For the ethylene chloride run[8,9] a 1:1 complex of aluminum chloride (133 g, 1.0 mol) and acetyl chloride (78.5 g, 1.0 mol) was prepared in 500 ml of ethylene chloride. This solution was added dropwise over 3 hr to a mechanically stirred solution of *o*-xylene (106 g, 1.0 mol) and 750 ml of ethylene chloride in a 3-l., three-necked flask. The reaction mixture was hydrolyzed by pouring it onto a slurry of ice-concentrated hydrochloric acid. The layers were separated. The organic layer was washed with water, 5% sodium bicarbonate solution, and water before being dried over calcium chloride. Rotary evaporation left 140 g (94%) of 3,4-dimethylacetophenone (essentially 100% pure by glpc), bp 100° (5 mm) and $n^{20}{}_{D}$ 1.5385 [lit.[7b] bp 95-97° (4 mm), $n^{20}{}_{D}$ 1.5381].

Ir and nmr analyses were run on the crude reaction products from the runs where glpc showed the presence of only one component. In this manner the products from runs 6, 10, and 11 (Table I) were positively identified as 3,4-dimethylacetophenone, 2,5-dimethylacetophenone, and 2,4-dimethylacetophenone, respectively. The nmr of 3,4-dimethylacetophenone showed a singlet at δ 2.28 (6 H), aromatic methyls; a singlet at 2.44 (3 H), acetyl methyl; a doublet at 7.10 (J = 7.5 cps, 1 H), aromatic hydrogen in the 5 position; a doublet at 7.61 (J = 7.5 cps); and an overlapping singlet at 7.64 (2 H) assigned to the aromatic hydrogen in the 6 position and the aromatic hydrogen in the 2 position, respectively. The nmr of 2,5-dimethylacetophenone showed a singlet at δ 2.22 (3 H), aromatic methyl in the 5 position; a broadened singlet at 2.38 (6 H), aromatic methyl in the 2 position and acetyl methyl; a singlet at 6.99 (2 H), aromatic hydrogens in the 3 and 4 positions; and a singlet at 7.37 (1 H), aromatic hydrogen in the 6 position. The nmr of 2.4-dimethylacetophenone showed a singlet at δ 2.25 (3 H), aromatic methyl in the 4 position, a singlet at 2.40 (3 H), aromatic methyl in the 2 position; a singlet at 2.46 (3 H), acetyl methyl; a broad band at 6.98 (2 H), aromatic hydrogens in the 3 and 5 positions, and a doublet at 7.57 (J = 7.5 cps, 1 H), aromatic hydrogen in the 6 position.

Registry No.—*o*-Xylene, 95-47-6; *n*-xylene, 108-38-3; *p*-xylene, 106-42-3; 3,4-dimethylacetophenone (**1**), 3637-01-2; 2,4-dimethylacetophenone (**2**), 89-74-7; 2,5-dimethylacetophenone, 2142-73-6.

A Facile and Economic Synthesis of Ethanol-OD[1]

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The use of large quantities of deuterium-labeled solvents is often precluded due to economic considerations. In some of our studies we required large quantities of ethanol-OD of high isotopic purity and thus were forced to find a low-cost procedure for its preparation. Previously, the most attractive procedure employed the acid-catalyzed deuterolysis of tetraethylorthocarbonate.[3] The current prohibitively high cost of tetraethylorthocarbonate, and the fact that only 2 moles of product are produced per mole of starting material, precluded the use of this material. Triethylorthocarbonate[4] and diethyl oxalate[5] have been used as starting materials; however, the costs are somewhat greater, and the utilization of starting material is poorer. Aluminum ethoxide[6] has also been employed as a starting material giving excellent yields of product. Aluminum ethoxide is quite expensive; however, it can be synthesized separately.[7] Several exchange procedures have been reported but none are suitable for the preparation of high isotopic purity ethanol-OD.

We have found that the uncatalyzed deuterolysis of tetraethylorthosilicate, followed by distillation of the ethanol-OD from the residual silicon dioxide under reduced pressure, produces 90% yields (based on the availability of all four ethoxyl groups) of ethanol-OD of very high isotopic (no O–H detectable by nmr) and chemical purity (>99.7%). The reaction may be carried out on a multiple mole basis. The cost of the ethanol-OD prepared by this procedure is roughly five cents per gram (based on the cost of the chemicals used) and is *considerably* cheaper than presently commercially available ethanol-OD of lower isotopic purity.

Although we have not extended this procedure to other alkanols-OD, a number of tetraalkylorthosilicates are available thus potentially providing sources of alkanols-OD considerably below current commercial prices.

Experimental Section

Preparation of Ethanol-OD.—The following procedure is typical although the quantities may be increased or decreased. A mixture of 104.2 g (0.5 mole) of tetraethylorthosilicate (Aldrich Chemical Co.) and 40 g (2 moles) of deuterium oxide (99.8%, Diaprep Inc.) is stirred in a stoppered distillation flask at room temperature until a viscous, miscible mixture is obtained (approximately 24 hr). The distillation flask is attached to a distillation head and condenser and subjected to distillation at 2 mm, collecting the product in a flask immersed in a Dry Ice–acetone bath, until no further product is produced. The ethanol-OD (90% average yield) displayed practically no O–H absorption in the infrared spectrum and no detectable OH in the nmr (<0.5%). The gas-liquid partition chromatogram indicated the presence of 0.2% D_2O, the remainder being C_2H_5OD.

Registry No.—Ethanol-OD, 925-93-9.

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[1] Supported by the Petroleum Research Fund of the American Chemical Society, Grant 1225-Al, 3.

[2] Alfred P. Sloan Research Fellow, 1967–1969.

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The Preparation of Fluorodinitroacetonitrile and Fluorodinitroacetamide[1]

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Chlorination of the dinitroacetonitrile anion was found to produce the chloro derivative $ClC(NO_2)_2CN$ in moderate yield.[2] Therefore, it was of interest to determine the course of reaction upon fluorination in aqueous media since it has been suggested that fluorina-

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[2] C. O. Parker, *et al.*, *Tetrahedron*, **17**, 89 (1962).

tion in this media is predominantly electrophilic in nature.[3] Accordingly, aqueous fluorination of sodium dinitroacetonitrile produced fluorodinitroacetonitrile in moderate yield. The reaction proceeded smoothly

$$NaC(NO_2)_2CN + F_2 \longrightarrow FC(NO_2)_2CN + NaF$$

even with fluorine concentrations as high as 50 vol %. The product was removed from the aqueous mixture by an additional helium purge. Pure fluorodinitroacetonitrile is a colorless liquid with bp 74° and fp −13°. The composition of the compound was established by elemental analysis. Table I presents the characteristic infrared absorption bands. The F^{19} nmr spectrum of $FC(NO_2)_2CN$ consists of a singlet at +91.4 ppm *vs.* CCl_3F).

Table I

Infrared Spectrum of $FC(NO_2)_2CN$[a]

Absorption bands, μ
4.40 (m sharp)
6.12 (v s)
7.47 (wk sh)
7.74 (s)
9.20 (m s)
11.83 (m s sharp)
12.59 (s)

[a] Abbreviations are m = medium, v = very, wk = weak, sh = shoulder, and s = strong.

Variation of the fluorine concentration, the reaction temperature and the ratio of reactants employed did not increase the yield of product above 30–35%. Increasing the concentration of $NaC(NO_2)_2CN$ in the reaction mixture resulted in the isolation of substantial amounts of acetonitrile upon fluorination. The formation of acetonitrile is probably a result of attack by the fluorine on oxygen or nitrogen to form unstable intermediates which would hydrolyse in the aqueous media. Possible hydrolysis products such as fluorine nitrate, and nitrate ion, were also found. The amount of acetonitrile in the fluorination product could be suppressed by use of dilute reaction mixtures containing as little as 3% $NaC(NO_2)_2CN$. Another reason for the moderate yield of product was the hydrolysis of $FC(NO_2)_2CN$ to fluorodinitroacetamide.

$$FC(NO_2)_2CN + H_2O \longrightarrow FC(NO_2)_2CONH_2$$

Fluorodinitroacetamide was obtained in quantitative yield by adding the stoichiometric amount of water to a HCl-saturated ether solution of fluorodinitroacetonitrile. The product was isolated by evaporation at 0° and extraction with methylene chloride. Fluorodinitroacetamide formed white feathery crystals, mp 32°. The infrared spectrum of $FC(NO_2)_2CONH_2$ contained peaks not present in the spectrum of the nitrile at 2.90 and 5.75 μ. The compound is soluble in water and attempts to isolate an alkali metal salt of the amide were not successful.

Experimental Section

Materials.—Sodium dinitroacetonitrile was prepared by the literature method.[4] The fluorine was obtained from General Chemical Co. and was used after it was passed through a NaF scrubber.

Fluorodinitroacetonitrile.—A solution of 10 g (65 mmoles) sodium dinitroacetonitrile in 300 ml of water was placed in a 500-ml, four-necked flask equipped with a magnetic stirrer, thermometer, and two gas inlet tubes. After cooling to 0°, a stream of 25% fluorine in helium was introduced at a rate of 1 l./hr. The temperature was maintained at 0° and the fluorination product was swept out of the reaction mixture by an additional stream of helium which was introduced through a gas dispersion tube. The off-gas was passed through four traps at −78° and then vented in order to avoid collecting fluorine nitrate which was sometimes formed. The fluorination was continued until the yellow color in the cyanodinitromethide ion faded away. In order to achieve complete removal of the product from the solution, the helium sweep was maintained for another hour. The combined fractions of all four −78° traps were dried over Drierite and condensed into a −30° trap. Fluorodinitroacetonitrile (2.6 g), mp −13°, was obtained in a 29% yield. Its vapor pressure at 25° was 65 mm.

Anal. Calcd for $C_3FN_3O_4$: C, 16.11; N, 28.19. Found: C, 16.16; N, 28.10.

Fluorodinitroacetamide.—Fluorodinitroacetonitrile (3 g, 20 mmoles) was condensed into a mixture of 30 ml of ether and 0.4 ml of water which had been saturated with hydrogen chloride. The hydrolysis proceeded smoothly on thawing. After standing for 1 hr at room temperature all volatile material was pulled off, keeping the reaction flask in a bath of 20°. The remaining semisolid was dissolved in 15–20 ml of methylene chloride and shaken over BaO to remove excess hydrogen chloride. Crystallization of the product took place when the solution was cooled slowly to −70°. The hygroscopic fluorodinitroacetamide was obtained in a 96% yield. It melted at 32° after sublimation under high vacuum.

Anal. Calcd for $C_2H_2FN_3O_5$: C, 14.38; H, 1.20; N, 25.15. Found: C, 14.91; H, 1.01; N, 24.87.

Registry No.—Fluorodinitroacetonitrile, 15562-09-1; fluorodinitroacetamide, 15562-10-4.

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The Reaction of Asparagine, Glutamine, and Derivatives with Phosgene

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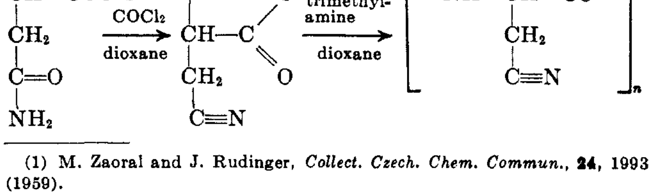
Several methods exist for the conversion of asparagine and glutamine derivatives into their corresponding nitriles.[1–4] An easy and convenient agent for the dehydration of these amino acids has now been found to be phosgene in dioxane. This reaction was discovered subsequent to the attempted preparation of the N-carboxy anhydride of asparagine by the usual procedure of passing phosgene through a dioxane sus-



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