublets.

Anal. Calcd. for $C_{15}H_{24}N_2Br_2$: C, 45.92; H, 6.12; N, 7.14; mol. wt., 392. Found: C, 45.93; H, 6.14; N, 7.14; mol. wt. (f.p. benzene), 402.

The effects of various initiators were shown by a series of experiments in which 11.2 g. (0.05 mole) of dibromomalononitrile was refluxed for 3 hr. in 20 ml. of 1-hexene with a small amount of initiator. These data are summarized in Table I.

3,8-Di-*n*-butyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (IIb).—Three grams of the low-melting 5,9-dibromo-7,7-dicyanotridecane was dissolved in 10 ml. of concentrated sulfuric acid by gentle warming. After cooling, the solution was diluted with sufficient water to give a 70% sulfuric acid concentration and then heated for 1 hr. on a steam bath. During this period hydrogen bromide was evolved. The mixture was then poured on ice, and the precipitated solid was isolated by filtration and dried. After crystallization from hexane, the dilactone melted at 102.5–103°, yield 1.07 g. (52%). The infrared spectrum showed a 5.70 μ γ-lactone carbonyl absorption.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02; mol. wt., 268. Found: C, 67.03; H, 8.87; mol. wt., 283.

Hydrolysis of the high-melting 5,9-dibromo-7,7-dicyanotridecane with sulfuric acid in the same manner gave a dilactone melting at 117–118° after crystallization from ethanol. The infrared spectrum showed a 5.65-μ absorption for γ-lactone carbonyl.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 66.73; H, 8.91.

1,5-Dibromo-1,5-diphenyl-3,3-dicyanopentane (VI).—A mixture of 2.24 g. (0.01 mole) of dibromomalononitrile, 2.1 g. (0.02 mole) of styrene, and a trace of copper powder was heated gently on a steam bath. After the mildly exothermic reaction subsided, the mixture was heated for one hour on the steam bath. It was then diluted with acetone and filtered, and the filtrate was evaporated to dryness. This left 2.3 g. of a mixture of isomers sintering above 105° and melting over the range 115–125°. After crystallization from alcohol, the mixture formed soft white plates melting over the range 134–140°.

The n.m.r. spectrum is shown in Table III.

TABLE III

Multiplicity	τ	Rel. intensity	Separation (c.p.s.)
1	2.60	5.2	...
3	4.81	0.9	7
2	7.15	2	8
	7.20		

Anal. Calcd. for $C_{19}H_{16}Br_2N_2$: N, 6.48; Br, 36.98. Found: N, 6.74; Br, 36.66.

1,3-Bis(1-bromo-3-cyanocyclobutyl)-2,2-dicyanopropane.—Dibromomalononitrile (4.48 g., 0.02 mole) and 3-methylenecyclobutanecarbonitrile (7.2 g., 0.08 mole) were mixed in a 100-ml. erlenmeyer flask, and a trace of copper powder was added. The reaction mixture was swirled manually and kept below 10° by intermittent immersion in a Dry Ice-acetone bath at −30° until the first separation of solid occurred and then was kept below 20°. About 40 min. was required for the reaction. The solid reaction mixture was taken up in acetone, filtered from the copper, and diluted with water to precipitate the adduct. The crude product from two runs was crystallized from aqueous acetone to yield 16.4 g. (56%) of 1,3-bis(1-bromo-3-cyanocyclobutyl)-2,2-dicyanopropane, m.p. 192–194°.

Anal. Calcd. for $C_{15}H_{14}N_4Br_2$: C, 43.92; H, 3.44; Br, 38.97; N, 13.66. Found: C, 43.38; H, 3.45; Br, 38.74; N, 13.66.

The Indirect Fluorination of Some Halogenated Aliphatic Nitriles[1]

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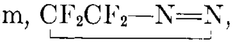
The reaction of argentic fluoride with dichloro- and difluoromalononitrile, tetrafluorosuccinonitrile, hexafluoroglutaronitrile and chlorodifluoroacetonitrile have been investigated. A number of interesting cyclization products have been identified including two new cyclic azoalkanes. The pyrolytic and spectroscopic properties of the latter have been examined.

Several fluorinating agents have been found effective in preparing highly fluorinated azoalkanes. Most notable among these are iodine pentafluoride,[2,3] argentic fluoride,[4,5] and elemental fluorine.[6,7] In addition, combinations such as argentous fluoride and bromine or sodium fluoride and chlorine have been successfully employed.[8] Recently Emeleus and Hurst[9] reported the first fluorinated cyclic azo system,  $CF_2CF_2—N{=}N$, by passing cyanogen over a heated bed of argentic fluoride.

During the course of the present research it was found that dichloro- and difluoromalononitrile undergo analogous cyclizations with argentic fluoride under autogenous pressure. The resulting new compounds were, respectively, 4,4-dichloro-3,3,5,5-tetrafluoro-1-pyrazo-

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[1] A portion of the research reported in this publication was supported by the Advanced Research Projects Agency to which grateful acknowledgment is hereby made.

[2] O. Ruff and W. Willenburg, *Ber.*, **73B**, 724 (1940).

[3] J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

[4] J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 4553 (1960).

[5] O. Glemser, H. Schröder, and H. Haeseler, *Z. Anorg. Allgem. Chem.*, **282**, 80 (1955).

[6] J. A. Attaway, R. H. Groth, and L. A. Bigelow, *J. Am. Chem. Soc.*, **81**, 3599 (1959).

[7] P. Robson, V. C. R. McLoughlin, J. B. Hynes, and L. A. Bigelow, *ibid.*, **83**, 5010 (1962).

[8] W. J. Chambers, W. C. Tullock, and D. D. Coffman, *ibid.*, **84**, 2337 (1962).

[9] H. J. Emeleus and G. L. Hurst, *J. Chem. Soc.*, 3276 (1962).

line $\underline{CF_2CCl_2CF_2N{=}N}$ (I) and hexafluoro-1-pyrazoline, $\underline{CF_2CF_2CF_2N{=}N}$ (II). However, in attempting to extend this series it was found that tetrafluorosuccinonitrile and hexafluoroglutaronitrile also underwent ring closure but in each case with the elimination of one or both of the nitrogen atoms.

In addition to the well known cleavage and rearrangement products CF_4, C_2F_6, $(CF_3)_2NF$, the reaction of difluoromalononitrile with argentic fluoride at 100° yielded II, b.p. −1.5°(extrapolated), in approximately 15% conversion. Confirmation of this novel structure was afforded by its molecular weight, and by n.m.r. and mass spectroscopy. In addition, the gas phase near-ultraviolet spectrum exhibited an intense absorption centering at 382 mμ, indicating the presence of an azo linkage. In order to establish the validity of this assignment, the absorption maxima for a number of related fluorinated compounds also were measured and the results are summarized in Table I.

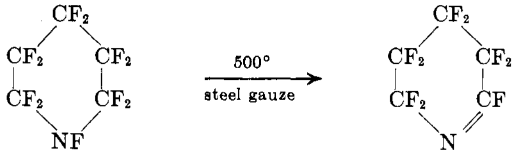
TABLE I
VAPOR PHASE ULTRAVIOLET ABSORPTION MAXIMA OF SOME FLUORINATED AZO SYSTEMS

Compound	Absorption maxima, mμ
I	360
II	382
$CF_3N{=}NCF_3$	365[a]
$CF_3N{=}NC_2F_5$	377
$C_2F_5N{=}NC_2F_5$	384
$CClF_2N{=}NCF_3$[b]	372
$CClF_2CF_2N{=}NCF_3$[b]	376
$CClF_2CF_2N{=}NCF_2CClF_2$	382[c]
$\overline{CF_2CF_2N{=}N}$	330[d]

[a] See ref. 2. [b] See ref. 14. [c] Determined in chloroform solution. [d] See ref. 9.

The rather narrow range in which all of these systems, except the highly strained four-membered ring, absorb suggests that ultraviolet spectrophotometry is of considerable diagnostic value in confirming the presence of the N=N group in highly fluorinated compounds.

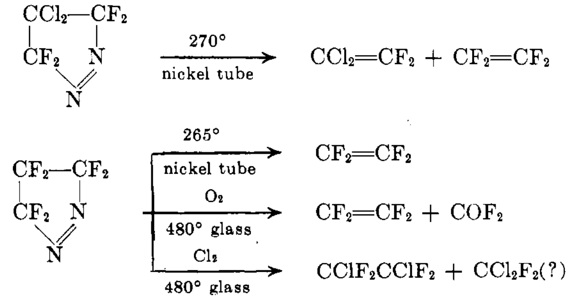
The analogous reaction of tetrafluorosuccinonitrile with argentic fluoride failed to yield a cyclic azo compound but, instead, afforded perfluorocyclobutane and perfluoropyrrolidine in addition to known cleavage products. By comparison, it is interesting to note that the direct fluorination of tetrafluorosuccinonitrile also produced perfluoropyrrolidine and in somewhat better yield but no cyclo-C_4F_8.[10,11] In the case of the next higher homolog, hexafluoroglutaronitrile, the reaction with argentic fluoride afforded three cyclic products, nonafluoro-1-piperideine,[12,13] perfluoropiperidine, and perfluoro-N-methylpyrrolidine,[12] each of which has been reported previously. The first of these compounds was also prepared by the pyrolytic defluorination of perfluoropiperidine in 50 to 60% yield as depicted. This reaction appears to be quite general since it recently was reported that the defluorination of perfluoropyrrolidine under identical conditions produced heptafluoro-1-pyrroline.[10]



In order to determine the feasibility of preparing chlorinated azoalkanes by the argentic fluoride method, the reaction with chlorodifluoroacetonitrile was examined briefly. When rocked at 100° in the presence of an excess of the fluorinating agent, this nitrile produced the new 2,2 -dichlorooctafluoroazoethane, $CClF_2CF_2N{=}NCF_2CClF_2$ (b.p. 82°), in approximately 45% conversion. In view of this result, the analogous reaction with dichloromalononitrile was attempted but preliminary experiments indicated that it was considerably more vigorous than those previously discussed. However, it was found that a milder reaction could be obtained when the reactants were warmed together slowly from −80° to room temperature and later to 50°. In this manner, the interesting new compound I (b.p. 67°) was obtained in approximately 25% conversion. Its structure was confirmed by conventional analysis as well as by n.m.r. and ultraviolet spectroscopy.

It should be noted that the action of elementary fluorine upon dichloro-[14] and difluoromalononitrile[11] has been studied. In each case, no cyclic products were isolated under any of the experimental conditions employed.

It has been proposed by a number of workers that the formation of fluorinated azoalkanes from their corresponding nitriles proceeds through a nitrene intermediate in which the nitrogen atom is electron deficient (R_fN:).[4,7,8] Therefore, it seems reasonable to assume that the cyclic azo compound reported by Emeleus and the two that are presented in the present publication are formed by the intramolecular coupling of two nitrenes.



The pyrolytic reactions of I and II are of considerable importance since they not only aid in the structural confirmation of the parent compounds but also indicate a definite pattern of thermal decomposition. The initial step in these reactions is undoubtedly the elimination of nitrogen. Apparently, the diradical thus formed then dissociates to yield a two-carbon olefin and difluorocarbene. In the absence of a carbene acceptor, CF_2: dimerizes, while, in the presence of oxygen or chlorine, carbonyl fluoride or dichlorodifluoromethane are the resulting products. The postulation that CF_2: is an intermediate in these reactions is supported by the recent work of Mahler[15] who reported that CF_2:

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(10) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Am. Chem. Soc.*, **84**, 3409 (1962).

(11) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, **85**, 1606 (1963).

(12) R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 3407 (1962).

(13) H. Ulrich, E. Kober, H. Schroeder, R. Rätz, and C. Grundmann, *J. Org. Chem.*, **25**, 2585 (1962).

(14) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, in press.

(15) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

reacts with oxygen and chlorine to yield these observed compounds.

Experimental

Apparatus and Materials.—The pressure reactions used in this work were carried out in Hoke stainless steel cylinders each equipped with a valve and pressure gage. Chromatographic separations were made with a Micro-Tek 1500 Chromatograph using Kel-F oil on Chromosorb-P (60–80 mesh) as the stationary phase. Analytical separations were made with a column 15 ft. × 0.25 in., and semipreparative separations with a column 15 ft. × $^3/_8$ in., both at room temperature. Infrared absorption spectra were measured on a Beckman IR-8 spectrophotometer, while the ultraviolet spectra were examined using a Beckman DB spectrophotometer.

The argentic fluoride was freshly prepared by the direct fluorination of silver fluoride at 250°. The nitriles which have been studied were synthesized by methods which have been described in detail in recent papers.[11,14]

The Fluorination of Difluoromalononitrile.—Difluoromalononitrile (16.6 g., 0.16 mole) was condensed into a 300-cc. steel cylinder which had previously been charged with argentic fluoride (185 g., 1.27 moles). The cylinder was then rocked at 100° for 25 hr., after which the product was transferred under vacuum into a trap cooled to −180°, yielding 10 cc. of yellow liquid. Analysis by chromatography and infrared showed the product to contain CF_4, C_2F_6, CF_3CN, $(CF_3)_2NF$, $CF_2(CN)_2$ and the new hexafluoro-1-pyrazoline ($CF_2CF_2CF_2N{=}N$, II). This compound, which was formed in about 15% conversion, was purified by semipreparative chromatography. When condensed, II was a liquid, b.p. (extrapolated) −1.5°, mol. wt. 182 (calcd. 178), ΔH_{vap} 5.81 kcal./mole, and Trouton's constant 21.4 cal./deg. mole. The infrared spectrum showed significant absorptions at 7.18, 7.51, 7.88, 8.24, 9.29, and 10.20 μ. The gas phase ultraviolet spectrum showed an absorption maximum at 382 mμ. The mass cracking pattern exhibited the following *m/e* values in order of decreasing relative intensity: 31 (CF^+), 100 ($C_2F_4^+$), 69 (CF_3^+), 50 (CF_2^+), 150 ($C_3F_6^+$), 81 ($C_2F_3^+$), 74 ($C_3F_2^+$), 131 ($C_3F_5^+$), and 76 ($C_2F_2N^+$). The F^{19} n.m.r. spectrum showed two peaks at +26.1 (CF_2-N) and +63.7 p.p.m. (CF_2–C), referred to trifluoroacetic acid with relative areas 2:1 in complete accord with the assigned structure.

The Fluorination of Dichloromalononitrile.—The dichloromalononitrile (27 g., 0.2 mole) was condensed into a 300-cc. cylinder which had previously been charged with argentic fluoride (146 g., 1.0 mole). The cylinder was next allowed to come slowly to room temperature and rocked for 16 hr. Then it was rocked at 50° for an additional 24 hr., the maximum pressure indicated at any time being 45 p.s.i. After this the product was transferred under vacuum into traps in series at −80° and −180°, yielding higher and lower boiling portions, respectively. The latter (1.4 cc.) was analyzed by chromatography and infrared, and shown to contain CF_4, C_2F_6, CF_3CN, CF_3NF_2, $CClF_3$, $CF_3N{=}NCF_3$, and CCl_2F_2. The former (15 cc.) was distilled through a 6-in. Vigreux column to give three fractions: (1) b.p. 25–60° (2 cc., complex); (2) b.p. 60–75° (8 cc., mainly I); and (3) residue [5 cc., mainly $CCl_2(CN_2)$]. Fraction 2 was separated by semipreparative chromatography to give pure 4,4-dichloro-3,3,5,5-tetrafluoro-1-pyrazoline, $CF_2CCl_2CF_2N{=}N$ (I), which was obtained in approximately 25% conversion.

Compound I was a yellow liquid which boiled at 67° under atmospheric pressure. The infrared spectrum showed three strong peaks at 7.79, 8.10, and 10.83 μ, while the near ultraviolet spectrum exhibited an absorption maximum at 360 mμ. The F^{19} n.m.r. showed one peak at +13.9 p.p.m. (CF_2–N), referred to trifluoroacetic acid.

Anal. Calcd. for $C_3Cl_2F_4N_2$: C, 17.1; Cl, 33.6; F, 36.0. Found: C, 17.1; Cl, 33.2; F, 35.9.

Small amounts of an unsaturate with an infrared absorption band at 5.82 μ also were isolated from fraction 2, but the quantity was insufficient for structure determination.

The Fluorination of Tetrafluorosuccinonitrile.—Tetrafluorosuccinonitrile (11 g., 0.07 mole) was condensed into the cylinder previously charged with argentic fluoride (75 g., 0.51 mole), and rocked 14 hr. at room temperature, and then 24 hr. at 100°. After cooling, the product was vacuum transferred into two traps at −80° and −180°. The lower boiling fraction (3 cc.) was examined by chromatography and infrared and found to contain C_2F_6, $(CF_3)_2NF$ (major component), C_4F_8 (cyclic), $(CF_2CN)_2$, and perfluoropyrrolidine, $CF_2CF_2CF_2CF_2NF$. The last product was purified by semipreparative chromatography and had physical properties identical with those previously reported.[10] The higher boiling portion (1 cc.) was very complex and presumably polymeric.

The Fluorination of Hexafluoroglutaronitrile.—Hexafluoroglutaronitrile (16 g., 0.08 mole) was treated with argentic fluoride under autogenous pressure (80 g., 0.55 mole) for 24 hr. at 100°. The product was vacuum transferred yielding low and high boiling portions which were examined by chromatography and infrared. The former (1 cc.) was found to contain CF_4 and C_2F_6, together with C_3F_8 and $(CF_3)_2NF$ as major components, and some $(CF_3)_2NH$. The latter fraction (5 cc.) consisted of perfluoropiperidine, nonafluoro-1-piperideine, the physical properties of which are discussed later on, and a component which showed only one peak chromatographically over Kel-F. However, the infrared spectrum of this material indicated that it was a mixture of perfluoro-N-methylpyrrolidine[16] and an unidentified unsaturated compound. Analysis by n.m.r. showed absorptions at −22.7, −20.2, +6.3, +15.7, +18.0, +50.0, and +58.0 p.p.m. relative to trifluoroacetic acid. The peaks at −20.2, +18.0, and +58.0 p.p.m. were assigned to perfluoro-N-methylpyrrolidine and are in good agreement with those reported by Haszeldine.[12]

The Fluorination of Chlorodifluoroacetonitrile.—Chlorodifluoroacetonitrile (33 g., 0.3 mole) was treated with argentic fluoride (130 g., 0.89 mole) analogously to the other nitriles, the mixture being rocked at 100° for 36 hr. Then the product was vacuum transferred and separated into a lower boiling (11 cc.) and a higher boiling (18 cc.) fraction in the usual manner. The former was examined by chromatography and infrared and found to contain CF_4, CF_3Cl, $(CF_3)_2NF$, $CClF_2CF_3$, and $CClF_2$-CN. The higher boiling portion was distilled using a 6-in. Vigreux column to give three fractions: (1) b.p. 20–68° (1 cc. complex); (2) b.p. 68–78° (8 cc., mainly $CClF_2CF_2N{=}NCF_2$-$CClF_2$); (3) b.p. 81–85° (6 cc., 95% $CClF_2CF_2N{=}NCF_2CClF_2$), and residue (3 cc.).

Pure $CClF_2CF_2N{=}NCF_2CClF_2$ was obtained by redistillation of fraction 3, b.p. 82° (762 mm.), mol. wt., 293 (calcd. 299), in approximately 45% conversion. The vapor phase infrared spectrum showed major absorptions at 8.15, 8.48, 8.60, 9.00, 9.25, 10.32, and 10.75 μ. The ultraviolet spectrum in chloroform solution gave a broad absorption centered at 382 mμ. The F^{19} n.m.r. spectrum showed two peaks at −5.8 p.p.m. ($CClF_2$) and +32.6 (CF_2), referred to CF_3COOH, with relative areas as 1:1.

Anal. Calcd. for $C_4Cl_2F_8N_2$: C, 16.05; Cl, 23.8; F, 50.5. Found: C, 16.1; Cl, 23.8; F, 50.6.

The residue was shown to contain mostly tris(chlorodifluoromethyl)-*sym*-triazine since the major absorptions in its infrared spectrum were identical with those of the product of the hydrogen chloride catalyzed trimerization of $CClF_2CN$ which boiled at 165 to 167°.

The Pyrolysis of Hexafluoro-1-pyrazoline.—This reaction was carried out in a 2-ft. length of $^3/_8$-in. o.d. nickel tubing, of which the central section (18 in.) was electrically heated. In operation, II was allowed to evaporate slowly from a cooled trap into a stream of dry nitrogen (10 l./hr.) and the mixture then passed through the pyrolysis tube The exit gases were continuously monitored by infrared before being collected in cooled traps. At 245° no reaction occurred, but at 255° $CF_2{=}CF_2$ appeared in the product together with unchanged sample, while at 265° $CF_2{=}CF_2$ only could be detected in the exit gas. The experiment was then repeated using a Pyrex glass pyrolysis tube. In this case no reaction occurred up to 280°, but at 480° $CF_2{=}CF_2$ was the only detectable product. When a slow stream of oxygen was introduced along with the sample at 480° the product contained COF_2 as well as $CF_2{=}CF_2$, while a similar introduction of dry chlorine produced $CClF_2CClF_2$ and probably CCl_2F_2.

The Pyrolysis of 4,4-Dichloro-3,3,5,5-tetrafluoro-1-pyrazoline.—A small sample of this compound on carrier nitrogen was pyrolyzed in the nickel tube as just described. At 270° the infrared spectrum of the exit gases indicated the presence of $CCl_2{=}CF_2$ and $CF_2{=}CF_2$. Examination by chromatography and infrared showed that the mixture contained 80% of the former and 20% of the latter.

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[16] R. N. Haszeldine, private communication.

The Pyrolytic Defluorination of Perfluoropyrrolidine.—This reaction was carried out in a 3-ft. length of $^3/_8$-in. o.d. stainless steel retubing, of which the central section (2 ft.) was packed with steel wool and electrically heated. Before each reaction the tube was heated to the required temperature and hydrogen passed through it for a few hours, after which it was purged with dry nitrogen. The reactant was vaporized slowly from a cooled trap and carried through the tube on a stream of nitrogen (9 l./hr.). In this manner perfluoropyrrolidine (1.7 cc.) at 500° yielded approximately 1 cc. of product, which on examination by analytical chromatography and infrared was shown to contain about 80% of heptafluoro-1-pyrroline, which was subsequently purified by preparative chromatography.

The pure $CF_2CF_2CF_2CF{=}N$ was a colorless liquid, b.p. 22° (extrapolated), mol. wt., 198 ± 4 (calcd. 195), obtained in approximately 50% yield. The infrared spectrum exhibited a sharp band at 5.81 μ (C=N). Other strong bands were located at 7.02, 7.42, 7.69, 8.07, 8.32, 8.76, 9.64, and 10.30 μ. When it was treated with an excess of 10% sodium hydroxide in a sealed tube at room temperature for 24 hr. it was completely hydrolyzed to ammonia and sodium tetrafluorosuccinate. The free acid, obtained by the acidification and ether extraction of the hydrolysis product gave a dianilinium salt, m.p. 223–225° (lit.[17] m.p. 223–225°). A mixture melting point with an authentic sample showed no depression.

The Pyrolytic Defluorination of Perfluoropiperidine.—This compound (3.5 cc.) was defluorinated in an analogous manner to that just described to yield the previously reported nonafluoro-1-piperideine[12,13] in 50 to 60% yield. After purification by preparative chromatography, it was found to be a colorless liquid, b.p. 42.5° (extrapolated), av. mol. wt., 243 ± 3 (calcd. 245), ΔH_{vap} 6.87 kcal./mole and Trouton's constant 21.8. The infrared spectrum exhibited a strong absorption at 5.70 μ (C=N). Other strong absorptions were located at 7.37, 7.58, 8.01, 8.31, 8.58, 9.26, and 10.42 μ. The mass spectrum exhibited the following principal *m/e* values in order of decreasing relative intensity: 69 (CF_3^+), 31 (CF^+), 145 ($C_3F_5N^+$), 50 (CF_2^+), 100 ($C_2F_4^+$), 76 ($C_2F_2N^+$), 95 ($C_3F_3N^+$), 131 ($C_3F_5^+$), 93 ($C_3F_3^+$), 176 ($C_4F_6N^+$), and a weak parent ion at 245 ($C_5F_9N^+$). The F^{19} n.m.r. spectrum showed five peaks at −24.1 p.p.m. (=CF), +17.1 p.p.m. (CF_2–N), +46.2 p.p.m. (CF_2–CF=), +58.8 p.p.m. (CF_2), and +59.9 p.p.m. (CF_2), referred to CF_3COOH, the relative areas of which were in accord with the assigned structure.

A small sample (0.2 cc.) of this unsaturate was hydrolyzed at room temperature in a sealed tube by an excess of 10% sodium hydroxide. The resulting basic solution liberated ammonia on boiling, but did not effervesce when acidified. The ether extract of the acid solution readily yielded the anilinium salt of hexafluoroglutaric acid, m.p. 221–222° (lit.[18] m.p. 218–220). The other products of this defluorination were found to be identical with the mixture of perfluoro-N-methylpyrrolidine and the unsaturate produced by the fluorination of hexafluoroglutaronitrile with argentic fluoride.

Acknowledgment.—We are indebted to Dr. Wallace S. Brey of the University of Florida for the n.m.r. data and to Dr. Charles Colburn and Dr. Grover Paulett for the mass spectra presented here. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

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[17] M. W. Buxton, *et al.*, *J. Chem. Soc.*, 3830 (1952).

[18] D. E. Evans and J. C. Tatlow, *ibid.*, 1184 (1955).

The Cyclization of Propynyl Carbanilates to 2-Oxazolidones

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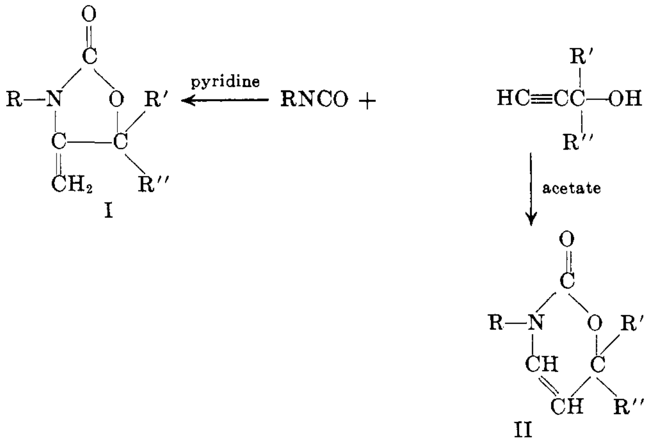
Propynyl carbanilates undergo facile cyclization to 4-methylene-2-oxazolidones with basic catalysts or by simply heating the appropriate isocyanate and alcohol. A discussion of the proof of structure as determined by nuclear magnetic resonance data is included.

The ease with which propynylureas cyclized intramolecularly to 2-imidazolones[1] with a wide variety of reagents (strong acids, phosphorus pentachloride, and base) encouraged us to speculate on the mechanism of cyclization of analogous propynyl carbanilates. Recent literature disclosed the formation of 2-oxazolidones I with pyridine as a catalyst[2] and 1,3-oxazin-2-ones II with sodium acetate.[3]

On repeating this work with *m*-chlorophenyl isocyanate and 1-ethynylcyclohexanol, the same product Ie was obtained with pyridine, sodium acetate, or more simply by heating the isocyanate and alcohol or the pre-formed carbanilate. Mixture melting points were not depressed and infrared and nuclear magnetic resonance spectra were identical. Similar results were obtained with Ia–g.

Five-membered heterocyclic carbonyl compounds derived from ureas and carbanilates can be differentiated from the corresponding six-membered rings by the carbonyl shift to higher frequency for the smaller ring.[1b] Infrared spectra of the products prepared by any of the methods gave the characteristic absorption band for C=O at 5.70–5.75 μ indicative of the five-membered ring. The spectra also showed absorption for $>C{=}CH_2$



I

II

a, R = phenyl; R′ = R″ = H
b, R = 3,4-dichlorophenyl; R′ = R″ = H
c, R = phenyl; R′R″ = pentamethylene
d, R = 3,4-dichlorophenyl; R′ = ethyl; R″ = methyl
e, R = 3-chlorophenyl; R′R″ = pentamethylene
f, R = 3,4-dichloro; R′ = R″ = methyl
g, R = 3,4-dichloro; R′R″ = pentamethylene

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[1] (a) P. J. Stoffel and A. J. Speziale, *J. Am. Chem. Soc.*, **84**, 501 (1962); (b) *J. Org. Chem.*, **27**, 3079 (1962); (c) in press.

[2] M. D. Cameron, U. S. Patent 2,844,950 (July 22, 1958).

[3] S. L. Shapiro, V. Bandurco, and L. Freedman, *J. Org. Chem.*, **26**, 3710 (1961).