mixture was brought to pH 1 with 2 *N* H_2SO_4 and the insoluble product was collected by filtration. The filtrate was concentrated *in vacuo* and the residue was dissolved in 40 ml of H_2O and neutralized with 40% NaOH. Chilling gave 2.4 g (82%) of crystals, mp 305-308°. These crystals were purified by dissolving them in 25 ml of H_2O made basic with diethylamine; the solution was treated with charcoal and then neutralized with acetic acid. Chilling gave 1.6 g of a white solid: mp 299-301°; R_f 0.28 (system 2).

Anal. Calcd for $C_{10}H_{13}ClN_2O_4S$: C, 41.03; H, 4.48; N, 9.57. Found: C, 41.10; H, 4.56; N, 9.33.

8-Chloro-10a-methyl-10,10a-dihydro-1H-imidazo[3,4-*b*][1,2]-benzothiazine-1,3(2H)-dione 5,5-Dioxide (5).—A mixture of 11.9 g (0.05 mol) of 4 in 75 ml of $ClSO_3H$ was stirred at 25° for 3 hr. The mixture was added dropwise with stirring to 500 g of ice, and a white solid, mp 143-154°, was collected by filtration. This was immediately added to 150 ml of concentrated NH_4OH, and the mixture was heated on a steam bath for 1 hr. After standing for 18 hr at 25° the pH was brought to 1 with concentrated HCl, and the resulting solid was collected by filtration. This was dissolved in dilute NH_4OH, treated with charcoal, and reprecipitated at pH 1 to give 10.8 g (72%) of product, mp 265-268°. Another base-acid purification gave white crystals: mp 267-269°; R_f 0.71 (system 3); nmr (CF_3COOH), δ 1.92 (S, 3, CH_3), 3.58 (S, 2, $-CH_2-$), 7.56 (m, 2) and 7.93 (d, 1, J = 8 Hz).

Anal. Calcd for $C_{11}H_9ClN_2SO_4$: C, 43.93; H, 3.02; N, 9.32. Found: C, 43.87; H, 3.16; N, 9.15.

6-Chloro-3-methyl-3,4-dihydro-2H-benzothiazine-3-carboxylic Acid 1,1-Dioxide (6).—A stirred mixture of 7.5 g (0.025 mol) of 5 and 39.4 g (0.25 mol) of $Ba(OH)_2 \cdot 8H_2O$ in 150 ml of H_2O was refluxed for 48 hr. After cooling, the pH was adjusted to 1 with concentrated H_2SO_4. The solid was collected and stirred for 30 min with ethanol. Concentration of the ethanol gave an oil which crystallized when triturated with dilute HCl to give 4.4 g of product, mp 127-152°. This was purified by dissolving in dilute NaOH and reprecipitating at pH 1 with dilute HCl. Two such treatments gave 3.7 g (53%) of product: mp 158-160°; R_f 0.72 (system 4).

Anal. Calcd for $C_{10}H_{10}ClNO_4S$: C, 43.56; H, 3.66; N, 5.08. Found: C, 43.80; H, 3.77; N, 4.86.

The nmr peaks (CF_3COOH) for **2,5-dimethylbenzenesulfonamide** were at δ 2.38 (S, 3, 5-CH_3), 2.67 (S, 3,2-CH_3), 7.45 (broad S, 2), and 8.02 (S, 1). The nmr peak for the CH_3 of toluene (CF_3COOH) is at δ 2.30.

Registry No.—**1**, 16793-24-1; **2**, 16793-21-8; **3**, 16793-22-9; **4**, 16793-23-0; **5**, 16793-19-4; **6**, 16793-20-7.

Fluoroalkylpyridines. A Novel Rearrangement

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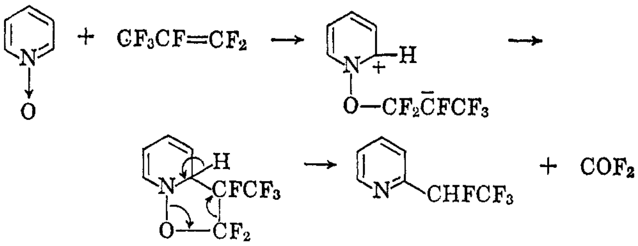
Rearrangements have been shown to occur in pyridine N-oxide chemistry.[1] For instance, pyridine N-oxide and acetic anhydride produced 2-pyridyl acetate, while 2-picoline N-oxide and acetic anhydride yielded 2-pyridylmethyl acetate and 6-methyl-2-pyridinol. Although the reaction of pyridine N-oxide and 2-bromopyridine to give 1-(2-pyridyl)-2-(1H)-pyridone is not a rearrangement, it does show the cyclization that occurs in pyridine N-oxide reactions. Other rearrangements in pyridine N-oxide reactions are also known.[1]

The similarity of pyridine N-oxides to nitrones should also be mentioned because it further supports the intermediates postulated below. For example, nitrones of the 1-pyrroline N-oxide type have been treated with olefinic compounds to form isoxazolidines.[2,3]

The novel rearrangement described below furnishes another preparative method for certain alkylpyridines. Alkylpyridines have been obtained previously in a variety of ways: from natural sources, by cyclizations of N-containing compounds; and by alkylation of the pyridine nucleus. These have been reviewed and have been reported by many investigators.[4-7] Our new method of alkylation produces 2-polyfluoroalkylpyridines. Treatment of pyridine N-oxides with terminally unsaturated perfluoroalkenes has yielded 2-polyfluoroalkylpyridines, probably through rearrangement of a postulated isooxazolidine intermediate. For example, pyridine N-oxide and hexafluoropropylene have yielded 2-(1,2,2,2-tetrafluoroethyl)pyridine. One possible mechanism that can account for the product is represented in Scheme I.

SCHEME I



Carbonyl fluoride was found in the off-gases but not in stoichiometric or large amounts, however. Whether some carbonyl fluoride had reacted to give other products was not investigated. Furthermore, solids were always obtained in the short-path distillation of the crude reaction mixture. These air-sensitive solids, when added to water and worked up, provided additional product. No attempt was made to identify these solids. It was later found that the crude reaction mixture could be added directly to water and the resulting mixture then either steam distilled or extracted with an organic solvent. No other reaction variables were investigated.

Mass spectral and nuclear magnetic resonance (F and H) data are consistent with the structures of the 2-polyfluoroalkylpyridines derived from the N-oxides of pyridine and the three picolines. In the case of the 3-picoline product, nmr data indicate it to be an 80:20 mixture of 2- and 6-substituted 3-picoline, respectively.

Experimental Section

Gases were analyzed on a vapor phase fractometer containing a column of DC 200 on Chromosorb P; liquids were analyzed, identified, and isolated on a column containing SE-30 on Chromosorb W. Only medium and strong absorbance bands are re-

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(1) E. N. Shaw, "The Chemistry of Heterocyclic Compounds, Pyridine and Its Derivatives," Part II, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 4.

(2) G. R. Delpierre and M. Lamchen, *J. Chem. Soc.*, 4693 (1963).

(3) B. G. Murray and A. F. Turner, *ibid.*, *C.*, 1338 (1966).

(4) L. E. Tenenbaum, "The Chemistry of Heterocyclic Compounds, Pyridine and Its Derivatives," Part II, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 5.

(5) D. Bryce-Smith, *et al.*, *Chem. Ind.* (London), 495 (1964).

(6) R. C. Myerly and K. G. Weinberg, *J. Org. Chem.*, **31**, 2008 (1966).

(7) G. J. Janz and A. R. Monahan, *ibid.*, **29**, 569 (1964).

ported from the infrared spectra obtained on an Infracord 337. Nmr spectra were run on chromatographically isolated fractions to which were then added trifluoroacetic acid as external standard for F^{19} spectra and tetramethylsilane in carbon tetrachloride as external reference standard for H^1 spectra.

2-(1,2,2,2-Tetrafluoroethyl)pyridine.—To a 500-ml stainless steel pressure vessel were added 99.7 g (1.05 mol) of pyridine N-oxide and 80 g (0.53 mol) of hexafluoropropylene, and the resulting mixture was heated at 62° for 16.5 hr. Then the gases (5.1 g) were bled off at ambient temperatures to a residual pressure of one atmosphere. The off-gas contained CO_2, COF_2, CF_3CFHCF_3, and a small amount of $CF_3CF{=}CF_2$. The residue (174 g of brown liquid) from the pressure vessel was transferred to a suitable flask and was distilled by short-path distillation at a pot temperature of 25–90° (0.1 mm) to yield 92 g of slightly colored oil. This oil was added to 300 ml of water with stirring. After all the carbon dioxide had evolved, the water layer was made basic (pH 8) with 50% aqueous KOH. The bottom (oil) phase was then separated, the water phase was washed twice with 20-ml portions of methylene chloride, and the organic phases were combined and dried ($MgSO_4$). After the salt was removed by filtration and the solvent removed by flash evaporation under reduced pressure, the remaining liquid was distilled at 142° (ambient pressures) on a spinning-band column to yield 42 g (44% yield based on hexafluoropropylene) of a colorless oil: n^{28}D 1.4109; mol wt (*m/e* found by mass spectroscopy) 179 (calcd 179); infrared spectrum, 1600 (m, doublet), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.75 (doubled doublet, CF_3), 121.6 (doubled quartet, CFH); H^1 spectrum (ppm), 5.41 (doubled quartet, CFH), 6.49–7.27 (complex bands, H_3, H_4, H_5), 8.04 (doublet, H_6).

Anal. Calcd for $C_7H_5F_4N$: C, 46.95; H, 2.81; F, 42.43; N, 7.82. Found: C, 47.08; H, 3.06; F, 42.15; N, 7.56.

6-(1,2,2,2-Tetrafluoroethyl)-2-picoline.—To a 100-ml stainless steel pressure vessel were added 14.5 g (0.14 mol) of 2-picoline N-oxide and 10 g (0.067 mol) of hexafluoropropylene. After the mixture was heated at 68° for 67 hr and then cooled, the gases (4.3 g) were removed and were found to consist mainly of CO_2 and CF_3CFHCF_3. The remaining contents of the pressure vessel were distilled by short-path distillation at a pot temperature of 25–63° (0.01 mm) to give 9.1 g of yellow liquid. Isolation and purification of the product was made by vpc to give a colorless liquid (19% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 154°; n^{25}D 1.4189; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1600 (m doublet), 1275 (s), 1190 (s), 1400 (s); F^{19} nmr spectrum (ppm), 0.68 (doubled doublet, CF_3), 121.1 (doubled quartet, CHF); H^1 spectrum (ppm), 1.88 (singlet, CH_3), 6.41–7.13 (broad lines, H_3, H_4, H_5), 5.32 (doubled doublet, CFH).

Anal. Calcd for $C_8H_7F_4N$: C, 49.75; H, 3.65; F, 39.34; N, 7.25. Found: C, 50.39; H, 4.14; F, 40.00; N, 7.39.

2- and 6-(1,2,2,2-Tetrafluoroethyl)-3-picoline.—To a 100-ml stainless steel vessel were added 21.8 g (0.2 mol) of 3-picoline N-oxide and 15.0 g (0.1 mol) of hexafluoropropylene, and the resulting mixture was heated at 60° for 16.5 hr. The work-up procedure, similar to that used for the 2-picoline N-oxide reaction, gave a colorless oil (36% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 166°; n^{26}D 1.4248; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1610 (s), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.59 (doubled doublet, CF_3), 119.6 (doubled quartet, CFH); H^1 spectrum (ppm), 2-substituted 3-picoline, 1.82 (str doublet, CH_3), 5.56 (doubled quartet, CFH), 6.96, 6.60, 7.91 (H_4, H_5, H_6, respectively) 6-substituted 3-picoline, 1.68 (wk singlet, CH_3), 5.56 (doubled quartet, CFH), 7.87, 6.91, 6.78 (H_2, H_4, H_5, respectively).

Anal. Calcd for $C_8H_7F_4N$: C, 49.75; H, 3.65; F, 39.34; N, 7.25. Found: C, 49.95; H, 4.17; F, 39.94; N, 7.25.

2-(1,2,2,2-Tetrafluoroethyl)-4-picoline.—To a 60-ml stainless steel pressure vessel were added 21.8 g (0.20 mol) of 4-picoline N-oxide and 15.0 g (0.10 mol) of hexafluoropropylene, and the resulting mixture was heated at 47–74° for 17.5 hr. The work-up procedure, similar to that used for the 2-picoline N-oxide reaction, gave a colorless oil (36% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 166°; n^{26}D 1.4248; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1610 (s), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.53 (doubled doublet, CF_3), 121.7 (doubled quartet, CHF); H^1 spectrum (ppm), 1.71 (singlet, CH_3), 6.88, 6.50, 7.88 (H_3, H_5, H_6, respectively, 5.41 (doubled quartet, CHF).

Anal. Calcd for $C_8H_7F_4N$: C, 49.45; H, 3.65; F, 39.34; N, 7.25. Found: C, 50.46; H, 3.86; F, 39.23; N, 7.26.

Miscellaneous.—Short-path distillation of the crude reaction mixture to yield the crude product can be eliminated if the mixture is added directly to water. The procedure can be continued as in the preparation of 2-(1,2,2,2-tetrafluoroethyl)pyridine, or it can be modified to include steam distillation.

Registry No.—2-(1,2,2,2-Tetrafluoroethyl)pyridine, 16876-47-4; 6-(1,2,2,2-tetrafluoroethyl)-2-picoline, 16876-48-5; 6-(1,2,2,2-tetrafluoroethyl)-3-picoline, 16876-49-6; 2-(1,2,2,2-tetrafluoroethyl)-3-picoline, 16876-50-9; 2-(1,2,2,2-tetrafluoroethyl)-4-picoline, 16876-51-0.

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Reaction of Aziridines with Benzoic Anhydride

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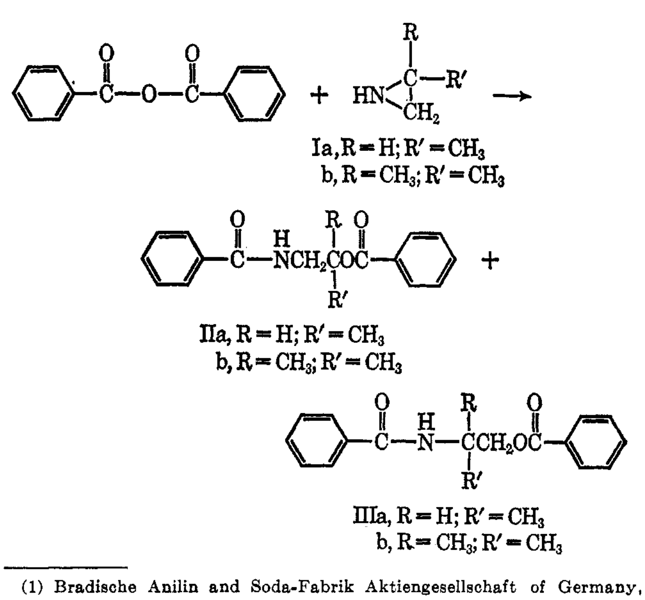
At least two examples of the reaction of anhydrides with aziridines are reported in the patent literature. Ester amides were prepared from N-alkylethylenimines and anhydrides of saturated monocarboxylic acid,[1] while poly(ester amides) were obtained from the reaction of N-alkylethylenimines and phthalic anhydride.[2] In both of these cases, only one isomer is possible through ring opening of the aziridine moiety.

We wish to report on the reactions of 2-methylethylenimine (Ia) and 2,2-dimethylethylenimine (Ib) with benzoic anhydride in acetone or tetrahydrofuran. The quantitative identification of the reaction products from these reactions was accomplished with the aid of



Ia, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

IIa, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

IIIa, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

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[1] Bradische Anilin and Soda-Fabrik Aktiengesellschaft of Germany, British Patent, 784,058 (1957).

[2] Bradische Anilin and Soda-Fabrik Aktiengesellschaft of Germany, British Patent, 784,059 (1957).