

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

The Action of Elementary Fluorine upon Organic Compounds. XXIV. The Jet Fluorination of Hydrogen Cyanide, Cyanogen, Methylamine and Ethylenediamine. Pyrolysis and Fluorinolysis of Selected Products¹

BY PETER ROBSON,² VICTOR C. R. McLOUGHLIN,³ JOHN B. HYNES⁴ AND LUCIUS A. BIGELOW

RECEIVED JUNE 26, 1961

A study has been made of the jet fluorination of HCN, (CN)₂, CH₃NH₂ and H₂NCH₂CH₂NH₂ under a wide variety of operating conditions. Each of these compounds yielded the products CF₃NF₂, (CF₃)₂NF, (CF₃)₃N and CF₃N=NCF₂ in varying amounts, indicating that these fluorinations may have operated, in part at least, through a common mechanism. There were also formed the new compounds NF₂CF₂CF₂NF₂, CF₃NFCHF₂, CF₃NFCF₂CF₃ and CF₃N=NCF₂CF₃, the last two of which have been synthesized independently by the co-fluorination of HCN and CF₃CN. The results of the pyrolysis and fluorinolysis of several products are presented in support of the proposed mechanism.

An earlier paper in this series⁵ has dealt with the direct fluorination of methylamine and ethylenediamine in the T or concentric ring reactors. In addition to CF₄, the former yielded only C₂F₆, CF₃NF₂, CF₃CF₂NF₂ and (CF₃)₂NF, but no nitrogen balance; the latter gave mostly CF₃NF₂, CF₃CF₂NF₂ and the unexpected CF₃N=NCF₂.

This paper describes in detail the jet fluorination of hydrogen cyanide, cyanogen, and their corresponding saturated derivatives, methylamine and ethylenediamine. Strangely enough all four of these compounds yielded in addition to CF₄ and other substances, the same products of fluorination, alkylation and dimerization, namely, CF₃NF₂, (CF₃)₂NF, (CF₃)₃N and CF₃N=NCF₂. They were formed in widely varying amounts depending upon the operating conditions used and the nature of the compound being fluorinated, but their appearance in each case furnished a strong indication that these fluorinations must, in part at least, follow a common mechanism.

Specifically, HCN fluorinated at the molar reaction ratio (F₂: sample: N₂) of 4:1:32 at 150° yielded pure CF₃NF₂ in 60 mole per cent. yield, which represents a practicable preparative method. Under other conditions it also yielded a small amount of CHF₃, identified by vapor phase chromatography and infrared. Since no C₂F₆ was formed in the HCN fluorinations, it was assumed that no significant concentration of ·CF₃ radicals could have been present in the reaction mixtures.

Next, (CN)₂ at the fluorination ratio of 8:1:8 and 200° gave the new NF₂CF₂CF₂NF₂ (crude yield, 22 mole %), purified by rectification and V.P.C., b.p. (extrapolated) -1.6°, mol. wt. 202-204 (calcd. 204). The corresponding infrared, n.m.r. and mass spectra were all consistent with the assigned structure. There were also formed small amounts of CF₃NFCF₂CF₃ and CF₃N=NCF₂CF₃ isolated by accumulation, rectification and V.P.C. These compounds were independently synthesized as described later. In addition, cyanogen also yielded

NF₃, C₂F₆ and CF₃CF₂NF₂ as might have been expected.

The fluorination of CH₃NH₂ at 5:1:50 and 150° produced the same principal products as HCN, and also two isomeric compounds in small amounts which were separated and purified by chromatography. The first of these was the known (CF₃)₂NH, positively identified by infrared, while the second was the new CF₃NFCHF₂, b.p. (extrapolated) -7.5°, the corresponding infrared and mass spectra of which were completely consistent with the proposed structure.

Finally, the fluorination of H₂NCH₂CH₂NH₂ yielded a very complex mixture of substances, including all the expected products, together with much NF₃ and smaller amounts of CHF₃, C₂F₆ and (CF₃)₂N-N(CF₃)₂, all separated by V.P.C. and identified by their known infrared spectra. The mixture also contained small amounts of CF₃NFCHF₂, (CF₃)₂NH₂, NF₂CF₂CF₂NF₂, CF₃NFCF₂CF₃ and CF₃N=NCF₂CF₃, separated in the usual manner.

The new compounds CF₃NFCF₂CF₃ and CF₃N=NCF₂CF₃ were prepared by the co-fluorination of HCN and CF₃CN at the molar reaction ratio (HCN:CF₃CN:F₂:N₂) of 1:1:5:16 in the jet reactor at 100°. The product on rectification yielded a portion, b.p. -5° to -3° (11 vol. %), which was separated by V.P.C. into three components, namely (CF₃)₃N, CF₃NFCF₂CF₃ and CF₃N=NCF₂CF₃. The last two were shown by their infrared spectra to be identical with similar material from other fluorinations. The structures of these new compounds were elucidated by mass spectroscopy, and the presence of the azo linkage in CF₃N=NCF₂CF₃ was demonstrated by its ultraviolet absorption spectrum. A larger sample of CF₃NFCF₂CF₃ was subsequently prepared by a different route to be described in detail in a forthcoming paper. The extrapolated boiling point was -4.0°, mol. wt. 220-224 (calcd. 221), and the n.m.r. spectrum was completely in accord with the assigned structure. Evidence from relative chromatographic retention times indicated that the boiling point of CF₃N=NCF₂CF₃ was close to 0°.

In all more than 80 runs have been made during the course of these studies, but few clear trends have been observed. Naturally, as the operating conditions became milder, cleavage was reduced and the formation of dimeric materials or high boiling residues was increased. An exception appears to be that in the fluorination of HCN an increase in

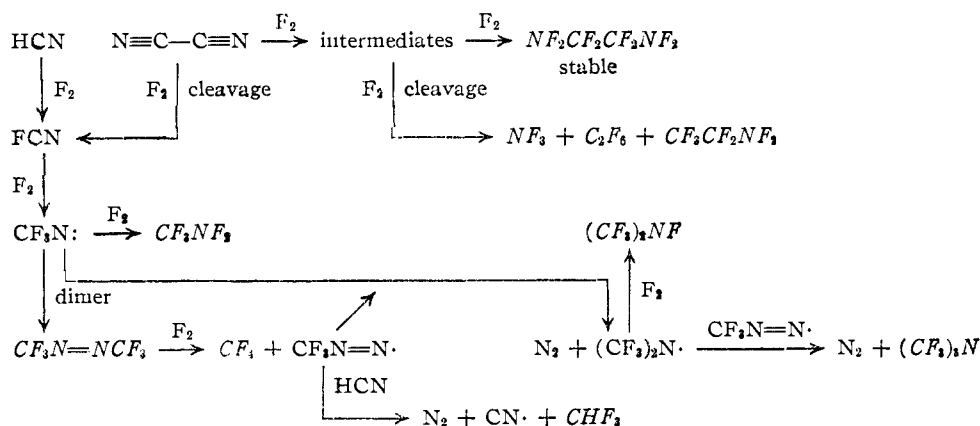
(1) This paper has been constructed in part from the Doctorate thesis submitted by John B. Hynes to the Graduate School of Duke University in June, 1961. Most of this material was presented at the New York Meeting of the American Chemical Society in September, 1960. The work was supported by the Office of Ordnance Research, to which grateful acknowledgment is hereby made.

(2) O.O.R. Research Associate, 1959-1960.

(3) O.O.R. Research Associate, Oct. 1959-Jan. 1961.

(4) O.O.R. Research Assistant, 1958-1960.

(5) J. A. Gervasi, M. Brown and L. A. Bigelow, *J. Am. Chem. Soc.*, **73**, 1679 (1950).



the dilution ratio progressively favored the formation of CF_3NF_2 , leading eventually to the 60 mole per cent. yield previously referred to. It is possible that as the dilution was increased, $\text{CF}_3\text{N}\cdot$ radicals (see below) would be less likely to dimerize.

In considering a possible common mechanism for these fluorinations, it is clearly recognized that such reactions may well take place by several different pathways simultaneously. It is believed, however, that the following scheme representing the fluorination of both hydrogen cyanide and cyanogen accounts well for most of the products actually formed, which are italicized.

Here it is assumed that both fluorinations may pass through FCN which rapidly accepts fluorine to form the nitrene, $\text{CF}_3\text{N}\cdot$, a structure similar to that already proposed by Young.⁶ The nitrene could readily dimerize to the isolated azo compound, which should undergo fluorinolysis to give the intermediate $\text{CF}_3\text{N}=\text{N}\cdot$. The latter could easily alkylate the nitrene with the evolution of nitrogen to form both $(\text{CF}_3)_2\text{NF}$ and $(\text{CF}_3)_3\text{N}$. Since no C_2F_6 was formed by the fluorination of HCN , it is unlikely that $\cdot\text{CF}_3$ radicals could have been responsible for this alkylation. In the direct addition of fluorine to cyanogen, the fragments formed, as indicated, probably resulted from the cleavage of the partially fluorinated intermediates rather than by the fluorinolysis of $\text{NF}_2\text{CF}_2\text{CF}_2\text{NF}_2$, which has been shown to be quite resistant to fluorine. Inasmuch as CH_3NH_2 and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ could, during fluorination, undergo both substitution and dehydrofluorination to form HCN and $(\text{CN})_2$, respectively, it was not surprising that these yielded similar products on fluorination. However, in the diamine case much cleavage of intermediates also took place, so that only a little of the perfluoro compound was formed. Incidentally the small amount of CHF_3 formed by the fluorination of HCN and the amines was presumably produced by the abstraction of hydrogen atoms from unreacted material by $\text{CF}_3\text{N}=\text{N}\cdot$ radicals.

The co-fluorination of HCN and CF_3CN referred to above would presumably lead to the formation of the nitrenes, $\text{CF}_3\text{N}\cdot$ and $\text{CF}_3\text{CF}_2\text{N}\cdot$, which on coupling would form $\text{CF}_3\text{N}=\text{NCF}_2\text{CF}_3$. This, in turn, on fluorinolysis could produce not only $\text{CF}_3\text{N}=\text{N}\cdot$, but also $\text{CF}_3\text{CF}_2\text{N}=\text{N}\cdot$, and these rad-

icals could easily alkylate the respective nitrenes to form ultimately the $\text{CF}_3\text{NFCF}_2\text{CF}_3$ actually isolated.

Several fluorinolyses and pyrolyses were run in support of the mechanisms just postulated. The former were operated in the jet reactor, and the latter in a heated copper tube. It was found that when pure $\text{CF}_3\text{N}=\text{NCF}_3$ was fluorinated at the molar ratio (F_2 :sample) of 3.8:1 and no dilution, at 150° , 90% of the sample was consumed, and much CF_4 together with small amounts of CF_3NF_2 and $(\text{CF}_3)_2\text{NF}$ were formed, but no C_2F_6 , indicating the absence of $\cdot\text{CF}_3$ radicals in the mixture. Here it appears that $\text{CF}_3\text{N}=\text{N}\cdot$ radicals alkylated the azo compound with the formation of $(\text{CF}_3)_2\text{N}-\text{NCF}_3$, which on further fluorinolysis yielded $(\text{CF}_3)_2\text{NF} + \text{CF}_3\text{NF}_2$.

Next, the fluorinolysis of pure $\text{NF}_2\text{CF}_2\text{CF}_2\text{NF}_2$ at the ratio of 15:1:50 (F_2 :sample: N_2) at 200° consumed only 10% of the sample and yielded small amounts of CF_4 and NF_3 , together with considerable $\text{CF}_3\text{CF}_2\text{NF}_2$, showing that this material was quite resistant to fluorine even at the indicated temperature.

Also, when a complex mixture containing the two azo compounds was similarly fluorinated at 3:1:8 and 200° , the azo compounds disappeared, and equivalent amounts of CF_4 and C_2F_6 were formed. This indicates again that the mixed azo compound might serve as a source of C_2F_6 when present in a mixture being fluorinated.

The pyrolysis of $(\text{CF}_3)_2\text{NF}$ diluted with helium at the ratio of 1:24 at 540° consumed 95% of the sample, and yielded mostly CF_4 and $(\text{CF}_3)_3\text{N}$, together with small amounts of CF_3NF_2 and C_2F_6 , indicating that both alkylation and dealkylation had occurred. It appears that the molecule was cracked into $\text{F}\cdot + (\text{CF}_3)_2\text{N}\cdot$ and $\cdot\text{CF}_3 + \text{CF}_3\text{NF}$, in which case all of the products may be accounted for by a recombination of these radicals while other possible coupling products would probably be unstable at this temperature.

Then the compound $\text{CF}_3\text{CF}_2\text{NF}_2$, when diluted with helium at the ratio of 1:26 and pyrolyzed at 450° , was completely decomposed, yielding CF_4 , C_2F_6 , $n\text{-C}_4\text{F}_{10}$, NF_3 , CF_3NF_2 , $(\text{CF}_3)_2\text{NF}$ and $(\text{CF}_3)_3\text{N}$. If it is assumed that the $\text{CF}_3\text{CF}_2\text{NF}_2$ was cracked into (1) $\text{F}\cdot + \text{CF}_3\text{CF}_2\text{NF}$; (2) $\text{CF}_3\text{CF}_2\cdot + \cdot\text{NF}_2$; (3) $\text{CF}_3\cdot + \cdot\text{CF}_2\text{NF}_2$; and (4) if the rearrangement $\text{CF}_3\text{CF}_2\text{NF} \rightarrow (\text{CF}_3)_2\text{N}\cdot$ is allowed, then all of the

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

products can be accounted for by a recombination of these radicals. After the tube had aged, however, so that the increased porosity at the surface favored defluorination, CF_3CN was formed, while NF_3 , CF_3NF_2 and $(\text{CF}_3)_2\text{NF}$ disappeared from the mixture.

Finally, when pure $\text{NF}_2\text{CF}_2\text{CF}_2\text{NF}_2$ diluted with helium at the ratio of 1:24 was pyrolyzed at 360° , the sample was completely consumed, and there were formed: CF_4 , C_2F_6 , C_3F_8 , *n*- C_4F_{10} , $(\text{CF}_3)_3\text{N}$, CF_3CN and $\text{CF}_3\text{N}=\text{CF}_2$. At 255° , $\text{CF}_3\text{CF}_2\text{NF}_2$ and $\text{CF}_3\text{N}=\text{NCF}_3$ were also formed, but were themselves decomposed at the higher temperature. The mechanism involved here was very complex, but it may be that the compound was primarily cracked into (1) $\text{F}\cdot + \text{NFCF}_2\text{CF}_2\text{NF}_2$; (2) $\cdot\text{NF}_2 + \cdot\text{CF}_2\text{CF}_2\text{NF}_2$; and (3) $2\cdot\text{CF}_2\text{NF}_2$; while the presence of CF_3CN and $\text{CF}_3\text{N}=\text{CF}_2$ indicated defluorination.

The products of fluorinolysis and pyrolysis just listed were separated by V.P.C. and/or identified by infrared. On the whole the formation of these products supported the general fluorination mechanism postulated earlier.

The investigation which has just been described has made clear the close relationship which exists between the reactions of elementary fluorine with hydrogen cyanide, cyanogen and the related amines, presumably involving a common mechanism which has been suggested. This knowledge should be of value as a basis for further studies of the fluorination of organic compounds of carbon, nitrogen and fluorine which are now actively in progress.

Experimental Part

Apparatus.—The fluorinations of methylamine and ethylenediamine were carried out in the two-stage jet reactor fully described previously.⁷ For all other fluorinations, a single stage, single jet reactor was employed, which was a logical development of the first jet reactor⁸ and the modification mentioned above. In it the two stages were effectively combined by constructing the reactor body from 2.5" brass pipe, 45" long with independent electrical heaters 30, 20 and 40 cm. in width located at the base, middle and near the top of the reactor body. Two horizontal thermometer wells were situated 19" and 33" above the base. The bottom of the reactor was lead-sealed by a cap carrying the conventional jet assembly equipped with the usual sample, diluent and fluorine connections, a 1/32" jet and a Meker tube set 3" above the base cap. The top of the reactor was also lead-sealed, and the cap carried a 3/8" exit tube. This improved model was originally designed and placed in service in this Laboratory by Mr. Shunji Nagase. The general assembly, including fluorine cylinder, reactor, sodium fluoride tube, refrigerated trap and accessories, has been described in detail before.

Materials.—Cylinder fluorine (99%) was supplied by the General Chemical Co., and was passed over sodium fluoride pellets to remove traces of HF, and then metered directly into the reactors. The hydrogen cyanide and cyanogen were obtained from the American Cyanamid Co.; and the methylamine (97%) from the Matheson Co. They were metered directly from the commercial cylinders warmed by infrared lamps. The ethylenediamine (98%) furnished by the Eastman Kodak Co. was dried over KOH before use. The diluent employed was Airco nitrogen (OP grade).

Purification and Identification of Products.—When sufficient material was available (above 5 cc.) the product was rectified in a Booth-Podbielniak low temperature precision still, the molecular weights of the fractions being

continuously measured by a vapor density balance. For further purification of fractions obtained by rectification, and for purposes of identification, a Perkin-Elmer model 154 vapor fractometer was employed. Volatile materials (b.p. below 0°) were separated by the solid adsorbents, Florisil or silica gel, while partition columns using dimethyl phthalate, hexadecane, Kel-F oil or polypropylene glycolon-Celite were successful in resolving less volatile mixtures. Highly purified compounds were isolated for b.p., m.p. and spectroscopic measurements by combining fractions from several injections and by using columns up to 3/8" in diameter. Infrared measurements were frequently carried out on components eluted from the column by expanding the eluent into glass syringes and transferring the highly diluted components into an evacuated 10-cm. gas cell. All infrared measurements were made with a Perkin-Elmer model 21 double beam spectrophotometer.

Fluorination of HCN.—In all, 35 fluorinations have been carried out, and the results of 10 representative runs are summarized in Table I.

TABLE I
THE FLUORINATION OF HYDROGEN CYANIDE

Run	Temp., °C.	Ratio	Mole % of total crude condensate—			
			CF_4	CF_2CF_2	$(\text{CF}_3)_2\text{NF}$	$(\text{CF}_3\text{N})_2$ Residue
1	250	4:1:4	89
2	200	4:1:4	58	25	5	..
3	150	4:1:4	51	34	7	..
4	100	4:1:4	42	15	6	2 3
5	30	4:1:4	23	27	.. ^a	..
6	100	4:1:8	37	39	4	5 5
7	100	4:1:12	28	45	2	.. 1
8	100	4:1:20	24	47	2	.. 10
9	100	4:1:24	20	51	3	.. 10
10	150	4:1:32	23	60	6	..

^a Unreacted HCN prevented further separation by rectification.

The approximate observed densities determined by weighing known volumes of the liquified samples as used in calculating the mole percentages were: CF_4 , 1.75; CF_3NF_2 , 1.60; $(\text{CF}_3)_2\text{NF}$, 1.70; $\text{CF}_3\text{N}=\text{NCF}_3$, 1.70; and high boiling residue, 1.80. In the calculations the densities of transitions were considered to be the mean of the densities of the adjacent fractions.

In a typical procedure, based on run 4, HCN (0.06 mole/hr.), diluted with N_2 (0.24 mole/hr.), was passed through the jet into the reactor, heated to 100° , while F_2 (0.24 mole/hr.) was allowed to rise around the jet. Thus the molar reaction ratio ($\text{F}_2:\text{HCN}:\text{N}_2$) was 4:1:4. The product was led through a sodium fluoride absorption tube at 30° , and then condensed in two glass traps in series cooled by liquid oxygen. After 6 hr. the crude product (19.5 cc.) was rectified, and the results are shown in detail in Table II.

The individual fractions were examined by V.P.C. and infrared, showing that (1) was CF_4 with no NF_3 ; (3) was CF_3NF_2 free from C_2F_6 ; (5) was $(\text{CF}_3)_2\text{NF}$ with no CF_2CF_2 ; and (6) was $\text{CF}_3\text{N}=\text{NCF}_3$; while (4) was a mixture of (3) and (5). Fraction 2 was separated by V.P.C. into two components which infrared analysis showed were mixtures of mostly CF_4 containing about 5% CO_2 and CF_3NF_2 containing about 5% CHF_3 . Fraction 7 was accumulated from several fluorinations and carefully redistilled to give $(\text{CF}_3)_3\text{N}$, b.p. -9.5° to -6.5° , mol. wt. 221 (known b.p. -7 to -6° ,⁹ mol. wt. calcd. 221), positively identified by infrared. The residue, b.p. -6.5° to 0° , mol. wt. 220-230, was shown to be a complex, inseparable mixture of at least 5 components by V.P.C.

Fluorination of Cyanogen.—In all 18 fluorinations have been carried out, and the results of 7 representative runs are summarized in Table III.

Here the approximate observed densities were $\text{CF}_4 + \text{NF}_3$, 1.70; $\text{C}_2\text{F}_6 + \text{CF}_3\text{NF}_2$, 1.65; $(\text{CF}_3)_2\text{NF} + \text{CF}_3\text{CF}_2\text{NF}_2$, 1.70; and $\text{NF}_2\text{CF}_2\text{CF}_2\text{NF}_2$, 1.75; and the calculations were as indicated above.

In a typical procedure, based on run 3, cyanogen (0.03 mole/hr.), diluted with N_2 (0.24 mole/hr.), and F_2 (0.24

(7) A. F. Maxwell, F. E. Detoro and L. A. Bigelow, *J. Am. Chem. Soc.*, **82**, 5827 (1960).

(8) B. A. Tyckowski and L. A. Bigelow, *ibid.*, **77**, 3007 (1955).

(9) R. N. Hazeldine, *J. Chem. Soc.*, 102 (1951).

TABLE II
 THE RECTIFICATION OF FLUORINATED HYDROGEN CYANIDE

Fraction	Boiling range, °C.	Mol. wt. range	Volume, cc.	Yield, %		Composition
				Vol.	Molar	
1	-128 to -126	85-87	6.5	33	42	CF ₄
2	-126 to -76	88-108	5.5	28	30	
3	-76	121	3.5	18	15	CF ₃ NF ₂
4	-75 to -37	127-162	0.75	4	2	
5	-36.5	169-171	1.75	9	6	(CF ₃) ₂ NF
6	-30	163-166	0.6	3	2	CF ₃ N=NCF ₃
7	-30 to 0	170-206	1.0	5	3	

 TABLE III
 THE FLUORINATION OF CYANOGEN

Fraction	Temp., °C.	Ratio	Mole % of total crude condensate				Residue
			CF ₄ + NF ₃	C ₂ F ₆ + CF ₃ NF ₂	(CF ₃) ₂ NF + CF ₃ CF ₂ NF ₂	NF ₂ CF ₂ CF ₂ NF ₂	
1	175	8:1:8	13	14	26	18	..
2	200	8:1:8	16	18	39	22	..
3	250	8:1:8	30	27	19	13	..
4	250	8:1:24	39	24	20	5	3
5	250	8:1:40	39	20	19	6	4
6	250	4:1:0	53	23	9	6	..
7	250	4:1:8	44	25	5	3	4

 TABLE IV
 THE RECTIFICATION OF FLUORINATED CYANOGEN

Fraction	Boiling range, °C.	Mol. wt. range	Volume, cc.	Yield, %		Composition
				Vol.	Molar	
1	-133 to -121	77-82	3.5	19	30	CF ₄ + NF ₃
2	-121 to -81	86-127	1.5	7.5	10	
3	-81	128-129	5.0	27	27	C ₂ F ₆ + CF ₃ NF ₂
4	-81 to -38	135-166	0.3	1.5	1.0	
5	-38 to -37	169-171	4.5	24	19	(CF ₃) ₂ NF + CF ₃ CF ₂ NF ₂
6	-37 to -7 (500 mm.)	185-207	4.0	21	13	

mole/hr.) were admitted to the reactor at 250° in the usual manner. Thus the molar reaction ratio (F₂:(CN)₂:N₂) was 8:1:8. The product coming from the top of the reactor was condensed directly in refrigerated traps in the usual manner. After 6 hr. the crude product (18.5 cc.) was rectified, and the results are shown in detail in Table IV.

Fraction 1 was shown to be a 2:1 mixture of CF₄ and NF₃ by infrared. Similarly fraction 3 was shown to be a 1:1 mixture of C₂F₆ and CF₃NF₂, and (5) was a 3:2 mixture of (CF₃)₂NF and CF₃CF₂NF₂. Fraction 5 was accumulated from many fluorinations (45 cc. in all) and re-distilled to give CF₃CF₂NF₂ (12 cc., 95% pure by V.P.C.), b.p. -35.5° to -35°, mol. wt. 170-171 (known b.p. -34.3,¹⁰ mol. wt. calcd. 171). The transitions 2 and 4 were shown to be mixtures of the adjacent fractions 1 and 3 and 3 and 5, respectively. Fraction 6 was accumulated from many fluorinations and carefully fractionated, with the results shown in Table V.

TABLE V

THE RECTIFICATION OF ACCUMULATED FRACTION 6, TABLE IV

Fraction	Boiling range, °C.	Mol. wt. range	Volume, cc.
1	-35 to -2	165-200	7.5
2	-2 to -1	200-206	18.0
3	-1 to -0.5	202-204	15.0
4		200-210	2.5 discarded

The forerun, fraction 1, was separated by V.P.C. into (CF₃)₂NF, CF₃CF₂NF₂ and CF₃N=NCF₃, identified by infrared, together with small amounts of the components of fraction 2. Fraction 2 contained some (CF₃)₂NF, CF₃CF₂NF₂ and CF₃N=NCF₃ (by infrared), but mostly NF₂CF₂CF₂NF₂ (85%), (CF₃)₂N (3%), CF₂NFC₂F₅ (4%) and CF₃N=NCF₃ (4%) by V.P.C. The last two named

(10) G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, 2762 (1951).

new compounds will be described later. Fraction 3 was pure NF₂CF₂CF₂NF₂, b.p. (extrapolated) -1.6°, mol. wt. 202-204 (calcd. 204). Its n.m.r. spectrum was in good agreement with the proposed structure having bands at -92.4 p.p.m. (assigned to N-F) and +39.9 p.p.m. (C-F) referred to CF₃COOH. The peak areas were in the ratio 1.17:1. The mass spectrum of the compound exhibited the following most abundant m/e values in the order of decreasing intensity: 69 (CF₃⁺), 100 (C₂F₄⁺), 114 (C₂F₄N⁺), 31 (CF⁺), 50 (CF₂⁺), 64 (CF₂N⁺), 119 (C₂F₅⁺), 83 (CF₃N⁺), 33 (NF⁺), 45 (CFN⁺), 52 (NF₂⁺).

Fluorination of Methylamine.—In all, 19 fluorinations have been carried out in the two-stage jet reactor; and the results of four representative runs are given in detail in Table VI.

TABLE VI

THE JET FLUORINATION OF METHYLAMINE

Run	Temp., °C.	Liquid volume % of total crude condensate				Residue
		CF ₄	Transition	CF ₃ NF ₂	(CF ₃) ₂ NF	
1	250	60	15	..	9	16
2	200	44 ^a	19	13 ^b	13	4
3	150	43 ^a	12	10 ^b	13	12
4	100	31 ^a	24	16 ^b	9	5

^a Contains some NF₃ by infrared. ^b Contains some C₂F₆ by infrared.

The removal of the HF formed in these fluorinations was incomplete, so that the crude products were contaminated with much subliming SiF₄, making rectification difficult. Consequently the percentages of CF₄ and CF₃NF₂ recorded may be inaccurate, due to the unusually large transition fraction between -120° and -80°. Better results were obtained by operating a large scale typical fluorination under the conditions of run 3, as follows. Methylamine (0.05 mole/hr.) and N₂ (2.5 moles/hr.) were passed through the jet of the reactor at 150° while fluorine (0.25 mole/hr.) was admitted around the jet such that the molar reaction ratio was 5:1:50. The products were

TABLE VII

THE RECTIFICATION OF FLUORINATED METHYLAMINE

Fraction	Boiling range, °C.	Mol. wt. range	Volume, cc.	Yield, % (vol.)	Composition
1	-126 to -125	85	14	40	CF ₄
2	-124 to -82	79-115	4	12	..
3	-77	119-121	6	17	CF ₃ NF ₂
4	-38 to -36	169-170	3	9	(CF ₃) ₂ NF
5	-30 to -29	166	2.5	8	CF ₃ N=NCF ₃
6	-12 to -10	187-196	1.5	4	(CF ₃) ₂ N + CF ₂ NFCHF ₂
7	-6 to 0	185-198	0.5	1	..
8	0 to 50	2.0	6	Complex
9	Non-volatile	1.0	3	Unstable

TABLE VIII

THE FLUORINATION OF ETHYLENEDIAMINE

diluent flow rate constant at 2.6 m./hr., temp. 140°

Run	Ratio F ₂ :sample:N ₂	Liquid volume % of total crude condensate					
		CF ₄	Trans. -120° to -80°	CF ₃ NF ₂	(CF ₃) ₂ NF	CF ₃ N=NCF ₃	Residue
1	16:1:130	33 ^a	25	17 ^b	12 ^c	8 ^c	5
2	11.5:1:130	30	17	23 ^b	8	3 ^c	20
3	10.5:1:100	25	6	25 ^b	6 ^c	6 ^c	27
4	8:1:110	22	7	28 ^b	12 ^c	10 ^c	6

^a Contains over 30% NF₃ by infrared. ^b Contains some C₂F₆ by infrared. ^c Estimated chromatographically.

TABLE IX

THE RECTIFICATION OF FLUORINATED ETHYLENEDIAMINE

Fraction	Boiling range, °C.	Mol. wt. range	Volume, cc.	Liq. vol. % of condensate
1	-130 to -128	78-83	5	33
2	-128 to -80	71-85	2.5	17
3	-78	116-118	2.5	17
4	-37 to -30	160-170	2.0	13
5	-30 to 0	170-220	1.3	9
6	0 to 30		0.5	3
7	30 and up		1.5	10

passed through a NaF tube at 80°, and then condensed in refrigerated traps in the usual manner. The crude product after 24 hr. of operation amounted to 35 cc. The results of the subsequent rectification are presented in Table VII.

Fractions 3, 4 and 5 after several redistillations were shown by infrared to be essentially pure as indicated in the table. Transitions not included were relatively insignificant. Fraction 2 was shown to be composed of CF₄, CF₃NF₂, CHF₃ and SiF₄ by V.P.C. and infrared. Fraction 6 was separated by V.P.C. into (CF₃)₂N, identified by b.p., mol. wt. and infrared; and a new compound CF₃NFCHF₂, b.p. -29° at 295 mm., mol. wt. 146 (calcd. 153). The extrapolated b.p. to 1 atm. was -7.5°, while the Δ*H* vap and Trouton's constant were approximately 5.8 kcal./mole and 22.0 kcal./deg. mole, respectively. The infrared spectrum showed the presence of C-H (3.30μ) and N-F (10.11μ) bonding, while the mass spectrum gave the following m/e values in order of decreasing relative intensity: 51 (CHF₂⁺), 69 (CF₃⁺), 46 (CHF₂N⁺), 31 (CF⁺), 50 (CF₂⁺), 32 (CHF⁺), 27 (CHN⁺), 153 (C₂H₂NF₆⁺) (parent ion), and a minor peak (0.2% relative intensity) at 33 (NF⁺). These data were consistent with the structure CF₃NFCHF₂. Its known isomer (CF₃)₂NH (b.p. -6.7°¹¹) was isolated from fraction 7 by V.P.C. and identified by its mol. wt., infrared and mass spectrum. At least six other components were shown to be present in fractions 7 and 8, but resolution by V.P.C. was not feasible.

Fluorination of Ethylenediamine.—In all, 11 fluorinations have been carried out, using the two-stage jet reactor and the results of four representative runs are given in detail in Table VIII.

The detailed procedure for one other typical run will now be described. Nitrogen (0.4 mole/hr.) carried ethylenediamine at the rate of 0.029 mole/hr. from a simple saturator maintained at 86°. The gas stream was further diluted

with N₂ (2.2 moles/hr.), and then passed through the jet into the reactor heated to 175° where it met and reacted with fluorine (0.24 mole/hr.), so that the over-all molar reaction ratio was 8:1:90. The products were passed over NaF at 80° and then condensed in refrigerated traps in the usual manner. After 8.3 hr., 2 cc. of non-volatile and 15 cc. of volatile product had been collected. The latter was then rectified, and the results are given in detail in Table IX.

Transitions not indicated were relatively insignificant. Fraction 1 was a 1:1 mixture of CF₄ and NF₃ by infrared; 2 was a mixture of CF₄, NF₃, CHF₃, SiF₄ and CF₃NF₂ by V.P.C. and infrared, while 3 was CF₃NF₂ with a little CHF₃ by infrared. Fraction 4 was separated by V.P.C. into two major components, shown to be (CF₃)₂NF and CF₃N=NCF₃ by infrared, together with an unidentified

minor component. Fraction 5 was separated by V.P.C. into five components, shown by infrared to be (CF₃)₂N, CF₃N=NCF₃, CF₃NFC₂F₅, CF₂NFCHF₂ and NF₂CF₂CF₂NF₂ in the order of amount produced as estimated by chromatography. Fraction 6 contained two known compounds, identified by infrared as (CF₃)₂N-N(CF₃)₂ and (CF₃)₂NH, together with two unknown components.

Synthesis of CF₃NFC₂F₅ and CF₃N=NCF₃.—When CF₃CN was fluorinated in the jet reactor at 100° and an over-all molar reaction ratio of 3:2:9 (F₂:CF₃CN:N₂), the only products isolated were C₂F₆ and C₂F₅N=NCF₃, some nitrile being recovered. This is in good agreement with previous fluorinations in a packed T-reactor.¹² Accordingly the co-fluorination of HCN and CF₃CN was carried out in order to prepare the mixed compounds CF₂NFC₂F₅ and CF₂N=NCF₃. This was done by metering CF₃CN (0.04 mole/hr.), HCN (0.04 mole/hr.) and N₂ (0.64 mole/hr.) through the jet of the reactor, at 100°, while fluorine (0.20 mole/hr.) flowed around the jet. The gaseous product was freed from HF and condensed in the usual manner. After 8 hr. the crude product (28 cc.) was rectified to give (1) CF₄, C₂F₆, CF₃NF₂ and CF₃CN (16 cc.), b.p. -130° to -70°, mol. wt. 80-130; (2) CF₃CN and (CF₃)₂NF (6 cc.), b.p. -70° to -34°, mol. wt. 120-170; (3) (CF₃)₂NF and CF₃N=NCF₃ (1.5 cc.), b.p. -34° to -5°, mol. wt. 160-190; (4) (CF₃)₂N, CF₃NFC₂F₅ and CF₃N=NCF₃ (3.0 cc.), b.p. -5° to -3°, mol. wt. 220-260; and (5) residue (1.0 cc.) b.p. above -3°. Fractions 1, 2 and 3 were identified by infrared and V.P.C. Fraction 4 was separated into its three component parts by V.P.C. The first was shown to be (CF₃)₂N. The second, CF₂NFC₂F₅, in the mass spectrometer gave the following m/e values in order of decreasing intensity: 69 (CF₂⁺), 119 (C₂F₄⁺), 50 (CF₂⁺), 31 (CF⁺), 12 (C⁺), 152 (C₂F₆N⁺), 114 (C₂F₄N⁺), 76 (C₂F₂N⁺), 45 (CFN⁺) and 202 (C₂F₅N⁺). A smaller peak at 221 (C₃F₉N⁺) was believed to represent the parent ion. A pure sample of this compound, prepared by a different route to be reported later, gave mol. wt. 220-224 (calcd. 221) and b.p. (extrapolated) -4°. The n.m.r. spectrum showed absorptions at -3.40 p.p.m. (CF₂-N); +11.41 p.p.m. (CF₂-CF₂); +17.45 p.p.m. (N-F) and +39.6 p.p.m. (CF₂). The relative areas were also in accord with the assigned structure. The third component, CF₃N=NCF₃, was light yellow in color, and showed a broad absorption maximum in its ultraviolet spectrum from 365 to 380 mμ. The corresponding ultraviolet absorption maximum for CF₃N=NCF₃ was 365 mμ.¹³ The infrared spectrum was in accord with the proposed structure and the mass spectrum gave the following m/e values in order of decreasing intensity: 69 (CF₂⁺),

(11) O. Ruff and W. Willeberg, *Ber.*, **73B**, 724 (1940).(12) J. A. Attaway, R. H. Groth and L. A. Bigelow, *J. Am. Chem. Soc.*, **81**, 3599 (1959).

119($C_2F_4^+$), 31(CF^+), 50(CF_2^+), 100($C_2F_4^+$), 64(CF_2N^+), 114($C_2F_4N^+$), 45(CFN^+) and 109 ($C_2F_2N_2^+$). There was also a small peak at mass 197($C_2F_7N_2^+$), while the absence of peaks at 33 and 52 indicated that there was no N-F bonding in this compound.

Fluorinolyses.—1. When $CF_3N=NCF_3$ (0.04 mole/hr.) was allowed to react with fluorine (0.15 mole/hr.) in the jet reactor, the only products formed were CF_4 (15 parts), CF_3NF_2 (1 part) and $(CF_3)_2NF$ (1 part). At 150°, 10% of the $CF_3N=NCF_3$ was returned unchanged, while at 30°, 25% did not react. 2. When F_2 , $NF_2CF_2CF_2NF_2$ and nitrogen in the molar ratio 15:1:50 were introduced into the jet reactor at 200°, only 10% of the $NF_2CF_2CF_2NF_2$ underwent fluorinolysis to give CF_4 (1 part), NF_3 (2 parts), $CF_3CF_2NF_2$ (25 parts) and an unidentified compound (10 parts). The last mentioned had a very simple infrared spectrum with one absorption, a triplet, centered at 10.65 μ . 3. Fraction 2, Table V, which contained $(CF_3)_2NF$, $CF_3CF_2NF_2$, $CF_3N=NCF_3$, $(CF_3)_2N$, $CF_3NFC_2F_5$, $NF_2CF_2CF_2NF_2$ and $CF_3N=NC_2F_5$ was fluorinated at a molar reaction ratio of 3:1:8 at 200°. The product contained CF_4 and C_2F_6 with a little CF_3NF_2 as well as all of the original materials except $CF_3N=NCF_3$ and $CF_3N=NC_2F_5$. The amounts of CF_4 and C_2F_6 formed could account for the two azo compounds that underwent fluorinolysis, all estimated by V.P.C.

Pyrolyses.—The pyrolyzer consisted of a 60'' section of $3/8$ '' copper tubing electrically heated for the middle 48''. 1. At first $(CF_3)_2NF$ (0.024 mole/hr.) was mixed with helium (0.58 mole/hr.) and passed through the pyrolyzer

which had previously been thoroughly purged with helium at the operating temperature (540°). The products were condensed in a glass trap cooled by liquid oxygen, and after 1.25 hr. the product (3.0 cc.) was separated by V.P.C. The major components were CF_4 and $(CF_3)_2N$ with small amounts of CF_3NF_2 , C_2F_6 and unchanged $(CF_3)_2NF$, all identified by infrared. 2. Next $CF_3CF_2NF_2$ (0.02 mole/hr.) and helium (0.52 mole/hr.) were passed through the pyrolyzer at 450°. After 2 hr. the condensed product (4.0 cc.) was separated by V.P.C. The major products as identified by infrared were CF_4 , C_2F_6 , $n-C_4F_{10}$, NF_3 , CF_3NF_2 , $(CF_3)_2NF$ and $(CF_3)_2N$. A small amount of C_3F_8 was also detected. This pyrolysis was repeated several times during which the composition of the product obtained gradually changed until it remained constant as: CF_4 , C_2F_6 , C_3F_8 , $n-C_4F_{10}$, CF_3CN and $(CF_3)_2N$. 3. Finally, $NF_2CF_2CF_2NF_2$ (0.025 mole/hr.) diluted with helium (0.60 mole/hr.) was pyrolyzed at 255°. After 0.5 hr. the condensed product (1.3 cc.) was separated by V.P.C. and identified by infrared as CF_4 , C_2F_6 , $CF_3CF_2NF_2$, CF_3CN , $CF_3N=NCF_3$ and unchanged $NF_2CF_2CF_2NF_2$. At 360°, the products were CF_4 , C_2F_6 , C_3F_8 , $n-C_4F_{10}$, $(CF_3)_2N$, CF_3CN and $CF_2N=CF_2$.

Acknowledgment.—We would like to thank Dr. Wallace S. Brey, University of Florida, for the n.m.r. spectrum of $CF_3NFC_2F_5$, and Dr. John Ruth, Liggett and Myers Research Laboratory, Durham, N. C., for the mass spectra given above.

[COMMUNICATION NO. 2134 FROM THE KODAK RESEARCH LABORATORIES, RESEARCH LABORATORIES, EASTMAN KODAK CO. ROCHESTER 4, N. Y.]

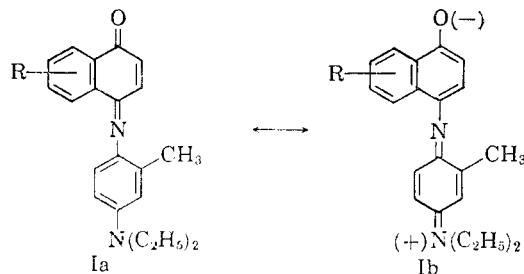
Indoaniline Dyes. V.¹ Some Dyes Derived from Substituted α -Naphthols

BY A. P. LURIE, G. H. BROWN, J. R. THIRTLE AND A. WEISSBERGER

RECEIVED APRIL 25, 1961

The synthesis and properties of some substituted α -naphthols and the indoaniline dyes derived from them are reported. Effects of substituents and solvents on the absorption maxima of these dyes, prepared by oxidative condensation of the α -naphthol with 4-amino-3-methyl-N,N-diethylaniline, are explained in terms of electronic and hydrogen-bonding considerations.

An increased contribution of the polarized form (Ib) to the resonance hybrid representing the indo-



aniline dye (I) should cause both a bathochromic shift and an increase in the maximum extinction coefficient. This expectation is based on a study of the indoaniline dyes derived from phenols² and from 1-hydroxy-2-naphthamides.^{1,3} The effect of

substituents in positions other than 2 or 3 on the absorption of indoaniline dyes derived from 1-naphthol is the subject of the present paper.

The data obtained are summarized in Table I. Because an increase in the polarity of the solvent tends to favor the ionic form (Ib) of the dye, the bathochromic and hyperchromic effects observed in proceeding from cyclohexane to butyl acetate to methanol were to be expected.

A plot (Fig. 1) of σ -constants⁴ against $1/\lambda_{max}$ of the dyes derived from 6- and 7-substituted α -naphthols, using *para*-constants and *meta*-constants, respectively, results in straight-line relationships. In these positions, substituents which increase the electron density on the carbonyl oxygen of the dye cause hypsochromic shifts; those which decrease the electron density result in bathochromic shifts. Thus, a methoxy group in position 6, where it can exercise resonance effects, is electron-supplying and gives a hypsochromic shift relative to the dye from α -naphthol; the same group in position 7, owing to its electron-withdrawing inductive effect, causes a bathochromic shift.⁵

(1) Indoaniline Dyes. IV, C. R. Barr, G. H. Brown, J. R. Thirtle and A. Weissberger, *Phot. Sci. and Eng.*, **5**, 195 (1961).

(2) (a) P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **68**, 2235 (1946); (b) **69**, 152 (1947); (c) **71**, 2287 (1949).

(3) (a) B. S. Portnaya, I. I. Levkoev and N. S. Spasokukotskil, *Doklady Akad. Nauk SSSR*, **82**, 603 (1952); (b) N. S. Spasokukotskil, I. I. Levkoev and B. S. Portnaya, *ibid.*, **93**, 671 (1953); (c) B. S. Portnaya, N. S. Spasokukotskil, N. F. Turitsyna, T. P. Bobkova, G. I. Arbutov and I. I. Levkoev, *J. Gen. Chem. SSSR*, **28**, 2532 (1956); (d) N. F. Turitsyna, B. S. Portnaya, N. S. Spasokukotskil, T. P. Bobkova, G. I. Arbutov and I. I. Levkoev, *ibid.*, **26**, 2546 (1956).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188; H. H. Jaffé, *Chem. Revs.*, **63**, 191 (1953); σ^* -values were used when available.

(5) It has been brought to our attention, by one of the referees, that the absorption of substituted indigo and thioindigo dyes (*cf.*