

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-dimethylamino-phenyl]-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°;  $\lambda_{\text{max}}^{\text{EtOH}}$  245 ( $\epsilon$  7625), 273 (7850), 317 (2400), 320 (1350), and 445  $\text{m}\mu$  (44,000).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{ClN}_3$ : 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°;  $\lambda_{\text{max}}^{\text{EtOH}}$  250  $\text{m}\mu$  ( $\epsilon$  20,000).

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$ : C, 69.7; H, 6.26; N, 17.4. Found: C, 69.8; H, 6.33; N, 17.6.

**Compound IX.**<sup>11</sup>—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*-toluenesulfonate 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°,  $\lambda_{\text{max}}^{\text{EtOH}}$  518  $\text{m}\mu$  ( $\epsilon_{\text{max}}$  17,900).

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ : 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  $\text{C}_{17}\text{H}_{16}\text{ClN}_4$ : 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  $\lambda_{\text{max}}$  499  $\text{m}\mu$  ( $\epsilon_{\text{max}}$  43,800) while in acetone  $\lambda_{\text{max}}$  449  $\text{m}\mu$  ( $\epsilon_{\text{max}}$  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),  $d^{20}$  1.34.

*Anal.* Calcd for  $\text{C}_2\text{HClF}_2\text{N}_2$ : 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.

## Organic Fluoronitrogens.<sup>1</sup> VI. Reduction of Difluoramino Compounds with Iodide

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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  $\text{NF}_2$  is 1+, while that in the monofluoramino ( $>\text{NF}$ ) or the fluorimino group ( $=\text{NF}$ ) is 1–. Both inorganic and organic molecules containing these groups are capable of oxidizing iodide ion. This general reaction constitutes an important qualitative test.<sup>2–5</sup> However, the products of iodide reductions have been reported for only a few fluoronitrogens.

Among the inorganic materials, difluoramino undergoes a quantitative, four-electron reduction to ammonium ion,<sup>6</sup> whereas difluorodiazine is reduced only to nitrogen gas.<sup>7</sup> The reported iodometric reactions of organic fluoronitrogens are limited to the four-electron reduction of *N,N*-difluorourea,<sup>8</sup> which readily hydrolyzes to difluoramino, and to the two-electron reductions of some cyclic compounds containing the monofluoramino group.<sup>2,9</sup>

(1) Paper V in this series: R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(2) R. E. Banks, J. E. Burgess, and R. N. Haszeldine, *J. Chem. Soc.*, 2720 (1965).

(3) R. E. Banks and E. D. Burling, *ibid.*, 6077 (1965).

(4) J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

(5) J. G. Erickson, H. A. Brown, and D. R. Husted, *J. Heterocyclic Chem.*, **1**, 257 (1964).

(6) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

(7) M. Schmeisser and P. Sartori, *Angew. Chem.*, **71**, 523 (1959).

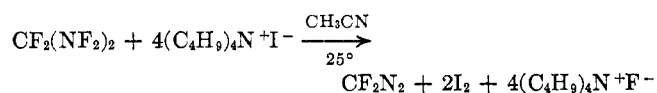
(8) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

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

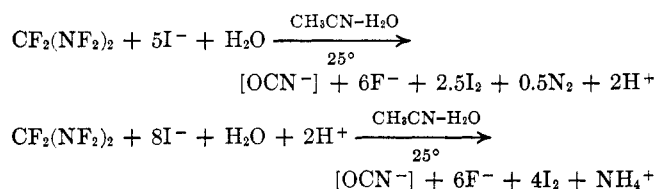
This paper describes the products of the reactions of iodide ion with the hydrolytically stable difluoramino compounds,  $\text{CF}_3\text{NF}_2$ ,  $\text{CF}_3\text{CF}_2\text{NF}_2$ ,  $(\text{CF}_3)_2\text{CFNF}_2$ ,  $\text{CF}_2(\text{NF}_2)_2$ , and  $\text{CCl}_2(\text{NF}_2)_2$ .

### Results

**Bis(difluoramino)difluoromethane.**—Bis(difluoramino)difluoromethane reacts stoichiometrically with tetrabutylammonium iodide in acetonitrile to produce difluorodiazirine. The reaction is complete within a few minutes at room temperature.<sup>10</sup>

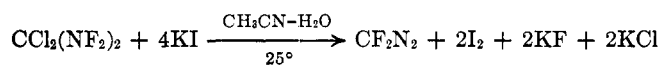


The yield of difluorodiazirine is lowered considerably when water is added to the acetonitrile solvent. Two side reactions lead to the formation of nitrogen gas and nitrogen(3-) reduction products. In systems con-

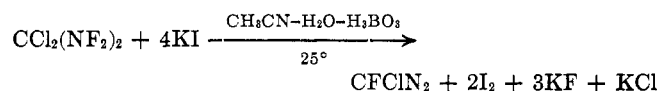


taining about 10% water, the conversion to difluorodiazirine is reduced to about 50 mole %. The yields of iodine and nitrogen indicate that the two side reactions take place to a similar extent; the  $n$  value is 2.6 electrons per nitrogen atom. Only the hydrolytic degradation products of cyanate ion are observed. Thus, the infrared spectrum of the solids from this reaction is nearly identical with that of the residue from an aged solution of potassium cyanate, potassium fluoride, and potassium iodide. In addition, carbon dioxide is observed in the gaseous phase.

**Bis(difluoramino)dichloromethane.**—The reaction of bis(difluoramino)dichloromethane with potassium iodide in 90% (v/v) acetonitrile-water is surprising in that difluorodiazirine is again one of the products; dichlorodiazirine is not produced. An attempt was



made to block the fluorination of the carbon during this reaction by adding boric acid to the system. This resulted in the formation of some chlorofluorodiazirine<sup>11</sup> in addition to the difluorodiazirine. These reactions



are not quantitative; however, increased yields of the diazirine products would be expected from an anhydrous acetonitrile solvent.

**2-Difluoramino-perfluoropropane.**—In 90% (v/v) acetonitrile-water containing 1 *M* potassium iodide and 1 *M* acetic acid, 2-difluoramino-perfluoropropane reacts

(10) Difluorodiazirine is also produced by the reductive defluorination of bis(difluoramino)difluoromethane with dicyclopentadienyliron(II), but a reaction time of several days is required at room temperature; see R. A. Mitsch, *J. Heterocyclic Chem.*, **3**, 245 (1966).

(11) A description of the properties of chlorofluorodiazirine and other substituted diazirines is given in R. A. Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *ibid.*, **2**, 371 (1965).

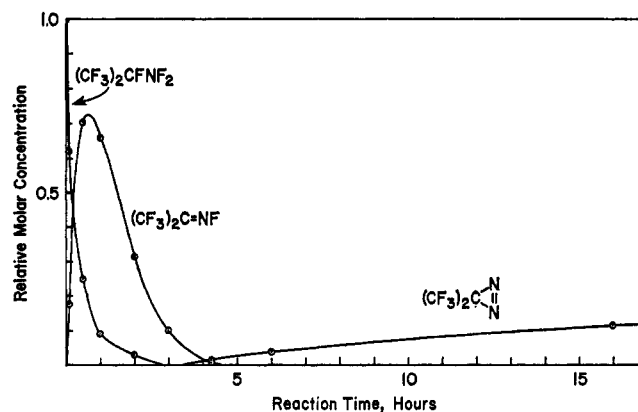
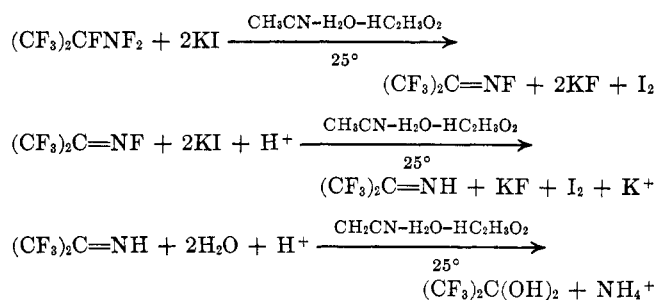


Figure 1.—The reduction of 2-difluoramino-perfluoropropane with iodide. Composition of the gas phase as a function of time.

over a period of several hours. The major portion of the reaction is straightforward. The difluoramino compound is first reduced in a two-electron step to the corresponding fluorimino compound.<sup>12</sup> The fluorimino, in turn, is reduced in a second two-electron step through the hydrolytically unstable imine to ammonium ion. In the absence of the acetic acid, ammonia ap-



pears in the gas phase as a final reduction product of the difluoramino group.

After about a 4-hr reaction time at room temperature, no additional iodine is produced in the acetonitrile-water system. However, if the iodine-containing solution is allowed to stand for several additional hours, a new gaseous product, 3,3-bis(trifluoromethyl)diazirine,<sup>13</sup> is produced. The composition of the gaseous phase of the 2-difluoramino-perfluoropropane reduction as a function of time is shown in Figure 1.

The yield of 3,3-bis(trifluoromethyl)diazirine is about 10 mole %, and removal of the maximal amount of the gaseous fluorimino intermediate from the reactor does not alter this value.

Thus, the precursor is nonvolatile, but its composition is unknown. All of the evidence indicates that both nitrogen atoms in the diazirine originate in the difluoramino groups of the starting material. Graham's disclosure<sup>14</sup> that certain substituted imines and di-

(12) The first step of the over-all reaction is similar to some reductive defluorination reactions of other difluoramino compounds with dicyclopentadienyliron(II). See R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 328 (1965).

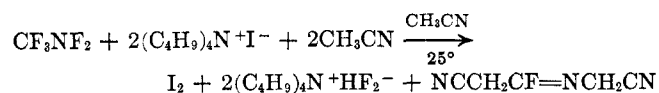
(13) The synthesis of 3,3-bis(trifluoromethyl)diazirine was originally reported by R. B. Minasyan, E. M. Rokhlin, N. P. Gambaryan, Yu. V. Zeifman, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 761 (1965). Subsequently, an improved method of preparation and limited spectral data were reported by D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 3617 (1966). The infrared spectrum is unusual in that the characteristic absorption for this type of structure is not observed in the 6.5- $\mu$  region. Like the halo diazirines, 3,3-bis(trifluoromethyl)diazirine absorbs rather strongly in the ultraviolet region but at much shorter wavelengths.

(14) W. H. Graham, *ibid.*, **88**, 4677 (1966).

fluoramine react to give diazirines suggests a mechanism involving an N-fluorodiaziridine intermediate. The over-all reaction consumes 3.6 g-ions of iodide per mole of fluoronitrogen, which is consistent with the yields of the diazirine and ammonium ion.

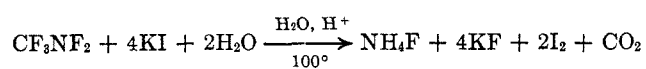
**Difluoramino-perfluoromethane.**—At room temperature difluoramino-perfluoromethane reacts completely with tetrabutylammonium iodide in acetonitrile within a few hours. The reaction rate decreases in other solvents:  $\text{CH}_3\text{CN} > (\text{CH}_3)_2\text{NCHO} > \text{CH}_3\text{OH} > \text{H}_2\text{O}$ . Thus, a complete reaction in water at  $100^\circ$  requires a period of about 10 days.

Generally, an approximate two-electron reduction takes place in dimethylformamide or acetonitrile as indicated by the quantity of iodine produced. The simplest product analogous to the first reduction product of 2-difluoramino-perfluoropropane is perfluoromethylenimine ( $\text{CF}_2=\text{NF}$ ), which was not observed in our analysis of the gaseous phase. Instead, it appears that solvolytic cleavage of two fluoride ions accompanies the reductive defluorination. Thus, a total of four g-ions of fluoride are produced from 1 mole of starting material. This leads us to propose the following reaction. A concentrated solution of the



products in acetonitrile exhibited fluorine nuclear magnetic resonance absorptions at  $\phi^* +39$  and  $+44$ . This region is reasonable for the  $\text{N}=\text{CF}$  moiety, and the two values may be related to isomeric structures. The material is very reactive toward solvents other than acetonitrile, and our attempts to isolate the reduction product by solvent extraction and by silica gel chromatography were unsuccessful.

In 1.0 M aqueous acid at  $100^\circ$  the reduction of the difluoramino group to ammonium ion is nearly quantitative, and all of the carbon is converted to carbon dioxide. Acidification with acetic acid led to a loss of



about one-third of the iodine produced during the 10-day reaction time. Substituting hydrofluoric acid reduced the loss to a negligible amount, but a period of 18 days was required for the reaction to go to completion. The yield of ammonium ion was confirmed by direct analysis. If no acid is added at the outset, nearly the same quantity of iodide is consumed. However, the final solids contain intermediate solvolysis products of cyanate ion, thus decreasing the yields of carbon dioxide and ammonium ion.

**Difluoramino-perfluoroethane.**—Only a few experiments were conducted with difluoramino-perfluoroethane. It reacts completely with tetrabutylammonium iodide in acetonitrile at  $25^\circ$  in less than 2 hr. No gaseous product was observed, and the solid reduction product was not identified. In 90% (v/v) acetonitrile-water containing 1.0 M potassium iodide and 0.5 M acetic acid, a period of nearly 24 hr was required for a complete reaction which consumed 2.2 moles of potassium iodide per mole of difluoramino-perfluoroethane. No significant quantities of gaseous products form, and the solids were not identified.

## Experimental Section

**Safety Precautions.**—Because some of the fluoronitrogens studied tend to be explosive, the safety precautions described previously<sup>1</sup> were closely followed.

**Materials.**—Difluoramino-perfluoroethane was obtained from Hynes Chemical Research Corp., Durham, N. C. Difluoramino-perfluoromethane and bis(difluoramino)difluoromethane were prepared by the method of Koshar, Husted, and Meiklejohn.<sup>1</sup> The 2-difluoramino-perfluoropropane was supplied by Dr. J. Lamar Zollinger.

Bis(difluoramino)dichloromethane was prepared in the course of this study.<sup>15</sup> Because this compound has not been disclosed previously in the open chemical literature, a brief description of its properties is given here. The structure was established by the infrared spectrum, which shows major absorptions at 9.49 (m), 9.64 (m), 10.27 (s), 10.94 (s), and 11.34  $\mu$  (s), the fluorine nmr spectrum, which shows a single, broad absorption at  $\phi^* -42.3$ , and the mass spectral fragmentation pattern given in Table I. Bis(difluoramino)dichloromethane is a colorless gas which does not appear to be affected by water, concentrated acids, alkali, or mercury at room temperature. The compound may be stored in glass.

TABLE I  
MASS SPECTRAL FRAGMENTATION PATTERN  
OF BIS(DIFLUORAMINO)DICHLOROMETHANE<sup>a</sup>

<i>m/e</i>	Ion	%	<i>m/e</i>	Ion	%
31	CF <sup>+</sup>	20.5	85	CF <sub>2</sub> Cl <sup>+</sup>	100.0
33	NF <sup>+</sup>	21.6	99	CNF <sub>2</sub> Cl <sup>+</sup>	69.0
35	Cl <sup>+</sup>	51.1	101	CFCl <sub>2</sub> <sup>+</sup>	28.4
47	CCl <sup>+</sup>	26.5	115	CNFC <sub>2</sub> <sup>+</sup>	29.9
61	CNCl <sup>+</sup>	29.4	134	CNF <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	32.8
80	CNFC <sup>+</sup>	93.4	151	CN <sub>2</sub> F <sub>4</sub> Cl <sup>+</sup>	33.5
82	CCl <sub>2</sub> <sup>+</sup>	44.6			

<sup>a</sup> Normal isotopic distribution for Cl<sup>35</sup> and Cl<sup>37</sup> was observed; Cl<sup>37</sup> fragments are not reported.

All of the difluoramino compounds were purified by gas chromatography or by distillation just prior to their use. Spectrograde acetonitrile was used because some less pure grades contained an impurity which reduces iodine. The other solvents and chemicals used were reagent grade.

**Reductions with Iodide.**—Gaseous samples of the difluoramino compounds, usually 0.15 mmole, were measured manometrically in a small, calibrated vacuum manifold and condensed into a previously evacuated 10-ml reaction flask containing 1.0 or 2.0 ml of a 1 M solution of iodide. Acetonitrile containing tetrabutylammonium iodide and 90% (v/v) acetonitrile-water containing potassium iodide were the most frequently used systems although acetic or hydrofluoric acid was added to some of the aqueous systems to ensure proper acidity. The reaction mixtures were warmed to  $25^\circ$  and stirred magnetically. A few tests were carried out in water at  $100^\circ$  with the glass reaction flasks sealed by fusion to prevent leakage.

**Methods of Analysis.**—The reactions were monitored by ultraviolet, infrared, or gas chromatographic analysis of the gas phase. The equipment used has been described previously.<sup>1,11</sup> The infrared and ultraviolet samples from incomplete reactions were returned to the reaction vessel. A segment of the vacuum manifold was used to collect and to inject the gas chromatographic samples, the size of which was limited to less than 2% of the total head space in the reaction flask. The relative molar responses of some of the gases to detection by thermal conductivity were determined empirically: N<sub>2</sub> (1.00), CO<sub>2</sub> (1.19), CF<sub>2</sub>N<sub>2</sub> (1.55), and CF<sub>2</sub>(NF<sub>2</sub>)<sub>2</sub> (2.25). At the end of each reaction, the iodine-containing liquid phase was divided into two portions, one of which was titrated with standard sodium thiosulfate (0.03 N); the other was reserved for analysis of the other non-volatile products by infrared, nmr, or wet chemical methods. Fluoride ion was determined photometrically with cerium(III)-alizarine complexone, and ammonium ion by the conventional distillation-titration method. The degradation products of

(15) The method of preparation of bis(difluoramino)dichloromethane is described in a forthcoming paper in this series by R. L. Rebertus and B. W. Nippoldt.

cyanate ion (other than carbon dioxide and ammonium ion) were identified by comparison of their infrared spectra with a series of reference spectra of the solids from hydrolyzed control solutions.

**Registry No.**—Bis(difluoramino)difluoromethane, 4394-93-8; bis(difluoramino)dichloromethane, 10394-50-0; 2-difluoraminoperfluoropropane, 662-23-7; difluoraminoperfluoromethane, 335-01-3; difluoramino-perfluoroethane, 354-80-3.

**Acknowledgment.**—The authors thank Vaughn Levin for technical assistance in carrying out many of the experiments. They also thank R. A. Meiklejohn and S. Kulver for interpreting the mass spectral data, and P. B. Olson for performing the elemental analyses. A portion of the work described in this communication was sponsored by the Advanced Research Projects Agency and was monitored by the Bureau of Naval Weapons.

## Tracer Studies of the Condensation of a Reissert Compound with 1,1-Diphenylethylene

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Received January 17, 1967

Mainly by a series of tracer studies, but also on the basis of other evidence, it has been established that the acid-catalyzed condensation of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with 1,1-diphenylethylene (II) affords a mixture of 2-(1-isoquinolyl)-3,3,5-triphenylpyrrolenine (III), 2-(1-isoquinolyl)-3,4,5-triphenylpyrrole (IV), and isoquinaldamide. Mechanisms are suggested for the formation of these products and also for several isomerization and cleavage reactions of III.

As mentioned in previous communications,<sup>1,2</sup> two isomeric products of molecular formula  $C_{31}H_{22}N_2$  are produced by the acid-catalyzed condensation of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with 1,1-diphenylethylene (II). One of these, a colorless compound of mp 194.0–194.5°, can be converted to the other, a yellow compound of mp 262.5–263.5°, either by treatment with 12 *N* sulfuric acid or by potassium hydroxide fusion. Also, prolonged hydrolysis of the colorless compound in 3.6 *N* sulfuric acid affords both the yellow compound and an equimolar mixture of 1-hydroxyisoquinoline (V)–2,3,5-triphenylpyrrole (VI).

A tracer study has now been carried out in which carbonyl- $C^{14}$ -labeled I and cyano- $C^{14}$ -labeled I were condensed with unlabeled II. In addition, unlabeled I was condensed with methylene- $C^{14}$ -labeled II, each of the three reactions being carried out in sulfuric acid-dioxane medium. A pure product of molecular formula  $C_{31}H_{22}N_2$  and mp 194.0–194.5° was isolated in each case, and these compounds were subjected to hydrolytic cleavage in hot, dilute sulfuric acid. Subsequent degradations of the labeled 2,3,5-triphenylpyrroles by the scheme outlined in Scheme I gave the carbon-14 distributions summarized in Table I.

TABLE I

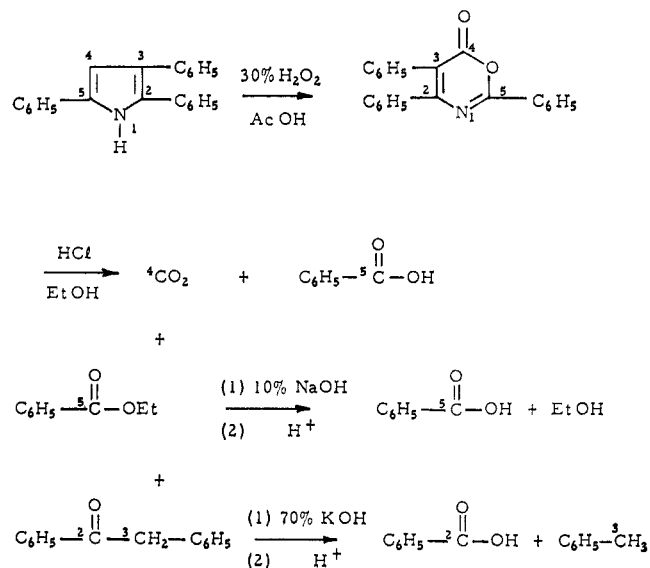
$C^{14}$  DISTRIBUTION IN THE HYDROLYTIC CLEAVAGE PRODUCTS

Specifically labeled precursor	Label in products	
	1-Hydroxyisoquinoline	2,3,5-Triphenylpyrrole
2-Benzoyl-1,2-dihydroisoquinaldonitrile-carbonyl- $C^{14}$	Inactive	100 ± 2% in 5 position
2-Benzoyl-1,2-dihydroisoquinaldonitrile-cyano- $C^{14}$	Inactive	100 ± 2% in 2 position
1,1-Diphenylethylene-2- $C^{14}$	Inactive	100 ± 2% in 4 position

(1) T. K. Liao and W. E. McEwen, *J. Org. Chem.*, **26**, 5257 (1961).

(2) T. T. Yee, W. E. McEwen, and A. P. Wolf, *Tetrahedron Letters*, 3115 (1965).

SCHEME I  
DEGRADATION OF 2,3,5-TRIPHENYLPYRROLE



Of the 24 theoretical structures<sup>3</sup> which may be written for a triphenyl(1-isoquinolyl)pyrrolenine, *only one* is consistent with the observed carbon-14 distribution

(3) The names of the 24 possible compounds are hereby provided, and the numbers in parentheses refer to the criteria, listed in the main text, which have been used to eliminate all but the correct structure from further consideration: 2,5,5-triphenyl-4-(isoquinolyl)pyrrolenine (1, 3), 3,5,5-triphenyl-2-(1-isoquinolyl)pyrrolenine (1, 2), 4,5,5-triphenyl-2-(1-isoquinolyl)pyrrolenine (1, 2, 3), 4,5,5-triphenyl-3-(1-isoquinolyl)pyrrolenine (1, 2, 3), 3,5,5-triphenyl-4-(1-isoquinolyl)pyrrolenine (1, 2, 3), 2,3,3-triphenyl-4-(1-isoquinolyl)pyrrolenine (1, 2, 3), 2,3,3-triphenyl-5-(1-isoquinolyl)pyrrolenine (1, 2), 3,3,4-triphenyl-2-(1-isoquinolyl)pyrrolenine (1, 2, 3), 3,3,4-triphenyl-5-(1-isoquinolyl)pyrrolenine (1, 2), 2,4,4-triphenyl-3-(1-isoquinolyl)pyrrolenine (1, 2, 4), 2,5,5-triphenyl-3-(1-isoquinolyl)pyrrolenine (1, 2, 4), *d*- and *l*-2,3,5-triphenyl-5-(1-isoquinolyl)pyrrolenine (1), *d*- and *l*-3,4,5-triphenyl-5-(1-isoquinolyl)pyrrolenine (1, 2, 3), *d*- and *l*-3,4,5-triphenyl-3-(1-isoquinolyl)pyrrolenine (1, 2, 4), *d*- and *l*-2,3,5-triphenyl-3-(1-isoquinolyl)pyrrolenine (1), *d*- and *l*-2,3,4-triphenyl-3-(1-isoquinolyl)pyrrolenine (1, 2, 3), *d*- and *l*-2,4,5-triphenyl-5-(1-isoquinolyl)pyrrolenine (1, 3), and 2-(1-isoquinolyl)-3,3,5-triphenylpyrrolenine (III), the correct structure.