The pyrolysis of IX at 650–700° gave small amounts of perfluorooöctane, perfluoroheptane and perfluorohexane with extensive decomposition of the starting material. Recent reports[6,18] on the pyrolysis of similar compounds under less drastic conditions demonstrated the possible free radical nature of these reactions.

The reaction of X with aluminum chloride was violent and could not be controlled effectively to obtain sufficient quantities of product for study.

A paper is in preparation by members of the Spectroscopy Group, Physical Measurements Branch, which will contain a more detailed discussion of the infrared spectra of the compounds reported in this paper. A study of the NMR spectra of these compounds was published recently by Muller, *et al.*[19]

**Acknowledgments.**—We are indebted to members of the Analytical Research Branch for the elemental analyses, the Spectroscopy Group for determination of the NMR and infrared spectra and to members of the Physical Measurements Branch for determination of some of the physical constants reported.

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[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

# Fluorocarbon Derivatives. II.[1] Cyclic Nitrides

BY THOMAS C. SIMMONS AND FRIEDRICH W. HOFFMANN[2] WITH R. B. BECK, H. V. HOLLER, T. KATZ, R. J. KOSHAR, E. R. LARSEN, J. E. MULVANEY, K. E. PAULSON, F. E. ROGERS, B. SINGLETON AND R. E. SPARKS

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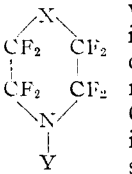
The electrofluorination of some secondary and tertiary cyclic amines in anhydrous hydrogen fluoride by the Simons process[3] was investigated. Pyridine, C-substituted pyridines and morpholine yielded the corresponding fully fluorinated, secondary cyclic nitrides, while N-substituted piperidines and 1-methylmorpholine gave the corresponding tertiary fluorocarbon nitrides. In all cases, considerable amounts of cleavage products also were formed; some of them were isolated in pure state and identified.

## Introduction

The electrofluorination of cyclic amines, such as pyridine, piperidine and 1-alkylpiperidines by the Simons process has been reported to yield the corresponding cyclic fluorocarbon nitrides[4,5]; however, the information given in the literature on this class of compounds is rather scanty.


I

While N-alkyl-substituted piperidines and related compounds, such as N-substituted morpholines, will be converted by electrofluorination in anhydrous hydrogen fluoride to the corresponding, unreactive, cyclic tertiary nitrides (I with X = O or $CF_2$, and Y = $C_nF_{2n+1}$), unsubstituted pyridine, piperidine, morpholine, as well as their C-substituted derivatives, are expected to yield the corresponding secondary cyclic nitrides (I with X = O or $CF_2$, and Y = F). The secondary nitrides, by virtue of their NF group, may possibly undergo chemical reactions allowing thus the introduction of cyclic fluorocarbon nitride groups into other molecules.

Only two secondary cyclic fluorocarbon nitrides appear to have been described in the literature, *i.e.*, perfluoropiperidine, obtained either by electrofluorination of pyridine or piperidine[5] or by fluorination of pyridine with cobaltic fluoride[6] and perfluoro-(2,6-dimethylpiperidine) prepared by Haszeldine[7] from 2,6-dimethylpyridine with cobalt trifluoride.

The purpose of this investigation was to study the general behavior of cyclic amines in the Simons cell and to characterize the resulting electrofluorination products. Pyridine, 4-alkyl-substituted pyridines and morpholine were chosen as starting materials for the preparation of secondary nitrides. N-methylmorpholine and 1,1′-dipiperidylmethane were expected to yield the corresponding tertiary fluorocarbon nitrides. The physical constants and analyses of the purified secondary and tertiary nitrides obtained in this study are listed in Table I.

## Experimental

**Electrochemical Fluorinations.**—With the exception of N-methylmorpholine, which was electrofluorinated in the 10-amp. cell (B), all other runs were performed in the 50-amp. cell (A) in the manner described previously.[1] The experimental conditions for the electrochemical fluorination runs and the major reaction products are listed in Table II. The crude liquid and gaseous products were subjected to the same preliminary purification with alkali or sodium fluoride, as described for the runs using dialkyl sulfides and disulfides[1] as starting materials.

The hydrogen fluoride employed was commercial grade, anhydrous material (Mathieson Chemical Corp. and Pennsylvania Salt Manufacturing Co.) which was distilled and dried electrolytically[1] before use. The organic starting materials were commercial products with the exception of 1,1′-dipiperidylmethane, b.p. 77.0–79.5° (2.6–2.7 mm.), $n^{25}D$ 1.4810, which was prepared by the method of Knoevenagel[8] from piperidine and formaldehyde.

Only the isolation of the major reaction products from the HF-insoluble liquid cell drainings and the cold trap condensates is described in the following for the various runs employing nitrogen-containing heterocyclic compounds as

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[1] Paper I of this series: F. W. Hoffmann and T. C. Simmons with co-workers, THIS JOURNAL, **79**, 3424 (1957).

[2] To whom inquiries about this paper should be directed: Chemical Research Division, Chemical Warfare Labs., Army Chemical Center, Maryland.

(3) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1947).

(4) E. A. Kauck and J. H. Simons, U. S. Patent 2,616,927 (1952).

(5) J. H. Simons, U. S. Patent 2,490,098 (1949).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 1966 (1950).

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TABLE I

FLUOROCARBON DERIVATIVES OBTAINED IN THE SIMONS CELL

| Compound | B.p., °C. | $n^{25}_D$ | $d^{25}_4$ | $MR_D$[a] | $AR_F$[b] | Analyses, %<br>Carbon<br>Calcd. | <br><br>Found | <br>Fluorine<br>Calcd. | <br><br>Found | <br>Nitrogen<br>Calcd. | <br><br>Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Perfluoro- | | | | | | | | | | | |
| -piperidine (II) | 49.5[c] | 1.2752[d,c] | 1.7043[c] | 28.56 | 1.24 | | | 73.84 | 73.6 | 4.95 | 4.92 |
| -dipiperidyl (III) | 72 (51 mm.) | 1.3022 | 1.870[e] | 53.17 | 1.17 | 22.74 | 22.1 | 71.95 | 73.2 | 5.31 | 4.0 |
| -1-methylpiperidine (IV) | 66 | 1.2754[d] | 1.7426 | 32.86 | 1.19 | 21.64 | 21.3 | 74.16 | 73.2 | 4.21 | 3.7 |
| -4-propylpiperidine (V) | 123.5 | 1.2965 | 1.8395 | 43.55 | 1.26 | 22.19 | 22.2 | 74.58 | 74.5 | 3.24 | 3.2 |
| -3-ethylhexane (VI) | 103 | 1.2744 | 1.809[e] | 41.67 | 1.24 | 21.93 | 22.2 | 78.07 | 78.1 | | |
| -4-isopropylpiperidine (VII) | 124.5 | 1.3010[d] | 1.8461 | 43.74 | 1.27 | 22.19 | 22.5 | 74.58 | 74.5 | 3.24 | 3.3 |
| -morpholine (VIII) | 15 (356 mm.) | | | | | 19.29 | 19.1 | 68.67 | 67.8 | 5.62 | 5.2 |
| -1-methylmorpholine (IX) | 51 | 1.2659 | 1.700[e] | 29.43 | 1.17 | 20.08 | 20.1 | 69.89 | 69.8 | 4.68 | 3.9 |

[a] Calcd. by the Lorentz–Lorenz equation. [b] The $AR_F$ values were calculated using the following atomic refractions: C, 2.42; N, 2.84; –O, 1.64. [c] B.p. 49–50°, $n^{25}_D$ 1.279, $d^{25}_4$ 1.738[6]; b.p. 48°, $n^{20}_D$ 1.281, $d^{20}$ 1.744.[5] [d] $n^{20}_D$. [e] $d^{25}_{25}$.

TABLE II

EXPERIMENTAL CONDITIONS OF ELECTROCHEMICAL FLUORINATION RUNS AND PRODUCTS OBTAINED

| Organic starting material | Amount used, g. | Concn. in HF, mole % | Volt | Amp. (av.) | Faradays | Products[a]<br>Compound | <br>g. |
|---|---|---|---|---|---|---|---|
| Pyridine (XII) | 2370 | 4.5 | 5.5-5.6 | 26 | 483 | $NF_3$ | 491 |
| | | | | | | II | 888 |
| | | | | | | III | 93 |
| | | | | | | X | 2346 |
| 1,1′-Dipiperidylmethane (XIII) | 1374 | 2.8 | 5.3-5.4 | 22.2 | 235 | $NF_3$ | 260 |
| | | | | | | II | 205 |
| | | | | | | IV | 178 |
| | | | | | | X | 1100 |
| 4-Propylpyridine (XIV) | 1695 | 5.0 | 5.4 | 30.3 | 295 | V | 85.7 |
| | | | | | | VI | 754 |
| 4-Isopropylpyridine (XV) | 1452 | 5.0 | 5.4 | 32.8 | 299 | VII | 260 |
| | | | | | | $C_8F_{18}$ isomers | 582 |
| Morpholine (XVI) | 675 | 3.3 | 5.2 | 29.4 | 80.8 | VIII | 260 |
| | | | | | | XI | 97 |
| N-Methylmorpholine (XVII) | 80 | 2.0 | 5.0-5.1 | 4.2 | 11.4 | IX | 33.7 |

[a] The amounts given are those of crude material.

starting materials. In runs where only portions of some of the cell crudes were worked up, the total weight of product given in Table II was calculated on the basis of the data obtained by processing the aliquots.

**Pyridine XII.**—The electrofluorination of 2370 g. of pyridine (Eastman Kodak, Karl Fischer Reagent) during 508 hr. of operation produced 5799 l. of hydrogen; 548 g. of liquid cell drainings; 3940 g. of Dry Ice–acetone condensate; and 698 g. of liquid nitrogen condensate.

The condensates collected at −78° throughout the run were combined and kept for removal of entrained hydrogen fluoride over sodium fluoride pellets in a refrigerator at about −15°. For distillation, this material was decanted from the sodium fluoride into a precooled round-bottom flask. A portion of 3759 g. was distilled in four batches through a 12-in. vacuum-jacketed column packed with nickel Heli-pak (Podbielniak, Inc.) and the following arbitrary cuts were taken: (1) b.p. up to 45°, 2774 g.; (2) b.p. 45–62°, 674 g.; (3) higher boiling residue, 69 g.

Fraction 1 consisted mainly of perfluoro-*n*-pentane (X). A portion of 681 g. of this fraction was distilled in a low temperature still at 486 mm. and yielded 526 g. of crude X, b. 17–23°, molecular weight 284–293 (calcd. 288). A higher boiling residue (1a) of 68 g. of liquid material remained in the flask; 14% loss during distillation and handling. Careful refractionation of the crude X at 460 mm. pressure gave an analytical sample, b.p. 16°, molecular weight 288 (reported b.p. 29.32°,[9] 29.3°)[10]; this sample melted at −128 to −124° with a plateau at −126 to −125° (reported[9] f.p. −125.65°).

Fraction 2 and the higher boiling residues 3 and 1a were combined (811 g.) and distilled through an 18-in. vacuum-jacketed column packed with nickel Heli-pak to give after 8.2 g. of forerun, b.p. 35–45°, 677.9 g. of crude perfluoropiperidine (II), b. 45–52.5°, and left 78 g. of higher boiling liquid. In an attached Dry Ice–acetone trap was collected 7.2 g. of low boiling material, presumably impure X which was discarded.

Careful refractionation of a 600-g. portion of the crude II through a modified Todd column of approximately 40 plates gave at atmospheric pressure after a small forerun of X and an intermediate fraction (b.p. up to 49.5°) 268.6 g. of pure II, b.p. 49.5–9.9°, $n^{20}_D$ 1.2754–1.2759. Redistillation of a portion of this material furnished an analytical sample, b.p. 49.5°, $n^{20}_D$ 1.2752, $d_{25}$ 1.7043 (reported, b.p. 49–50°, $n^{25}_D$ 1.279, $d_{25}$ 1.738[6]; b.p. 48, $n^{20}_D$ 1.281, $d_{20}$ 1.744[5]).

All the material boiling above 52.5° from the previous rectifications was combined and the mixture (670 g.) was fractionated through the Todd column. A major fraction (306 g.), b.p. 67–71°, $n^{25}_D$ 1.2756–1.2719, exhibited an infrared spectrum indicating the presence of residual hydrogen. This finding and the elemental analysis of the material suggest it to be a mixture of II and isomeric monohydrides of II.

*Anal.* Calcd. for $C_5F_{11}N$: C, 21.21; F, 73.82; N, 4.97. Found: C, 21.2; F, 72.1; N, 5.0. Calcd. for $C_5F_{10}HN$: C, 22.65; F, 71.68; N, 5.28.

Further distillation of the remaining material under reduced pressure yielded a constantly boiling fraction of 93 g. of a colorless, mobile liquid, b.p. 71–72° (51 mm.), which was tentatively identified by its analysis and nuclear magnetic resonance (NMR) spectrum as perfluoro-1,1′-dipiperidyl (III). The analytical sample was taken at 72° (51 mm.).

The liquid nitrogen trap condensate was evaporated and

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(9) J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

(10) L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1950).

the gas passed successively through large drying tubes filled with sodium fluoride pellets and Drierite, respectively. The recondensed gas was then distilled in a low temperature still to yield 491 g. of nitrogen trifluoride contaminated with approximately 5% of carbon tetrafluoride, as determined by mass spectrometric analysis. This material boiled at −128 to −122° and showed a molecular weight range of 70 to 72 (calcd. 71) (reported for $NF_3$,[11] b.p. −129.07°).

1,1′-**Dipiperidylmethane (XIII)**.—This run, performed in Cell A with an electrode pack of alternating iron cathodes and nickel anodes, yielded 130 g. of insoluble cell drainings; 1465 g. of Dry Ice–acetone condensate; and 260 g. of condensate in a liquid nitrogen trap. The latter condensate was screened and found to consist mainly of nitrogen trifluoride, b.p. −129 to −126°, molecular weight 74 (calcd. 71).

Distillation at atmospheric pressure of a portion of 136 g. of the Dry Ice condensate, after passing over sodium fluoride pellets, gave 69.3 g. of X, b. 28–30°, and left 62.1 g. of material boiling above 30°. In an attached cold trap was collected 7 g. of lower boiling material, presumably X, which was discarded. The remainder of the Dry Ice condensate was treated in the same manner. The material boiling above 30°, was combined with the liquid cell drainings and the mixture stabilized in the usual manner with aqueous potassium hydroxide. The dried, crude liquid product (470 g.) was then fractionated at atmospheric pressure to yield 97 g. of a mixture of X and II, b. 32–37.5°; 115 g. of II, b.p. 47.5–51°, $n^{20}_{D}$ 1.2754; 75 g. of a mixture of II and perfluoro-1-methylpiperidine (IV); 143 g. of IV, b. 63–66°, $n^{20}_{D}$ 1.2752–1.2754; and 21 g. residue (4% distillation loss). An analytical sample of IV was taken at 66°, $n^{25}_{D}$ 1.2754, $d_{25}$ 1.7426 (reported[4] 65–65.5° (730 mm.), $n^{24}_{D}$ 1.275, $d_{24}$ 1.760). The identity of IV was confirmed by its NMR spectrum.

**4-*n*-Propylpyridine (XIV)**.—Commercial XIV (Reilly Tar & Chemical Corp.) was fractionated through a 3-ft. heated column packed with glass helices and the fraction b. 185.5–187.5° collected.

The electrofluorination of 1695 g. of XIV in cell A with an electrode pack of alternating nickel anodes and iron cathodes gave 1795 g. of liquid cell drainings, 295 g. of Dry Ice–acetone condensate, and 300 g. of liquid nitrogen condensate. The condensate in the liquid nitrogen trap consisted mainly of nitrogen trifluoride which was identified by its infrared spectrum.[12,13] The material condensed at −78° boiled in the range from −50 to +17° and might have contained $C_3$ and $C_4$ cleavage products; it was not investigated further.

The liquid cell drainings were stabilized in the usual manner and a 1237-g. portion of the dried material (1515 g., 84.4% recovery) was fractionated through the Todd column to give 15 g. of forerun, b.p. 35–58°, and 30 g. of a colorless liquid distillate, b.p. 58–59°, $n^{20}_{D}$ 1.2578, possibly $C_6F_{14}$ (reported for perfluoro-2-methylpentane,[14] b.p. 57.7°, $n^{22}_{D}$ 1.2564). Further fractionation of the remaining crude product gave in addition to several intermediate, unidentified cuts 754 g. of perfluoro-3-ethylhexane (VI), b.p. 102–103°, and 85.7 g. of perfluoro-4-*n*-propylpiperidine (V), b.p. 121–124°; both yields are based on the total amount (1515 g.) of crude stabilized cell drainings.

The NMR spectrum of an analytical sample of VI, b.p. 103.0°, $n^{25}_{D}$ 1.2744, confirmed its identity. A middle cut of V, b.p. 123.5°, was taken for elemental and NMR analysis.

**4-Isopropylpyridine (XV)**.—Commercial XV (Reilly Tar & Chemical Corp.) was used without further purification as starting material in this run which yielded 1980 g. of HF-insoluble liquid product; 282.1 g. of Dry Ice–acetone trap condensate; and 280 g. of material condensed by liquid nitrogen. The condensate collected at −195° was mostly nitrogen trifluoride. No attempt was made to work up the Dry Ice condensate from this run.

A portion of 1538 g. of the crude, liquid cell product was stabilized in the usual manner and the dried recovered material (1378 g., 89.6% recovery) was fractionated at atmospheric pressure to yield the following main fractions: (1) crude perfluoroheptanes, colorless liquid, 74 g., $n^{20}_{D}$ 1.2713; (2) crude VI, 452 g., b. 100–104°, $n^{20}_{D}$ 1.2780; (3) colorless liquid, 305 g., b.p. 109–111°, $n^{20}_{D}$ 1.2880; (4) crude perfluoro-4-isopropylpiperidine (VII), 226 g., b.p. 122–128°, $n^{20}_{D}$ 1.3010; and 108 g. pot residue (4.2% distillation loss). The forerun, several intermediate cuts and the residue were not further investigated.

Fraction 1, which boiled in the range expected for perfluoroheptanes, is possibly a mixture of $C_7F_{16}$ isomers (reported for perfluoro-2,2,3-trimethylbutane,[15] b.p. 82°, $n^{30}_{D}$ 1.2676 with $\Delta n/\Delta t = -0.00045$, $n^{20}_{D}$ 1.2712 calcd.).

The NMR spectrum of fraction 2 showed it to contain the expected perfluoro-2-methyl-3-ethylpentane only as a minor component; the major part of this fraction gave a spectrum identical with that of VI obtained by electrofluorination of XIV. The spectrum was taken on an analytical cut, b.p. 101.5°, $n^{25}_{D}$ 1.2783. The calculated total yield of this material in the crude cell drainings was 582 g.

Fraction 3 could not be identified with certainty. The rather complex NMR spectrum seems to indicate the presence of a compound having the structure $(CF_3)_2CFCF(C_2F_5)CF_2CF_2NF_2$ or $(CF_3)_2CFCF(C_2F_5)CF_2NFCF_3$.

*Anal.* Calcd. for $C_8F_{19}N$: C, 20.4; F, 76.6; N, 2.97. Found: C, 22.1; F, 76.0; N, 1.8.

Analytical sample, b.p. 110°, $n^{20}_{D}$ 1.2885, $n^{25}_{D}$ 1.2864, $d_{25}$ 1.8635, $MR_D$ found 45.26, $AR_F$ 1.22, $MR_D$ calcd. 45.04 (using $AR_F$ 1.22).

Fraction 4 (260 g. total yield) (analytical sample, b.p. 124.5°, $n^{20}_{D}$ 1.3010) was identified by its NMR spectrum as VII.

**Morpholine (XVI)**.—XVI (675 g.) (Eastman Kodak, Yellow Label) yielded 644 g. of condensate in the Dry Ice–acetone cooled trap and 93 g. of material condensed by liquid nitrogen. No HF-insoluble liquid cell drainings were obtained in this run.

The condensate collected at −78° was evaporated from the traps and the gas bubbled through 10% aqueous potassium hydroxide to remove small amounts of acidic impurities. The washed gas was passed successively through small columns of sodium fluoride pellets and granular Drierite, respectively, and recondensed with Dry Ice–acetone. Fractionation of the condensate through a low temperature still gave after a small forerun 96.9 g. of perfluorodiethyl oxide (XI), b.p. 3.0–4.5° (730 mm.) (reported[16] b.p. 1.0°), molecular weight 248 (calcd. 254), which was identified by its NMR spectrum. A subsequent cut, b.p. 4.5–30°, of 100 g. consisted of a mixture of XI and perfluoromorpholine (VIII). Further distillation of the remaining charge yielded 260 g. of a colorless liquid, b.p. 30.3–33.0° (730 mm.), b.p. 17–21° (455 mm.), molecular weight 248–253 (calcd. 249), which was identified by its analysis and NMR spectrum as VIII. No attempt was made to identify the contents of the liquid nitrogen trap.

**1-Methylmorpholine (XVII)**.—XVII (80 g., 0.79 mole) (Eastman Kodak, Yellow Label) yielded 7 g. of HF-insoluble, liquid product and 55 g. of Dry Ice–acetone condensate which was found to boil above room temperature. No liquid nitrogen-cooled trap was attached to the cell in this run.

Fractional distillation of 55 g. of the combined products, after treatment with calcium sulfate and sodium fluoride, through a 25-cm. column packed with nickel Heli-pak gave 33.7 g. perfluoro-1-methylmorpholine (IX), b.p. 50.0–52.0°, $n^{25}_{D}$ 1.2679–1.2659 (analytical sample, b.p. 51.1–51.3°, $n^{25}_{D}$ 1.2659), which was identified by its elemental analysis and NMR spectrum. A small forerun and the column hold-up were not investigated further.

## Summary of Results

The results of the electrochemical fluorination of the cyclic amines were comparable in many respects to those obtained in the electrofluorination of alkyl sulfides. The starting materials formed in the electrolyte colored solutions which exhibited a high degree of conductivity. These amine–hydrogen fluoride solutions showed boiling points considerably higher than anhydrous hydrogen fluoride al-

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lowing, in general, the cell temperatures to rise during the electrolysis to 25–35° and in some cases even to 40° (in the runs with XIV and XV).

The electrofluorination runs gave, with the exception of the run with dipiperidylmethane, the fully fluorinated analogs and in all cases fluorinated cleavage products of the organic starting materials. The electrochemical fluorination of pyridine (XII) yielded, as expected, perfluoropentane (X), nitrogen trifluoride contaminated with about 5% of carbon tetrafluoride and as the main product perfluoropiperidine (II). The formation of perfluoro-1,1'-dipiperidyl (III) from XII is noteworthy. Condensations of this type occur possibly in all electrofluorinations but, in general, the resulting products are not formed in small runs in amounts sufficient for isolation and identification.

The electrofluorination of 4-*n*-propylpyridine (XIV) yielded some of the fully fluorinated analog V which according to its NMR spectrum appeared to be free of isomers. The NMR analysis of the perfluoro-3-ethylhexane (VI) fraction which had been formed in this run by rupture of the two carbon-to-nitrogen bonds indicated the absence of isomers but showed contamination with a small amount of other impurities.

The isomeric 4-isopropylpyridine (XV) gave in an analogous manner perfluoro-4-isopropylpiperidine (VII) which, however, appeared to contain V as a contaminant. The NMR analysis of the cleavage product $C_8F_{18}$ from this run indicated the major component to be VI with some perfluoro-2-methyl-3-ethylpentane, $(CF_3)_2CFCF(C_2F_5)_2$, present as an impurity. A similar conversion of a branched carbon skeleton to a straight chain has been observed in the electrochemical fluorination of *t*-butyl disulfide[1] which yielded as one of the cleavage products a perfluorobutane fraction consisting of approximately 85–90% of perfluoro-*n*-butane and 15–10% of perfluoroisobutane.

The only material which failed to give the perfluorinated analog was dipiperidylmethane (XIII). Only the cleavage products II, IV and X were obtained. It is interesting to note that in this run as well as in the electrofluorination of XIV, where the electrode pack consisted of alternating iron cathodes and nickel anodes, none, or at best only a relatively small yield, of the fully fluorinated analogs was formed. The amount of tarry materials obtained in the cells during these runs was correspondingly large. The electrochemical fluorination of XV employing an all-nickel electrode pack gave a larger yield of perfluorinated analog than the run with XIV using alternating iron and nickel electrodes (260 g. as compared to 85.7 g.). This observation was rather surprising since one might expect the more branched carbon skeleton of XV to be more susceptible to degradation than that of XIV.

The electrofluorination of morpholine (XVI) resulted in a relatively good yield of perfluoromorpholine (VIII) and a considerable amount of perfluorodiethyl oxide (XI) indicating extensive cleavage of the C–N bonds of the starting material. Similar results were obtained with 1-methylmorpholine (XVII) which yielded, as expected, the fully fluorinated analog IX and the cleavage product XI.

A detailed discussion of the NMR and infrared spectra of the various compounds obtained in this study will be published by members of the Spectroscopy Group, Physical Measurements Branch, of these laboratories in a forthcoming paper.

**Acknowledgments.**—We wish to express our appreciation to Dr. R. D. Dresdner of the University of Florida, Gainesville, for his valuable advice in the construction and operation of the electrochemical cells. The authors are also indebted to Mr. C. A. Rush and Mr. J. H. Rothstein for performing the analyses reported in this paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Neighboring Carbon and Hydrogen. XXIX. $\rho$–$\sigma$ Analysis of Acetolysis of Substituted Neophyl Arylsulfonates

BY R. HECK AND S. WINSTEIN

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In acetolysis of neophyl *p*-bromobenzenesulfonate, ionization is exclusively anchimerically assisted, only neighboring phenyl participating. Rates of aryl-assisted ionization of a series of substituted neophyl *p*-bromobenzenesulfonates have been measured and correlated with the aid of the Hammett $\rho$–$\sigma$ relation. Omitting the *p*-MeO group, log *k* of acetolysis is approximately linear in $\sigma$ with a slope $\rho$ of $-3.65$. The value of log *k* for the *p*-MeO substituent falls substantially above the line through the other points. By using $\sigma^+$-values of Brown and Okamoto which reflect a blend of inductive and resonance influences of the substituents more appropriate for an electron-demanding reaction, the *p*-MeO group may be treated along with the other substituents. The slope of the log *k vs.* $\sigma^+$ line is $-2.96$.

In connection with another investigation,[1] it became necessary to prepare *p*-benzhydrylneophyl alcohol (IX). The synthetic route employed involved preparation of the *p*-bromo- and *p*-carbomethoxyneophyl alcohols (III) and (V). Since these were available and the *p*-carbomethoxyneophyl alcohol was converted easily to the *p*-methyl analog, we were prompted to extend the previous study[2] of the effect of substituents on solvolysis rate of neophyl arylsulfonates. The results obtained and their analysis with the aid of Hammett's $\rho$–$\sigma$-relation[3] are given in the present article

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[1] P. Magee, R. Heck and S. Winstein, unpublished work.

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