[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

Fluorocarbon Nitrogen Compounds. V.[1] Nitrogen Trifluoride as a Reagent in Fluorocarbon Chemistry[2,3]

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The reaction of NF_3 in a hot tube with $CF_3CF{=}CF_2$ and with CF_3CN has been investigated. At 520° with C_3F_6 over NaF, NF_3 reacts as a fluorinating agent to give mainly iso-C_3- to C_6- fluorocarbons and fluorocarbon imines. Substitution of CsF for NaF allows reaction between the same reagents to proceed at 320°, in which case little cleavage occurs, very little C_3F_8 is formed, and reaction apparently takes place mainly by radical coupling, the major identified products being $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFNF_2$ and $(CF_3)_2C{=}NF$. In the reaction between CF_3CN and NF_3 over CsF at 520° only destructive fluorination is observed, CF_3NF_2, $(CF_3)_2NF$, $CF_3N{=}CF_2$ and $(CNF)_3$ being formed.

The few reports in the literature concerning NF_3 have indicated only its reaction with elements or simple compounds[5] and its recent use in the synthesis of other nitrogen fluorides.[6] The present work describes its reaction with $CF_3CF{=}CF_2$ and CF_3CN at 520°, in which NF_3 acts primarily as a fluorinating agent, and its reaction with C_3F_6 over CsF at 320°, in which NF_3 serves to introduce $=NF$ and $-NF_2$ groups into the fluorocarbon structures.

Under flow conditions in a nickel tube over NaF, no appreciable reaction between NF_3 and C_3F_6 was found below 450°. At 520°, with an estimated residence time of 103 sec., 87% of the C_3F_6 was converted to products in the relative mole ratios shown in Table I.

TABLE I

REACTION PRODUCTS OF C_3F_6 AND NF_3 AT 520°

Compound	Mole ratio in prod. (relative)	Compound	Mole ratio in prod. (relative)
$CF_3N{=}CF_2$	2.7	$(CF_3)_2CFCF_3$	3.1
$CF_3CF{=}NCF_3$	4.1	$(CF_3)_2CFCF_2CF_3$	2.5
$CF_3CF_2CF_3$	10.0	$(CF_3)_2CFCF_2CF_2CF_3$	1.4
$(CF_3)_2C{=}CF_2$	2.8	$(CF_3)_2CFCF(CF_3)_2$	1.0

These products were generally similar in nature to those obtained in high temperature vapor phase fluorination reactions,[7] and demonstrated the occurrence of the customarily observed processes—cleavage, alkylation and introduction of fluorine—which take place under these conditions. The predominance of the iso-alkane structure indicated that the initial attack had occurred on the CF_2 group of $CF_3CF{=}CF_2$, the resulting perfluoroisopropyl radical undergoing further reaction mainly by accepting fluorine to form $CF_3CF_2CF_3$ or by coupling with other radicals created by cleavage. The isohexane may have formed *via* radical addition of $(CF_3)_2CF\cdot$ to $CF_3CF{=}CF_2$; the absence of other compounds containing a normal chain permits the inference that the fluorocarbons were formed mainly by coupling and not by radical addition to the terminal carbon of the double bond. The formation of imines would seem to involve a nitrogen-containing free radical, but the nature of such a species and process is not clear.

Substitution of CsF as a catalyst[8] for NaF enabled the reaction to proceed at 320° with about the same residence time, the 200° temperature decrease permitting a much milder reaction and consequent retention in the products of a substantial percentage of the N–F bonds. The products and their relative mole ratios are given in Table II.

TABLE II

REACTION PRODUCTS OF C_3F_6 AND NF_3 AT 320°

Compound	Mole ratio in prod. (relative)	Compound	Mole ratio in prod. (relative)
$(CF_3)_2CFNF_2$	2.5	C_4F_9N	1.0
$(CF_3)_2C{=}NF$	3.0	C_3F_8	<1.0
$(CF_3)_2CFCF(CF_3)_2$	2.0	C_6F_{12}	2.0

It can be seen readily from the decreased amount of fluorocarbons smaller than C_6 that fragmentation was much reduced at the lower temperature. The surprising and virtually complete absence of C_3F_8 would seem to indicate that the intermediate $(CF_3)_2CF\cdot$ radicals coupled almost entirely with each other or with $NF_2\cdot$ radicals to form $(CF_3)_2CFCF(CF_3)_2$ and $(CF_3)_2CFNF_2$, respectively. Such an increased incidence of radical coupling with milder reaction conditions has been found in other investigations.[9] The three major products may have been formed by the sequence

$$CF_3CF{=}CF_2 + NF_3 \xrightarrow{CsF} (CF_3)_2CF\cdot + NF_2\cdot \quad (1)$$

$$(CF_3)_2CF\cdot + NF_2\cdot \longrightarrow (CF_3)_2CFNF_2 \quad (2)$$

$$2(CF_3)_2CF\cdot \longrightarrow (CF_3)_2CFCF(CF_3)_2 \quad (3)$$

$$(CF_3)_2CFNF_2 \xrightarrow{-2F} (CF_3)_2C{=}NF \quad (4)$$

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[1] For previous paper in this series see J. A. Young, W. S. Durrell and R. D. Dresdner, THIS JOURNAL, **81**, 1587 (1959).

[2] Presented in part before the Southeastern Regional Meeting, A.C.S., Gainesville, Fla., December 13, 1958.

[3] This work was supported by the Chemistry Branch, Office of Naval Research, and reproduction of all or any part of this paper is permitted for purposes of the United States Government.

[4] This paper includes work done by F. N. Tlumac submitted in partial fulfillment of the requirements for the M.S. degree, University of Florida.

[5] (a) O. Ruff and H. Wallauer, *Z. anorg. allgem. Chem.*, **196**, 421 (1931); (b) O. Ruff, *ibid.*, **197**, 273 (1931).

[6] (a) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1957); (b) C. B. Colburn, F. Johnson, A. Kennedy, K. McCollum, L. Metzger and C. Parker, *ibid.*, **81**, 6397 (1959).

[7] (a) J. A. Gervasi, M. Brown and L. A. Bigelow, *ibid.*, **78**, 1679 (1956); (b) E. H. Hadley and L. A. Bigelow, *ibid.*, **63**, 3302 (1940); (c) J. A. Attaway, R. H. Groth and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

[8] (a) W. H. Christie and J. A. Wethington, Abstracts, Southeastern Regional Meeting, A. C. S., Durham, N. C., November 14–16, 1957; (b) W. H. Christie, Doctoral Dissertation, University of Florida, 1958.

[9] (a) W. T. Miller and S. D. Koch, Jr., THIS JOURNAL, **79**, 3884 (1957); (b) J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **82**, 4553 (1960).

Loss of fluorine from the structure =CF–NF–, shown in eq. 4, has been shown by Bigelow to occur when $(CF_3)_2NF$ is passed through a hot metal tube.[7c]

For the reaction of CF_3CN with NF_3, a temperature of 520° was found necessary even when CsF was used. The products identified are shown in Table III.

TABLE III

Compound	Mole ratio in prod. (relative)
CF_3NF_2	2.2
$CF_3N{=}CF_2$	1.3
$(CF_3)_2NF$	1.0
$(CNF)_3$	1.4
CF_4	1.9

Since both reactants contain nitrogen, it was impossible to tell from the results whether the =NF and —NF_2 compounds were formed by coupling or by exhaustive fluorination of the nitrile group. At the high temperature used, the latter process appears more probable, particularly since conditions were so severe that no carbon–carbon bonds remained intact, no indications of $CF_3CF_2NF_2$ or C_3F_6 being found.

Experimental

Materials.—The NF_3 was prepared by the electrochemical process.[10] The crude NF_3, collected in liquid-air cooled traps, was purified by consecutive scrubbing with concentrated base and buffered aqueous KI until no test for OF_2 was observed even with starch, then dried over P_2O_5 and degassed until the material had a permanent vapor pressure of less than 1 mm. at liquid air temperature. Finally the purified material, mol. wt. 70.5–71.5, was analyzed by vapor phase chromatography and a purity of not less than 99% by wt. was indicated. The infrared spectrum agreed with that in the literature.[11]

Perfluoropropene was prepared by the pyrolysis of the sodium salt of perfluorobutyric acid,[12] the dissolved CO_2 being removed by passing the gas through strong alkali. The final product was 99% pure by chromatographic analysis.

Trifluoroacetonitrile was purchased from Penninsular ChemResearch, Gainesville, Fla., and refractionated before use.

Cesium fluoride was obtained from A. D. Mackay, New York, N. Y., and the NaF pellets from Harshaw Chemical Co., Cleveland, O.

Nuclear magnetic resonance spectra were made with a Varian Associates instrument operating at 40.0 mc. and utilizing an external standard of CF_3COOH for the determination of chemical shifts. The values are reported in parts per million (p.p.m.), negative values for low field. Infrared spectra were run on a Perkin–Elmer double beam instrument using a 5-cm. gas cell with NaCl windows. The one mass spectrogram was obtained on a model 620 Consolidated mass spectrometer.

Chromatographic analyses were performed with a model 154 Perkin–Elmer vapor fractometer, utilizing both fluorocarbon and hydrocarbon type stationary phases.[13] The preparative scale separations were done on a larger unit using 1″ o.d. tubes 2 meters long and packed with hexadecane on acid-washed Celite.[14]

Procedure.—Perfluoropropylene and NF_3 were allowed to escape from their respective cylinders through needle valves, metered through two capillary flow meters, and then passed through two concentric tubes extending into the reactor, which was a 12″ × 1″ i.d. nickel tube packed with sodium fluoride pellets or CsF powder and having a free volume of about 30 cc. As the products left the reactor, which was heated by a Hoskins furnace, they were collected in consecutive traps cooled by Dry Ice–acetone and liquid air. The exit of the second trap was protected by a drying tube and a counter flow of dry nitrogen to prevent air or water vapor from diffusing into the system. Very stringent precautions were taken to keep the packing from absorbing water, but even when the CsF was dried *in vacuo* at 500° blue products sometimes resulted whose formation was ascribed to traces of water or air. Only when the products were water-white were they examined further. The temperature was measured by a thermocouple in the center of the heated zone.

Mixing of C_3F_6 and NF_3 before admission to the heated zone resulted in a number of explosions. These were initially ascribed to impurities such as OF_2, H_2O, air or C_3F_7H, but they persisted even after every precaution was taken, and finally were prevented only by modifying the reactor as described above, so that the gases were not mixed until they had entered the hot part of the tube. Both starting materials invariably were present in the exit stream but no explosions ever occurred beyond the reaction zone. A number of small scanning trials were made, but only the two large scale runs made under optimum conditions are reported here.

Reaction of NF_3 with C_3F_6 over NaF.—One hundred and seventy-eight grams (1.19 moles) of C_3F_6 and 60 g. (0.85 mole) of NF_3 were fed into the system over 49 hours, equivalent to a flow rate of 0.024 mole/hr. olefin and 0.017 mole/hr. NF_3. The estimated residence time in the heated zone was 103 seconds. At the conclusion of this experiment 211 g. of material had collected in the Dry Ice cooled trap and 19 g. in the liquid air cooled trap.

The liquid air condensate was found to have a mol. wt. range of 80 to 100. Successive infrared spectra indicated that the most volatile fractions were mostly CF_4 and NF_3, while later fractions contained CF_4, some C_2F_6, and very little else.

The Dry Ice condensate was fractionated carefully. There was a forecut of 11 g. and then three fractions between −40.0° and −35.2°, all three fractions showing a weak infrared absorption at 5.54 μ. Bromination had no effect on the impurity responsible for this absorption, but it was removed successfully by treatment with aqueous alkali. Similar treatment of the combined fractions raised their average mol. wt. from 162 to 188, the material then having a chromatographic purity of at least 98% and giving an infrared spectrum identical with that of C_3F_8. Some 40 g. of the original 50 g. were thus recovered. It is probable that the impurity which was removed by base was $CF_3N{=}CF_2$, mol. wt. 133, b.p. −33°, for which the C=N infrared assignment is known to be 5.53 μ.

A fourth fraction isolated between −29 and −28.3° and amounting to 17 g. was identified as unreacted C_3F_6.

A fifth fraction, which was collected at −13.0° to −12.1°, had a constant mol. wt. of 183 and amounted to 21.0 g. This material showed a chromatography purity of 99%, gave an infrared absorption at 5.57 μ, and had the characteristic acrid smell of fluorocarbon imines. Basic hydrolysis of the material at room temperature was extremely slow; however, at 100° in a sealed tube with aqueous NaOH, ammonia was evolved quantitatively in accord with the formula C_3F_7N, calcd. mol. wt. 183. Its infrared spectrum did not agree with that of $CF_3CF_2N{=}CF_2$, nor did it hydrolyze as readily as this reported isomer.[15] The mol. wt. of 183, the slow hydrolysis to give NH_3, and the infrared peak at 5.57 μ all indicate that this compound was $CF_3CF{=}NCF_3$. The n.m.r. spectrum had gross peaks at values of −44.1, singlet (CF); −19.6, complex $(CF)_3$; and −4.5, complex (CF_3).

Anal. Calcd. for C_3F_7N: N, 7.65. Found: N, 7.61, 7.62.

The sixth and seventh fractions, isolated between −5.1° to −1.1° and −1.1° to 1.0°, had average mol. wts. of 223 and 231, and amounted to 12 and 25 g., respectively. Their infrared spectra manifested all the lines attributable to a mixture of $(CF_3)_2CFCF_3$ and $(CF_3)_2C{=}CF_2$. Chromatograms showed essentially only two components, whose area ratios showed them to be present in the same amounts by

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[10] J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

[11] J. H. Simons, editor, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., p. 498.

[12] J. D. LaZerte, L. T. Hals, T. S. Reid and G. H. Smith, THIS JOURNAL, **75**, 4525 (1953).

[13] T. M. Reed, *Anal. Chem.*, **30**, 221 (1958).

[14] T. M. Reed, J. F. Walter, R. R. Cecil and R. D. Dresdner, *Ind. Eng. Chem.*, **51**, 271 (1959).

[15] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3416 (1956).

weight as was calculated from their mol. wt. data. The olefin was not affected by bromination nor hydrolysis but was removed quantitatively either by alcoholysis or by reaction with HF, leaving in each case a chromatographically pure sample, mol. wt. 238. The infrared spectrum[16] of the purified material agreed with that from iso-C_4F_{10}, calcd. mol. wt. 238, known boiling point 1.0°.

An eighth fraction, 22 g., was isolated between 27.4° and 30.4°. It was far from a pure substance. The presence of both C≡N and C=N unsaturation was shown in the infrared spectrum, and ammonia was evolved on hydrolysis. Attempts to isolate the nitrogen compounds being unsuccessful, the fraction was subjected to strong basic hydrolysis and the remaining material, 96% pure chromatographically, was found to have a mol. wt. of 289. Its $n^{15}\text{D}$ was 1.2472, compared to 1.2475 for perfluoroisopentane reported by Rohrbach and Cady.[17]

The n.m.r. spectrum showed peaks at δ-values of −3 $(CF)_3$, 6 $(CF)_3$, 42 $(CF)_2$ and 109 (CF). Very small peaks at values of −12 and +52 were observed and probably came from isomeric impurities.

A final fraction was isolated between 53.5° and 58.5°, weighing 25 g. and having mol. wts. between 334 and 338. The mixture contained an insoluble subliming solid, in amounts too small to identify, which was removed by streaming the vapor past a Dry Ice cooled cold finger at reduced pressure, leaving a liquid that was clear even at −20°. Traces of unsaturated material, detected by infrared analysis, were removed by reaction with bromine. The purified residue, weighing 23 g., had mol. wt. 338, but chromatographic analysis on hexadecane showed two well defined peaks. By preparative scale chromatography this material was separated into two pure fractions, each having a mol. wt. of 338. The boiling point, 58.0°, and the refractive index, $n^{22}\text{D}$ 1.2560, of one fraction agreed with the properties of perfluoroisohexane reported by Rohrbach and Cady[15]; b.p. 57.4, $n^{22}\text{D}$ 1.2564. In this case the n.m.r. data were conclusive, giving δ-values of −3.5 (CF_3C), 4.5 $(CF)_3$, 38 $(CF)_2$, 47 $(CF)_2$ and 108 (CF), with area ratios of 6:3:2:2:1. The other chromatographic fraction, which was a solid at −80, amounted to a third of the original purified mixture, had the longer appearance time on the chromatographic column, was identified by a comparison infrared spectrum of the sample of $(CF_3)_2CFCF(CF_3)_2$ obtained in the catalytic reaction described below.

Reaction of NF_3 with C_3F_6 over CsF.—Eighty-eight grams (0.59 mole) of C_3F_6 was treated with 36 g. (0.51 mole) of NF_3 at 320° over a 46-hour period, with a residence time of about 135 sec. The catalyst was an anhydrous powder and every precaution was taken to keep it dry at all times. The liquid air condensate resulting from the reaction consisted essentially of 27 g. of unreacted NF_3, while the Dry Ice condensate, 97 g., was found during the subsequent fractionation to contain 42 g. of unreacted C_3F_6, b.p. −30 to −28°, mol. wt. 149. Unreacted C_3F_6 also was found in the fractions preceding and following this cut, but no measurable amount of pure C_3F_8 was detected.

The most volatile reaction product was found to boil at −13.0° to −11.7°, weighed 8 g., and had a mol. wt. of 182, a center fraction showing a chromatographic purity of 99% based on the major peak. Since it gave no infrared absorption below 6 μ, was not attacked readily by dilute alkali at room temperature, but did give a positive test for N–F with iodide, it was thought to be a C_3F_7N isomer containing no C=N—C unsaturation, possibly $CF_3CF_2CF{=}NF$, $(CF_3)_2C{=}NF$, or c-$(CF_2)_3NF$. The most probable structure $(CF_3)_2C{=}NF$ was indicated by a mass spectrogram which showed peaks only for masses 33 (NF), 69 (CF_3) and the parent peak. An infrared band at 6.05 μ could be assigned to C=NF. The n.m.r. spectrum showed four peaks at δ-values of 123 (NF), 12, 11.3, 8.3 and 1.0 with area ratios of approximately 1:2:2:5:1. No adequate explanation of this spectrum can be offered at this time.

Anal. Calcd. for C_3F_7N: C, 19.7; F, 72.8; mol. wt., 183. Found: C, 20.0; F, 72.9; mol. wt., 182.

A second fraction, weighing 7 g., was collected at −2.0° to 1.0°. Its purity was 97% and its mol. wt. 220, consistent with a formula C_3F_9N. A positive N–F test was obtained with KI. The n.m.r. data were in accord with the structure $(CF_3)_2CFNF_2$, with δ-values of 95 (CF), 0.3 (CF_3) and −97 (NF_2), and area ratios of 1:6:2, respectively. These figures eliminate from consideration the known compound $CF_3CF_2CF_2NF_2$.[18] An infrared spectrum showed that an impurity in the sample was probably perfluoroisobutene.

Anal. Calcd. for C_3F_9N: C, 16.3; F, 77.4; mol. wt., 221. Found: C, 16.8; F, 76.9; mol. wt., 220.

A third fraction, weighing 3 g. and boiling at 23.5–25.0°, had a mol. wt. of 233–234 but was only 91% pure by chromatographic estimates. It gave a positive N–F test but was not attacked under severe basic hydrolysis conditions, while its infrared spectrum showed a line at 5.54 μ, indicative of some sort of C=C or C=N unsaturation, but probably not of an imine nature in view of its resistance to hydrolysis. The elementary analysis figures were close to those necessitated by the formula derived from the mol. wt. C_4F_9N, but neither they nor the n.m.r. spectrum were sufficiently conclusive as to permit establishing a structure for this compound.

A fourth fraction was isolated which boiled between 52° and 54°, weighed 8 g., and had a $n^{25}\text{D}$ 1.2631. The mol. wt. of 298, obtained on material that was 94% pure chromatographically, corresponded to that of a C_6-olefin, and its infrared spectrum with a peak at 5.89 μ indicated that the unsaturation was not terminal. The n.m.r. of a center fraction that was 97% pure showed three peaks in the CF_3-region, −9.6, −9.0 and −5.0, one peak in the C–CF_2–C region, 40, and one peak at 6.2, indicative of a trifluoromethyl-2-pentane structure such as $CF_3CF{=}C(CF_3)CF_2CF_3$ or $(CF_3)_2C{=}CFCF_2CF_3$.

Anal. Calcd. for C_6H_{12}: F, 76.0; mol. wt., 300. Found: F, 75.6; mol. wt., 298

A final fraction was collected at 57–58°, weighed 8.5 g., had a mol. wt. of 338, and showed chromatographic purity of 96%. A refractionated sample of 98% purity had a $n^{22}\text{D}$ 1.2640, and melted at −27.7° to −27.0°. A n.m.r. analysis showed only two peaks, at −5.9 (CF_3) and 108 (CF), with area ratios very close to 6:1. These data, along with the analysis figures, conclusively establish the structure as $(CF_3)_2CFCF(CF_3)_2$.

Anal. Calcd. for C_6F_{14}: F, 78.7; C, 21.3; mol. wt., 338. Found: F, 78.8; C, 21.5; mol. wt., 338.

Reaction of CF_3CN with NF_3.—Two trials were made of this reaction, both giving essentially the results described. Twenty-two grams (0.31 mole) of NF_3 and 20 g. (0.21 mole) of CF_3CN were allowed to react over CsF at 520°, with a flow rate of 3.1 g./hr. of the mixture. The liquid air condensate from the reaction weighed 12 g. and the Dry Ice condensate 30 g.

Fractionation of the Dry Ice condensate gave 7 g. overhead (Dry Ice–acetone-cooled head) which was subsequently found to boil at −74°. The crude overhead showed an infrared band in the C≡N region; after this impurity had been removed by scrubbing with strong alkali the purified product of 96% main component on chromatographic analysis had a mol. wt. of 120–122, a b.p. of −74°, and gave a positive test for N–F with KI solution. The main impurity was believed to be CF_4. The boiling point of CF_3NF_2 is −74°[19] and its mol. wt. is 121.

A second fraction, 9 g., mol. wt. 157–159, was obtained at −40° to −35°. A chromatogram showed only two peaks, the material causing at least one of these apparently being unsaturated, since a strong line in the infrared spectrum was obtained at 5.55 μ. The unsaturated material was removed by scrubbing with aqueous alkali, the evolution of ammonia indicating that the unsaturation was of the imine type. The dried residue, mol. wt. 169–711, showed no residual unsaturation, gave a single chromatographic peak, and a positive test for N–F with KI solution. Its infrared and n.m.r. spectra agreed in all detail with the known spectra of $(CF_3)_2NF$.[20]

A third fraction, boiling point −33° to −30°, exhibited the same type of behavior as the previous fraction. Of the initial 5 g., mol. wt. 154–157, 2 g. remained after treatment with base, this remainder being identified in a similar manner

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(16) Reference 11, p. 469.

(17) A. H. Rohrbach and G. H. Cady, 114th Meeting, A. C. S., Div. Phys. and Inorg. Chem., Portland, Ore., 1948.

(18) N. Muller, P. D. Lauterbur and C. F. Svatos, THIS JOURNAL, **79**, 1807 (1957).

(19) (a) R. N. Haszeldine, *J. Chem. Soc.*, 3037 (1950); (b) G. E. Coates, J. Harris and T. J. Sutcliffe, *ibid.*, 2762 (1951).

(20) J. A. Young, W. S. Durrell and R. D. Dresdner, THIS JOURNAL, **81**, 1587 (1959).

as $(CF_3)_2NF$. It would seem from the boiling points, the infrared peak at 5.55 μ, the mol. wt. and the formation of ammonia on hydrolysis that the second component of these two fractions was $CF_3N{=}CF_2$, b.p. −33°, mol. wt. 133.

Distillation of the pot residue, 8 g., gave a major fraction boiling at 73.5–74.0° which had a mol. wt. of 135–137, melted at −40° to −38°, and reacted with water to give insoluble cyanuric acid. Reported[21] values for $(CNF)_3$ are m.p. −38°, b.p. 74°. The liquid air condensate, 12 g., had a mol. wt. of 88–115. Neither the mol. wt. range or the infrared spectrum was substantially modified by passage of the material through aqueous base. The spectrum showed weak evidence for NF_3 and strong indications of both CF_3NF_2 and CF_4.

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[21] A. F. Maxwell, J. S. Fry and L. A. Bigelow, THIS JOURNAL, **80**, 548 (1958).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, IND., AND OF SAINT LOUIS UNIVERSITY, ST. LOUIS, MO.]

Solvents of Low Nucleophilicity. I. Reactions of Hexyl Tosylates and Hexenes in Trifluoroacetic Acid and Other Acids[1]

BY PAUL E. PETERSON[2]

RECEIVED MARCH 24, 1960

The solvolysis of 2-hexyl tosylate in trifluoroacetic acid containing sodium trifluoroacetate occurred at approximately four times the rate of the solvolysis in formic acid, which has been regarded as the best ionizing solvent suitable for solvolysis studies. The substitution product from solvolysis in trifluoroacetic acid contained about 20% of 3-hexyl trifluoroacetate, the product which may arise *via* hydride shift, in addition to 2-hexyl trifluoroacetate. The substitution product from formic acid solvolysis, sometimes regarded as the best rearranging solvent, contained about 6% of 3-hexyl formate. Trifluoroacetic acid added readily to hexenes at 25°, yielding trifluoroacetates. Pyridine was found to be a suitable solvent for acylation of alcohols with trifluoroacetic anhydride.

Solvolysis reactions of the type thought to proceed *via* intermediate carbonium ions or their equivalent have been carried out in a variety of solvents, of which aqueous alcohol or aqueous dioxane, acetic acid and formic acid are perhaps the most important. Recently trifluoroacetic acid has been employed for some solvolyses of cyclooctane derivatives, and in each case the solvolysis products were quite unlike the products from solvolysis of the same starting materials in acetic acid. Thus solvolysis of cycloöctene oxide in trifluoroacetic acid gave exclusively products arising *via* a transannular hydrogen shift, while solvolysis with acetic acid containing sodium acetate gave 76% of normal products and only 24% of products arising *via* hydride shift.[3] In another study[4] the products obtained from solvolysis of 4-cycloöcten-1-yl brosylate in trifluoroacetic acid contained 31% of a product arising *via* a carbon shift and 12% of a product arising *via* an apparent hydrogen shift. Solvolysis of the same compound in acetic acid yielded no detectable products arising *via* carbon or hydrogen shift.[5] The reactions just mentioned are illustrations of the fact that although simple carbonium ion theory frequently can account adequately for products of reactions, the theory frequently does not allow prediction of the products.

Since the interpretation of the solvolysis reactions mentioned above is complicated by the proximity effects which may influence the reactions of cycloöctane derivatives, it was of interest to determine whether there are any unusual effects associated with carbonium ion reactions of simpler molecules in trifluoroacetic acid. The present work reports such a study involving reactions of the hexenes and derivatives of 2-hexanol and 3-hexanol. The choice of this system was determined in part by the fact that both the hexanols and the hexenes are well suited for gas chromatographic analysis.[6] In addition the system is well suited for the study of hydride shifts which may occur during carbonium ion reactions. The large percentage of hydrogen and carbon shift is the most striking common feature of the previously mentioned solvolysis reactions in trifluoroacetic acid. The equation (in Fig. 1) for solvolysis of 2-hexyl toluenesulfonate (2-hexyl tosylate), whose solvolysis is reported here, illustrates the pos-

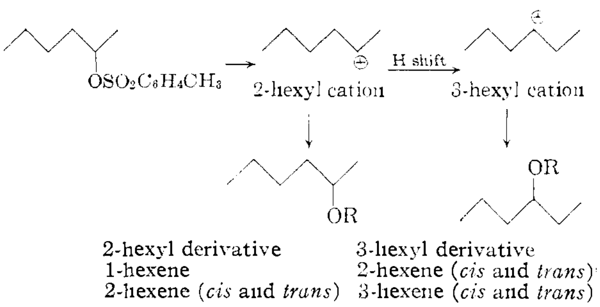

Fig. 1.

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