

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_D^{20} 1.5385 [lit.^{7b} bp 95–97° (4 mm), n_D^{20} 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-OD¹

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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. Triethylorthocarbonate⁴ and diethyl oxalate⁵ have been used as starting

materials; however, the costs are somewhat greater, and the utilization of starting material is poorer. Aluminum ethoxide⁶ 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% D₂O, the remainder being C₂H₅OD.

Registry No.—Ethanol-OD, 925-93-9.

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The Preparation of Fluorodinitroacetonitrile and Fluorodinitroacetamide¹

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Chlorination of the dinitroacetonitrile anion was found to produce the chloro derivative ClC(NO₂)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) Alfred P. Sloan Research Fellow, 1967–1969.

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