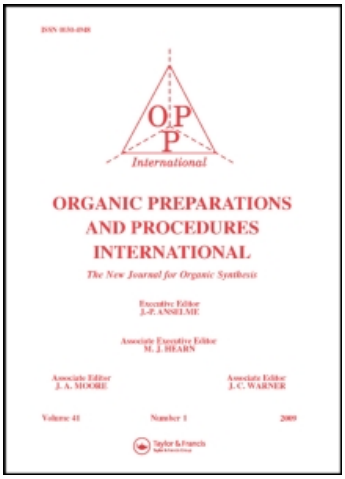

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A NEW, MILD PREPARATION OF 2,4,6-TRINITROFLUOROBENZENE

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We have had a long standing interest in the reactions and mechanisms of reaction of 2,4,6-trinitrophenyl (picryl) derivatives, including picryl ethers, with nucleophiles.[1,2] It has been suggested that picryl ethers are best prepared by reaction of the appropriate alcohol with picryl fluoride, in the presence of 1,4-diazabicyclo[2.2.2]octane, as catalyst.[3] However, the two common methods for preparation of the precursor fluoride have significant drawbacks. Our approach has been to use the versatile fluorinating agent, diethylaminosulfur trifluoride (DAST) to convert pyridinium picrate into picryl fluoride. Since its introduction by Middleton, DAST has been used to convert alcohols,[4]

$$(NO_2)_3C_6H_2O^- \ \overset{+}{H}NC_5H_5 + Et_2NSF_3 \longrightarrow (NO_2)_3C_6H_2F$$

including sterols[5] and carbohydrates,[6] as well as acid chlorides, to the corresponding fluorides.[4] α-Fluorothioethers have been prepared *via* a Pummerer-type rearrangement of sulfoxides.[7,8] However, to the best of our knowledge, DAST has not been used previously in phenolic fluorination. The similarity between the DAST reaction sequence[5-7] and that of $POCl_3$ with pyridinium picrate,[9] which is the standard route for making picryl chloride, led us to attempt this reaction as a new, mild method of preparing picryl fluoride. Low to moderate (20-40% crude) yields were obtained in several experiments from the reaction of DAST with pyridinium picrate, whether the latter was added as an isolated solid or formed *in situ* by addition of pyridine (1 equiv.) to a benzene or toluene solution of picric acid. In contrast to the $POCl_3$ reaction, picric acid reacts with DAST to give the fluoride, albeit in poor yields (<10%). Although the low to moderate yields may be partially due to the insolubility of the picrate in the aromatic solvents, reaction in $CHCl_3$ where the reagents are all soluble, failed to give more than traces of picryl fluoride after workup.

The length of time the reaction mixture is in contact with water during the workup, is critical; the longer the contact, the lower the yield and the worse the quality of the product. This is apparently the result of the great ease of hydrolysis of picryl fluoride and is common also to the other methods of synthesis.

By way of comparison, the halogen exchange between picryl chloride and KF at 185° leads only to partial conversion to the product (ca. 30% crude yield) after 5 hrs; repeated recrystallizations are required to obtain the pure fluoride.[10] The alternate syntheses rely upon various methods of nitration of 2,4-dinitrofluorobenzene.[3,11-13] One nitration method emphasizes the need for careful tempera-

ture control; the nitration is extremely slow below 140° (12-35 hrs), but at temperatures above 150° the reaction can become violent and only picric acid is isolated.[3] Yields from these generally vigorous procedures are typically moderate (purified yields: 43-50%).[3,11-13]

The ease of preparation and the relative speed of the DAST reaction, as well as safety considerations, make the present route an attractive alternative for the preparation of picryl fluoride, especially on a small scale.

EXPERIMENTAL SECTION

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Pyridine (BDH) was refluxed with and freshly distilled from CaH_2 prior to use. Pyridinium picrate was made in quantitative yield from picric acid (Eastman) and pyridine[9] and was thoroughly dried. Proton NMR spectra were recorded on a Bruker AM-400 spectrometer and are referenced to TMS.

Picryl Fluoride from Pyridinium Picrate.- Dry pyridinium picrate (3.6 g; 0.011 mol) was placed in a 3-neck round bottom flask, fitted with condenser and magnetic stirring bar. The assembly was immersed in an ice bath. Toluene (stored over 4Å molecular sieves) was added to the flask (ca. 300 mL) and the mixture was stirred, while it cooled to 0°. To this stirred suspension, was added one equiv. of diethylaminosulfur trifluoride (DAST; 1.6 mL, 2.0g, 0.012 mol). After stirring at 0° for 15 min, the reaction mixture was allowed to come to room temperature (ca. 45 min) and was then heated to 50-80° for a further 30 min. The brown suspension was then cooled and washed several times ***rapidly*** with warm, dilute (10% v/v) HCl. The toluene solution was then dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give a golden solid. No attempt was made to try to recover the relatively inexpensive starting picrate or picric acid, which was presumably left in the aqueous layer. After drying under high vacuum (< 0.1 Torr), the yield of crude picryl fluoride was 1.10 g (40%), mp. 110-119°. Recrystallization from CCl_4 afforded 0.64 g (23%) picryl fluoride, mp. 127-129°, lit.[3,10-13] 122-123° and 131-132° (dimorphic).^{1}H NMR(DMSO-d_6): δ 9.182 (d, $J_{F\text{-}H_{3,5}}$ = 5.2 Hz). Generally, the picryl fluoride was used immediately or was stored over silica gel in a desiccator in the refrigerator (ca. 10°).

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AN IMPROVED SYNTHESIS OF MONOESTERS OF PHOSPHORIC ACID

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Various methods are available[1] for the conversion of alcohols into their monophosphate esters. For those routes employing alcohols as substrates, direct phosphorylation with pyrophosphoric acid,[2] or phosphorous acid-Hg^{2+}-R_3N systems has been reported; in the former method, variable yields were observed while in the latter large excess of an alcohol is required. The phosphorylation of an alcohol *via* the nucleophilic cleavage of the P-Cl bond can be performed with a suitably protected reagent (e. g., *o*-phenylenephosphorochloridate[4]) or by a much simpler approach, in reaction with $POCl_3$, followed by selective hydrolysis of the monosubstituted intermediate. The first step (formation of **1**) can be successfully applied for primary alcohols and phenols, but selective hydrolysis of **1**, and the isolation of pure **2** can present problems. Cramer and Winter[6] reported the high-yield preparation of free acids **2** *via* the hydrolysis of **1** in aqueous acetonitrile in the presence of