

[CONTRIBUTION FROM HYNES CHEMICAL RESEARCH CORP. AND THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

## The Action of Elementary Fluorine upon Organic Compounds. XXVIII. The Direct Fluorination of Perhalonitriles<sup>1</sup>

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The nitriles  $\text{CClF}_2\text{CN}$ ,  $\text{CCl}_2(\text{CN})_2$ , and  $\text{CCl}_3\text{CN}$  have been fluorinated in a jet reactor under various conditions. The new saturated derivatives  $\text{CClF}_2\text{CF}_2\text{NF}_2$ ,  $\text{CCl}_2\text{FCF}_2\text{NF}_2$ ,  $\text{CCl}_3\text{CF}_2\text{NF}_2$ , and  $\text{CF}_3\text{CCl}_2\text{CF}_2\text{NF}_2$  were formed, together with a product which has been tentatively assigned the structure  $\text{NF}_2\text{CF}_2\text{CCl}_2\text{CF}_2\text{NF}_2$ . Also the interesting unsaturates  $\text{CClF}_2\text{CF}=\text{NF}$  and  $\text{CCl}_3\text{CF}=\text{NF}$  were produced, as well as a related azo derivative and other products. The influence of operating conditions on these reactions and the mechanisms involved are discussed.

This paper deals with a logical extension of our earlier work<sup>2</sup> on the direct fluorination of highly fluorinated dinitriles and describes the fluorination of a series of related nitriles containing chlorine.

Perhaps the most interesting observation made during this study was that even under quite vigorous operating conditions, most of the chlorine was not displaced from these molecules, even when the original structures were cleaved into fragments by fluorinolysis. Also the halogenated derivatives of acetonitrile were found for the first time to yield unsaturates of the type  $\text{RCF}=\text{NF}$  by controlled direct fluorination. However, no derivatives of this kind were formed by the fluorination of dichloromalononitrile. Furthermore fluorination of the more highly fluorinated dinitriles did not yield such unsaturates, but in some cases cyclization products were formed.<sup>2</sup>

The nitriles which have been fluorinated were  $\text{CClF}_2\text{CN}$  (I),  $\text{CCl}_2(\text{CN})_2$  (II), and  $\text{CCl}_3\text{CN}$  (III), and the reactions have been carried out for the most part in a single jet, single stage fluorination reactor in the usual manner.

On fluorination, compound I yielded the fully saturated product  $\text{CClF}_2\text{CF}_2\text{NF}_2$  (IV), together with the corresponding unsaturate  $\text{CClF}_2\text{CF}=\text{NF}$  (V). They were accompanied by the azo compound  $\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$  (VI), as well as the expected known cleavage products  $\text{CClF}_3$  and  $\text{CF}_3\text{CClF}_2$ . Under considerably more vigorous operating conditions involving both higher fluorination ratio and temperature, the molecule was almost completely cleaved and only traces of  $\text{CClF}_2\text{CF}_2\text{NF}_2$  were formed.

The fluorination of II yielded the new cleavage products  $\text{CF}_3\text{CCl}_2\text{CF}_2\text{NF}_2$  (VII) and  $\text{CCl}_2\text{FCF}_2\text{NF}_2$  (VIII) together with a substance which has been tentatively assigned the structure of the saturated adduct  $\text{NF}_2\text{CF}_2\text{CCl}_2\text{CF}_2\text{NF}_2$ . Other fragments included the known  $\text{CCl}_2\text{F}_2$ ,  $\text{CF}_3\text{CCl}_2\text{F}$ ,  $\text{CF}_3\text{CClF}_2$ ,  $\text{CF}_3\text{CCl}_2\text{CF}_3$ , and  $\text{CF}_3\text{CClF}_2\text{CF}_2$ , the last undoubtedly by rearrangement. The alkylation products  $(\text{CF}_3)_2\text{NF}$  and  $\text{CF}_3\text{NFC}_2\text{F}_5$  were also produced.

It appears that no unsaturates were formed during these fluorinations when the fluorination ratios were relatively high. The cleavage product  $\text{CCl}_2\text{FCF}_2\text{NF}_2$  was formed at  $175^\circ$ , but the reaction temperature had

to be lowered to  $110^\circ$  before significant quantities of the higher boiling products were obtained. It may be recalled that the fluorination of the analogous  $\text{CF}_2(\text{CN})_2$ <sup>2</sup> gave relatively good yields of the adduct  $\text{NF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{NF}_2$  and its primary cleavage product  $\text{CF}_3\text{CF}_2\text{CF}_2\text{NF}_2$  at  $160^\circ$ . Thus it is clear that the chlorinated nitrile  $\text{CCl}_2(\text{CN})_2$  is considerably more sensitive to fluorinolysis than its fluorinated analog.

Finally, when III was subjected to fluorination, the expected saturate  $\text{CCl}_3\text{CF}_2\text{NF}_2$  (IX) was formed, together with smaller amounts of the corresponding unsaturate  $\text{CCl}_3\text{CF}=\text{NF}$  (X). This time the more important cleavage products were the known  $\text{CCl}_3\text{F}$  and  $\text{CCl}_3\text{CF}_3$ , as might be predicted. In this way the mono-, di-, and trichloro derivatives on the  $\beta$ -carbon atom of  $\text{CF}_3\text{CF}_2\text{NF}_2$  have now been synthesized.

The new compounds which have been prepared during the course of this work together with their simpler physical properties are listed in Table I.

TABLE I  
PHYSICAL CONSTANTS OF NEW COMPOUNDS

| Compound  | B.p.,<br>°C.      | Mol. wt. |        | Approx.<br>yield,<br>vol. % |
|---|-------------------|----------|--------|-----------------------------|
|   |                   | Obsd.    | Calcd. |                             |
| IV $\text{CClF}_2\text{CF}_2\text{NF}_2$            | 3.6 <sup>a</sup>  | 186.5    | 187.5  | 12                          |
| V $\text{CClF}_2\text{CF}=\text{NF}$                | 9.7 <sup>a</sup>  | 147      | 149.5  | 15                          |
| VI $\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$  | 34.3 <sup>a</sup> | 245      | 232.5  | 10                          |
| VII $\text{CF}_3\text{CCl}_2\text{CF}_2\text{NF}_2$ | 66.7              | 264      | 254    | 15                          |
| VIII $\text{CCl}_2\text{FCF}_2\text{NF}_2$          | 44 <sup>a</sup>   | 199      | 204    | 9                           |
| IX $\text{CCl}_3\text{CF}_2\text{NF}_2$             | 82                | ...      | 220.5  | 10                          |
| X $\text{CCl}_3\text{CF}=\text{NF}$                 | 88                | 187      | 182.5  | 5                           |

<sup>a</sup> Extrapolated.

The basic reactions which took place during these fluorinations were the well-known processes of addition and of cleavage by fluorinolysis, accompanied to a minor extent only by the substitution of chlorine by fluorine. However, the ready formation of  $\text{CClF}_2\text{CF}=\text{NF}$  and  $\text{CCl}_3\text{CF}=\text{NF}$  was to some extent unexpected, since an earlier investigation in this Laboratory<sup>3</sup> had shown that the fluorination of  $\text{CF}_3\text{CN}$  under vigorous conditions in the T-reactor yielded  $\text{CF}_3\text{CF}_2\text{NF}_2$  and under mild conditions mostly  $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$ , but in no case was the presence of  $\text{CF}_3\text{CF}=\text{NF}$  detected. It was therefore decided to repeat the fluorination of  $\text{CF}_3\text{CN}$  using the jet reactor under intermediate conditions. In this case pure  $\text{CF}_3\text{CF}=\text{NF}$ ,<sup>4</sup> b.p.  $-32^\circ$  (extrap.), mol. wt. 130.5 (calcd. 133), was obtained, together with  $\text{CF}_3\text{CF}_2\text{NF}_2$  and the azo compound, thus establishing the generality of this reaction. However,

(1) Portions of this material were presented to the Second International Fluorine Symposium at Estes Park, Colo., in July, 1962, and to the Fluorine Symposium at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963. This work was supported by the Advanced Research Projects Agency, the Army Research Office (Durham), and in part by the Allied Chemical Corporation, to whom grateful acknowledgment is hereby made.

(2) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Am. Chem. Soc.*, **85**, 1606 (1963).

(3) J. A. Attaway, R. H. Groth, and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

(4) J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *ibid.*, **85**, 83 (1963).

it should be noted that  $\text{CF}_3\text{CF}=\text{NF}$  was only just resolved from its corresponding saturate by analytical chromatography, but could not be separated by preparative chromatography. It is therefore quite likely that traces of the unsaturate were formed during the earlier investigation, but were not detected with facilities then available.

Since n.m.r. spectroscopy has been invaluable in the structural confirmation of systems containing the  $\text{C}=\text{N}$  linkage, a comparison of the observed chemical shifts appears to be of significant diagnostic value for use in related research. Therefore the data for such systems in which fluorine is attached to the  $\alpha$ -carbon atom are summarized in Table II.

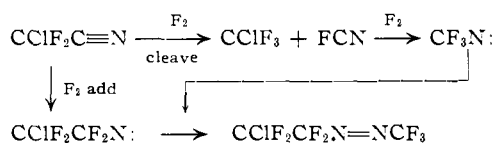
TABLE II  
F<sup>19</sup> N.M.R. CHEMICAL SHIFTS<sup>a</sup> FOR SOME FLUORINATED SYSTEMS CONTAINING THE  $\text{C}=\text{N}$  LINKAGE

| R                 | F<br>RC=NF |       | R <sub>1</sub>                | F<br>R <sub>1</sub> C=NR <sub>2</sub> |                    |
|-------------------|------------|-------|-------------------------------|---------------------------------------|--------------------|
|                   | CF         | NF    |                               | R <sub>2</sub>                        | CF                 |
| CF <sub>3</sub>   | +8.2       | -54.0 | CF <sub>3</sub>               | CF <sub>3</sub>                       | -44.1 <sup>5</sup> |
| CClF <sub>2</sub> | +4.4       | -54.2 | CF <sub>3</sub>               | C <sub>2</sub> F <sub>5</sub>         | -46.9 <sup>4</sup> |
| CCl <sub>3</sub>  | -5.4       | -59.9 | C <sub>2</sub> F <sub>5</sub> | CF <sub>3</sub>                       | -51.2 <sup>4</sup> |
|                   |            |       | C <sub>2</sub> F <sub>5</sub> | C <sub>3</sub> F <sub>7</sub>         | -53.1 <sup>4</sup> |
|                   |            |       | C <sub>3</sub> F <sub>7</sub> | CF <sub>3</sub>                       | -52.5 <sup>2</sup> |

<sup>a</sup> All absorptions are expressed in p.p.m. relative to  $\text{CF}_3\text{COOH}$ .

It will be noted that the location of the  $\alpha$ -fluorine resonance in the three acetaldimine derivatives is dependent upon the degree of chlorination of the halogenated alkyl group, the greatest shielding occurring in the case where this group is  $\text{CF}_3$ . This trend is similar, although as expected smaller in magnitude, to that observed for the chlorofluoromethanes and can presumably be rationalized in an analogous manner.<sup>6</sup> In the cases where the fluorine on nitrogen is replaced by a perfluoroalkyl group, the  $\alpha$ -fluorine resonance occurs at considerably lower field strength. This effect may be explained by the higher mesomeric contribution of the fluorine atom attached to nitrogen than that of a perfluoroalkyl group.

The formation of azo compounds during the direct fluorination of nitriles and amines has been known for some time and is therefore not surprising.<sup>3,7</sup> In the present case, for example, the conversion of  $\text{CClF}_2\text{CN}$  into  $\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$  (VI) may readily be accounted for as follows by the combination of two nitrenes, which of course were not isolated.



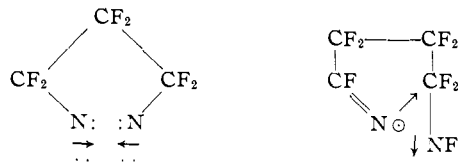
It is also of interest to consider the fact stated earlier that highly halogenated dinitriles do not yield unsaturates containing the  $\text{CF}=\text{NF}$  linkage, either on moderate direct fluorination<sup>2</sup> or upon reaction with  $\text{AgF}_2$ ,<sup>8</sup> but mostly cyclize instead. Such dinitriles offer two easy pathways to cyclization, as illustrated.

(5) R. D. Dresdner, F. N. Thumac, and J. A. Young, *J. Am. Chem. Soc.*, **82**, 5831 (1960).

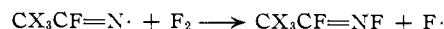
(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 321.

(7) P. Robson, V. C. R. McLoughlin, J. B. Hynes, and L. A. Bigelow, *J. Am. Chem. Soc.*, **83**, 5010 (1961).

(8) J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *J. Org. Chem.*, **28**, 2811 (1963).



The first of these represents the easy combination of two nitrenes to form a cyclic azo compound, while the second indicates a free radical attack with the expulsion of a stable  $\cdot\text{NF}_2$  radical to form a pyrrolene, to be followed by further fluorination. In either case the formation of a stable cyclic end product would be clearly indicated. On the other hand, in the case of the mononitriles where cyclization is definitely excluded, it is not surprising that under mild conditions the primary adduct in the fluorination should react to a significant extent with fluorine according to the equation



The remainder of the primary adduct would be expected to be converted into the nitrene and thence into the corresponding linear azo compound or the perhalogenated amine. Finally, the material reported here, together with that of the preceding paper of this series,<sup>2</sup> forms a suitable background for a comparison of the results of fluorinations by silver difluoride.<sup>8</sup> Also the relatively more reactive chlorine might serve as a convenient starting point for other significant reactions of these compounds.

## Experimental

**Apparatus and Materials.**—The fluorination reactors, operating techniques, and rectification procedures used in this work were essentially the same as those described earlier.<sup>2</sup> The chromatographic separations were made using a Micro-Tek Model 1500 gas chromatograph and Chromosorb-P, 60–80 mesh, as the solid support except as otherwise indicated. The infrared spectra were measured with a Beckman IR5A spectrophotometer equipped with NaCl optics. The ultraviolet spectra were measured by a Beckman DB spectrophotometer.

The fluorine, rated as better than 99% pure, was furnished in cylinders by the General Chemical Co., and was used as has frequently been described. The  $\text{CClF}_2\text{CN}$ , b.p.  $-19.5$  to  $-19^\circ$  (756 mm.), was synthesized from the ethyl ester of the corresponding acid by standard methods of ammonolysis and dehydration. The  $\text{CCl}_2(\text{CN})_2$ , b.p.  $96$ – $100^\circ$ , was prepared by the chlorination of commercial malononitrile.<sup>9</sup> The requisite ester, and also the  $\text{CCl}_3\text{CN}$ , b.p.  $82$ – $84^\circ$ , were furnished by Columbia Organic Chemicals, while the  $\text{CF}_3\text{CN}$  used was supplied by Peninsular Chem. Research, Inc. All samples subjected to spectroscopic or physical analysis were purified by gas chromatography and unless otherwise stated the F<sup>19</sup> n.m.r. spectra showed no stray fluorine peaks, thus further substantiating the chromatographic evidence.

**The Fluorination of  $\text{CClF}_2\text{CN}$ .**—This compound (45.9 g.) was fluorinated in a single jet single stage reactor at the flow rate of 0.034 m./hr., molar reaction ratio 3.1:1:10, at  $140^\circ$  for 12 hr., and yielded about 38 cc. of crude product, which was rectified in the usual manner with the results shown in Table III.

Fractions 4 and 5 were separated by preparative chromatography on a 15 ft.  $\times$   $\frac{3}{8}$  in. column over Kel-F (33%) at room temperature to give pure samples of  $\text{CClF}_2\text{CF}_2\text{NF}_2$ ,  $\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$ , and  $\text{CClF}_2\text{CF}=\text{NF}$ . The  $\text{CClF}_2\text{CF}_2\text{NF}_2$  (IV) was a colorless liquid, b.p.  $3.6^\circ$  (extrap.), mol. wt. 186.5 (calcd. 187.5), obtained in 12 vol. % yield. The infrared spectrum showed no unsaturation and was otherwise consistent. The mass spectrum exhibited the following principal ions in order of decreasing relative intensity ( $\text{Cl}^{37}$  ions omitted): 85 ( $\text{CClF}_2^+$ ), 69 ( $\text{CF}_3^+$ ), 135 ( $\text{C}_2\text{ClF}_4^+$ ), 31 ( $\text{CF}^+$ ), 100 ( $\text{C}_2\text{F}_4^+$ ), 50 ( $\text{CF}_2^+$ ), 116 ( $\text{C}_2\text{ClF}_3^+$ ), 119 ( $\text{C}_2\text{F}_3^+$ ), 66 ( $\text{CClF}^+$ ), 35 ( $\text{Cl}^+$ ), 12 ( $\text{C}^+$ ), 47 ( $\text{CCl}^+$ ), 33 ( $\text{NF}^+$ ), 83 ( $\text{CF}_3\text{N}^+$ ), and 45 ( $\text{CFN}^+$ ). The F<sup>19</sup> n.m.r. spectrum showed three

(9) E. Ott and B. Lopmann, *Ber.*, **55**, 1255 (1922).

TABLE III  
THE RECTIFICATION OF FLUORINATED  $\text{CClF}_2\text{CN}$

| Fraction | B.p., °C.  | Mol. wt. | Vol., cc. | Product  |
|----------|------------|----------|-----------|--|
| 1        | ...        | ...      | 5         | $\text{CF}_4$ , $\text{SiF}_4$ , $\text{CO}_2$ , $\text{CClF}_3$   |
| 2        | -41 to -39 | 136-154  | 10        | Mainly $\text{CF}_3\text{CClF}_2$ with $\text{CO}_2$ and $\text{CClF}_3$   |
| 3        | -22 to -19 | 109-117  | 13        | Mainly $\text{CClF}_2\text{CN}$  |
| 4        | -5 to -2.5 | 134-152  | 5         | $\text{CClF}_2\text{CN}$ (40%)<br>$\text{CClF}_2\text{CF}_2\text{NF}_2$ (30%)<br>$\text{CClF}_2\text{CF}=\text{NF}$ (30%)                        |
| 5        | Residue    | ...      | 3         | $\text{CClF}_2\text{CF}_2\text{NF}_2$ (30%)<br>$\text{CClF}_2\text{CF}=\text{NF}$ (30%)<br>$\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$ (40%) |

absorptions at  $-94.4$  ( $\text{NF}_2$ ),  $-6.8$  ( $\text{CClF}_2$ ), and  $+40.4$  p.p.m. ( $\text{CF}_2$ ); referred to  $\text{CF}_3\text{COOH}$ , relative areas 1.01:1.04:1.00.

The  $\text{CClF}_2\text{CF}_2\text{N}=\text{NCF}_3$  (VI) was a pale yellow liquid, b.p.  $34.3^\circ$  (extrap.), mol. wt. 245 (calcd. 232.5),  $\Delta H_{\text{vap}}$  7.08 kcal./mole, Trouton's constant 23.0 cal./deg. mole, obtained in 10 vol. % yield. The ultraviolet spectrum showed an absorption centered at  $376 \mu$ . The mass cracking pattern showed the following peaks in order of decreasing relative intensity ( $\text{Cl}^{37}$  ions omitted): 69 ( $\text{CF}_3^+$ ), 31 ( $\text{CF}^+$ ), 85 ( $\text{CClF}_2^+$ ), 50 ( $\text{CF}_2^+$ ), 135 ( $\text{C}_2\text{ClF}_4^+$ ), 100 ( $\text{C}_2\text{F}_4^+$ ), 66 ( $\text{CClF}^+$ ), 12 ( $\text{C}^+$ ), 35 ( $\text{Cl}^+$ ), 150 ( $\text{C}_3\text{F}_5^+$ ), 64 ( $\text{CF}_2\text{N}^+$ ), and 119 ( $\text{C}_2\text{F}_3^+$ ). The  $\text{F}^{19}$  n.m.r. spectrum showed three peaks at  $-4.7$  ( $\text{CClF}_2$ ),  $-0.4$  ( $\text{CF}_3$ ), and  $+34$  p.p.m. ( $\text{CF}_2$ ); referred to  $\text{CF}_3\text{COOH}$ , relative areas 2.2:2.7:2.0.

Finally, the  $\text{CClF}_2\text{CF}=\text{NF}$  (V) was also a colorless liquid, b.p.  $9.7^\circ$  (extrap.), mol. wt. 147 (calcd. 149.5),  $\Delta H_{\text{vap}}$  6.2 kcal./mole, and Trouton's constant 22.5 cal./deg. mole, obtained in 15 vol. % yield. The infrared spectrum exhibited a band at  $5.96 \mu$  ( $\text{C}=\text{NF}$ ) and was otherwise consistent. The  $\text{F}^{19}$  n.m.r. spectrum showed three peaks at  $-54.2$  ( $=\text{NF}$ ),  $-14.2$  ( $\text{CClF}_2$ ), and  $+4.4$  p.p.m. ( $=\text{CF}$ ); referred to  $\text{CF}_3\text{COOH}$ , relative areas 1.00:2.39:1.16.

The fluorination of  $\text{CClF}_2\text{CN}$  at 0.03 m./hr., ratio 7.2:1:16, at the higher temperature of  $175^\circ$  yielded 29.9 cc. of product, shown by rectification and chromatography to contain  $\text{CF}_4$  +  $\text{NF}_3$  (7 cc.),  $\text{CClF}_3$  (16 cc.),  $\text{C}_2\text{F}_5\text{Cl}$  (6.5 cc.), and only traces of  $\text{CF}_3\text{N}=\text{NCF}_3$  and  $\text{CClF}_2\text{CF}_2\text{NF}_2$ .

**The Fluorination of  $\text{CCl}_2(\text{CN})_2$ .**—This compound was fluorinated in a two-stage single jet reactor under five different operating conditions. In a representative run under fairly vigorous conditions,  $\text{CCl}_2(\text{CN})_2$  at the flow rate of 0.031 m./hr., molar reaction ratio ( $\text{F}_2$ :sample: $\text{N}_2$ ) 7.5:1:30.4, at  $175^\circ$  for 9.1 hr. yielded 40 cc. of crude product. The volatile portion (35 cc.) was passed through 10%  $\text{NaOH}$  solution, dried over  $\text{CaSO}_4$ , and rectified in the customary manner, with the results shown in Table IV.

TABLE IV  
THE RECTIFICATION OF FLUORINATED  $\text{CCl}_2(\text{CN})_2$

| Fraction | B.p., °C. (mm.)  | Mol. wt.  | Vol., cc. | Product   |
|----------|------------------|-----------|-----------|---|
| 1        | -122             | 83-88     | 8         | $\text{CF}_4$ + $\text{NF}_3$   |
| 2        | -78 to -75       | 119-140   | 4.5       | $\text{CF}_3\text{NF}_2$ + $\text{C}_2\text{F}_6$   |
| 3        | -39 to -38       | 158-160   | 3.2       | $(\text{CF}_3)_2\text{NF}$ impure   |
| 4        | -37 to -30       | 155-129   | 2.3       | Transition  |
| 5        | -29 to -28.2     | 121-122.5 | 2         | $\text{CCl}_2\text{F}_2$  |
| 6        | 0 to 2.5         | 192-165   | 5         | $\text{CF}_3\text{CCl}_2\text{F}$ with<br>$\text{CF}_3\text{NFC}_2\text{F}_5$ +<br>$\text{CF}_3\text{CClFCF}_3$ |
| 7        | -18 to 3.0 (288) | 165-210   | 2         | Transition  |
| 8        | 3.5-8 (288)      | 210-213   | 4         | $\text{CF}_3\text{CCl}_2\text{CF}_3$ +<br>$\text{CF}_3\text{CClFCClF}_2$  |
| 9        | ...              | ...       | 9         | Residue   |

The various fractions were further resolved chromatographically and identified spectroscopically in the usual manner. The known compounds  $\text{CCl}_2\text{F}_2$ ,  $\text{CF}_3\text{CCl}_2\text{F}$ ,  $\text{CF}_3\text{CClFCF}_3$ ,  $\text{CF}_3\text{CCl}_2\text{CF}_3$ , and  $\text{CF}_3\text{CClFCClF}_2$  (by rearrangement) were expected cleavage products, while the known alkylation products  $(\text{CF}_3)_2\text{NF}$  and  $\text{CF}_3\text{NFC}_2\text{F}_5$  may be accounted for as described previously.<sup>7</sup> The residue was shown by analytical chromatography to contain  $\text{CCl}_2\text{FCF}_2\text{NF}_2$  (VIII), which was then purified by preparative chromatography over Kel-F oil (28.6%) at room temperature.

The pure compound (4 cc.) was a colorless liquid, b.p.  $44^\circ$  (extrap.), mol. wt. 199 (calcd. 204),  $\Delta H_{\text{vap}}$  6.94 kcal./mole, Trouton's constant 21.9 cal./deg. mole, yield 9 vol. %, based on total product. The infrared spectrum indicated no unsaturation. The mass spectrum showed two chlorine atoms per molecule by isotope ratio. It exhibited the following principal  $m/e$  values in order of decreasing relative intensity ( $\text{Cl}^{37}$  ions omitted): 31 ( $\text{CF}^+$ ), 101 ( $\text{CCl}_2\text{F}^+$ ), 85 ( $\text{CClF}_2^+$ ), 151 ( $\text{C}_2\text{Cl}_2\text{F}_3^+$ ), 116 ( $\text{C}_2\text{ClF}_3^+$ ), 66 ( $\text{CClF}^+$ ), 47 ( $\text{CCl}^+$ ), 50 ( $\text{CF}_2^+$ ), 69 ( $\text{CF}_3^+$ ), 132 ( $\text{C}_2\text{Cl}_2\text{F}_2^+$ ), 33 ( $\text{FN}^+$ ), 168 ( $\text{C}_2\text{ClF}_3\text{N}^+$ ), 82 ( $\text{CCl}_2^+$ ), 52 ( $\text{NF}_2^+$ ), and 64 ( $\text{CF}_2\text{N}^+$ ), in accordance with the assigned structure. The  $\text{F}^{19}$  n.m.r. spectrum exhibited three peaks at  $-98.3$  ( $\text{NF}_2$ ),  $-4.8$  ( $\text{CCl}_2\text{F}$ ), and  $+36.1$  p.p.m. ( $\text{CF}_2$ ), referred to  $\text{CF}_3\text{COOH}$ , with relative areas 2.0:1.0:2.0.

Another run, operated at the flow rate of 0.025 m./hr., molar reaction ratio 9.2:1:19.5, and at a lower temperature of  $104$ - $113^\circ$  for 9 hr., yielded 28 cc. of crude product. On rectification it was found that the low boiling products previously mentioned had been formed, but the only significant portion was the residue boiling above  $60^\circ$  (16 cc.), which consisted chiefly of two compounds in the approximate ratio of 1:2 by peak areas. This was resolved by preparative chromatography over di-*n*-octyl phthalate (25%) at  $60^\circ$ . The first compound  $\text{CF}_3\text{CCl}_2\text{CF}_2\text{NF}_2$  (VII) was a colorless liquid, b.p.  $66.7^\circ$  (734 mm.), mol. wt. 264 (calcd. 254), obtained in 15 vol. % yield. The infrared spectrum indicated no unsaturation. The  $\text{F}^{19}$  n.m.r. spectrum exhibited three absorptions at  $-100.8$  ( $\text{NF}_2$ ),  $-2.3$  ( $\text{CF}_3$ ), and  $+29.8$  p.p.m. ( $\text{CF}_2$ ), referred to  $\text{CF}_3\text{COOH}$ , with relative areas 1.9:3.1:2.0.

*Anal.* Calcd. for  $\text{C}_3\text{Cl}_2\text{F}_7\text{N}$ : C, 14.2; Cl, 27.9; F, 52.4. Found: C, 14.4; Cl, 27.65; F, 51.7.

The second product was also a colorless liquid, b.p.  $86^\circ$  (746 mm.), mol. wt. 270, obtained in 30 vol. % yield. The infrared spectrum indicated no unsaturation. The  $\text{F}^{19}$  n.m.r. spectrum showed two major peaks at  $-100$  ( $\text{NF}_2$ ) and  $+32.5$  p.p.m. ( $\text{CF}_2$ ) referred to  $\text{CF}_3\text{COOH}$ , with relative areas 1.5:1.0. There were some minor peaks in the n.m.r. spectrum of this product, indicating the presence of isomeric impurities. On this basis the compound has been tentatively assigned the structure of the saturated adduct  $\text{NF}_2\text{CF}_2\text{CCl}_2\text{CF}_2\text{NF}_2$ , mol. wt. (calcd.) 287.

**The Fluorination of  $\text{CCl}_3\text{CN}$ .**—This compound (37.3 g.) was fluorinated in a single jet single-stage reactor at the flow rate of 0.043 m./hr., molar reaction ratio 3.4:1:12, at  $140^\circ$  for 6 hr. and yielded about 28 cc. of crude product. This was then subjected to a trap-to-trap separation at 1 mm. with traps at  $-80$  and  $-180^\circ$ . The lower boiling portion (1.5 cc.) was shown by chromatography and infrared to contain  $\text{CF}_4$ ,  $\text{SiF}_4$ ,  $\text{NF}_3$ , and  $\text{CF}_3\text{NF}_2$ .

The higher boiling fraction (27 cc.) was examined by analytical chromatography with a tricresyl phosphate (30%) column at  $100^\circ$  and shown to contain 10%  $\text{CCl}_3\text{F}$ , 40%  $\text{CCl}_3\text{CF}_3$ , 10%  $\text{CCl}_3\text{CF}_2\text{NF}_2$ , 5%  $\text{CCl}_3\text{CF}=\text{NF}$ , and 30%  $\text{CCl}_3\text{CN}$ . This same portion was then subjected to a crude fractionation, yielding a cut, b.p.  $75$ - $90^\circ$  (14 cc.), which was then separated by preparative chromatography on a 12 ft.  $\times$  0.25 in. column over tricresyl phosphate (30%) at  $100^\circ$  to yield pure  $\text{CCl}_3\text{CF}_2\text{NF}_2$  (IX) and  $\text{CCl}_3\text{CF}=\text{NF}$  (X). The  $\text{CCl}_3\text{CF}_2\text{NF}_2$  (IX) was a colorless liquid, b.p.  $82^\circ$ . Its infrared spectrum showed no unsaturation. The  $\text{F}^{19}$  n.m.r. spectrum showed two peaks at  $-103.5$  ( $\text{NF}_2$ ) and  $+31.5$  p.p.m. ( $\text{CF}_2$ ), referred to  $\text{CF}_3\text{COOH}$ , relative areas 1.05:1.

*Anal.* Calcd. for  $\text{C}_2\text{Cl}_3\text{F}_4\text{N}$ : C, 11.0; Cl, 48.2; F, 34.6. Found: C, 11.2; Cl, 48.0; F, 34.6.

The  $\text{CCl}_3\text{CF}=\text{NF}$  (X) was also a colorless liquid, b.p.  $88^\circ$ . Its infrared spectrum exhibited a band at  $6.01 \mu$  ( $\text{C}=\text{NF}$ ), and was otherwise consistent. Its  $\text{F}^{19}$  n.m.r. spectrum showed two peaks at  $-59.9$  ( $=\text{NF}$ ) and  $-5.4$  p.p.m. ( $=\text{CF}$ ); referred to  $\text{CF}_3\text{COOH}$ , relative areas 1.0:1.3.

*Anal.* Calcd. for  $\text{C}_2\text{Cl}_3\text{F}_2\text{N}$ : C, 13.2; F, 20.9. Found: C, 13.5; F, 21.4.

**The Fluorination of  $\text{CF}_3\text{CN}$ .**—This compound (17.5 g.) was fluorinated in the jet reactor at the flow rate of 0.031 m./hr., reaction ratio 3.8:1:14, at  $140^\circ$  for 6 hr., and yielded 12.5 cc. of crude product. This material was shown by chromatography and infrared to contain  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_3\text{CN}$ ,  $\text{C}_2\text{F}_5\text{NF}_2$ ,  $\text{CF}_3\text{CF}=\text{NF}$ ,  $\text{CF}_3\text{N}=\text{NC}_2\text{F}_5$ , and  $\text{C}_2\text{F}_5\text{N}=\text{NC}_2\text{F}_5$ . The  $\text{CF}_3\text{CF}=\text{NF}$  was obtained pure (0.4 cc.) by analytical chromatography in a 15 ft. column over Kel-F at room temperature. It was a colorless liquid, b.p.  $-32^\circ$  (extrap.), mol. wt. 130.5 (calcd. 133). The infrared spectrum exhibited an absorption at  $5.90 \mu$  ( $\text{C}=\text{NF}$ ) iden-

tical with that reported in earlier work.<sup>4</sup> The  $F^{19}$  n.m.r. spectrum showed three peaks at  $-54.0$  ( $=NF$ ),  $-2.8$  ( $CF_3$ ), and  $+8.2$  p.p.m. ( $=CF$ ), referred to  $CF_3COOH$ , with relative areas 1.0:2.2:1.2.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

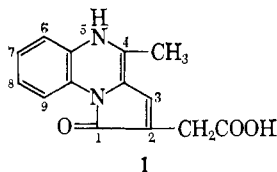
## Synthesis and Properties of Pyrrolo(1,2-*a*)quinoxalines<sup>1</sup>

BY EDWARD C. TAYLOR AND GORDON W. H. CHEESEMAN

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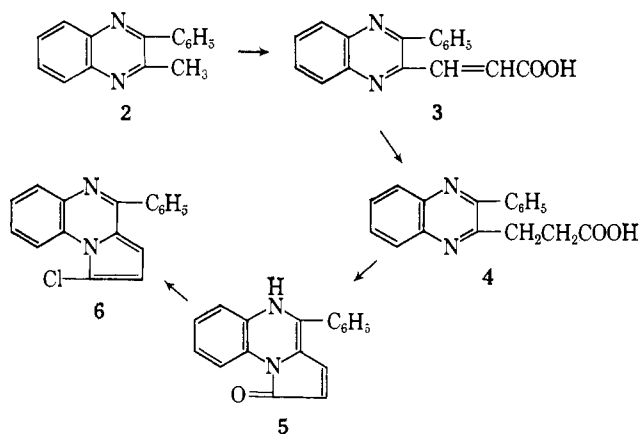
The reaction of 2,3-dimethylquinoxaline with maleic anhydride in glacial acetic acid has recently been shown to give 2-carboxymethyl-4-methylpyrrolo(1,2-*a*)quinoxalin-1(5H)-one (1). In the present study, it has been found that fusion of maleic anhydride with 2-methyl-3-phenylquinoxaline gives 2-carboxymethyl-4-phenylpyrrolo(1,2-*a*)quinoxalin-1(5H)-one (13). Decarboxylation of 13 gives 2-methyl-4-phenylpyrrolo(1,2-*a*)quinoxalin-1(5H)-one (14), the constitution of which is established independently by its synthesis in five steps from 2-methyl-3-phenylquinoxaline-1 N-oxide (19). Cyclodehydration of  $\beta$ -quinoxalypropanoic acids with sulfuric acid-acetic anhydride, polyphosphoric acid, or phosphorus oxychloride is shown to be a useful and general synthetic route to the pyrrolo(1,2-*a*)quinoxaline system. Various chemical reactions of these compounds are described and their ultraviolet and n.m.r. spectra discussed.

The reaction of 2,3-dimethylquinoxaline with maleic anhydride has recently been shown<sup>2</sup> to give 2-carboxymethyl-4-methylpyrrolo(1,2-*a*)quinoxalin-1(5H)-one (1) rather than the Diels-Alder adduct originally claimed. This novel entry into a 1,4-dihydroquinoxaline system, coupled with the interesting chemical



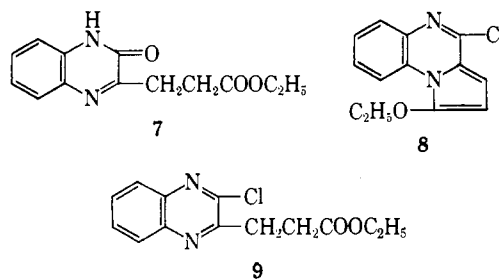
and physical properties of these tricyclic compounds, prompted us to look more closely into synthetic methods for their preparation and at their chemical properties. The present paper describes our more recent investigations in this field.

The synthesis of 4-methylpyrrolo(1,2-*a*)quinoxalin-1(5H)-one from 2,3-dimethylquinoxaline and chloral, as described in our first communication, has now been extended to the synthesis of the corresponding 4-phenyl derivative 5. Thus, the condensation of 2-methyl-3-phenylquinoxaline (2) with chloral followed by alkaline hydrolysis yielded the  $\beta$ -quinoxalypropanoic acid 3 which was catalytically reduced to the saturated propanoic acid 4. Cyclodehydration with a mixture of acetic anhydride and sulfuric acid then gave the tricyclic pyrroloquinoxaline 5. Although its spectral characteristics were similar to those of the corresponding 4-methyl derivative, it proved to be difficult to characterize, and for this reason was converted with phosphorus oxychloride into 1-chloro-4-phenylpyrrolo(1,2-*a*)quinoxaline (6). This compound showed a long wave length absorption band at  $346 m\mu$  in contrast to the long wave length absorption band at  $442 m\mu$  for the 1,4-dihydroquinoxaline derivative 5. The vinyl



hydrogens in positions 2 and 3 of compound 6 appeared in the n.m.r. spectrum ( $CCl_4$ ) as two doublets centered at 3.17 and 3.38  $\tau$  ( $J \sim 5$  c.p.s.).

It has been reported recently<sup>3</sup> that the quinoxalypropanoic acid ester 7 upon treatment with phosphorus oxychloride gave a mixture of 8 (in 18% yield) and 9 (in 45% yield). It thus appeared that this reagent might prove to be an effective cyclizing agent for quinoxalypropanoic acids such as 4 or 10. To test this possibility, the more readily available compound 10<sup>2</sup> was treated directly with phosphorus oxychloride



to give 1-chloro-4-methylpyrrolo(1,2-*a*)quinoxaline (12) in satisfactory yield. The n.m.r. spectrum ( $CCl_4$ )

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