The Ar(OH)(CH_2OH) type of compounds, which do not polymerize in alkaline medium, should in principle be methylated selectively. Optimum conditions may be discovered by keeping in view that (1) methylation of the alcoholic group is favored as the DMS/substrate ratio exceeds 1 and the temperature of the reaction is raised (toward 50 °C), and (2) methylation of the phenolic group, which takes place via salification, can be prevented when LiOH/DMS and LiOH/substrate ratios are at least 3 and the reaction temperature is lowered (toward 20 °C).

Registry No.—HkH, 501-30-4; HkM, 6269-25-6.

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Phase Transfer Catalysis. Preparation of Aliphatic and Aromatic Sulfonyl Fluorides

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Received October 21, 1976

We wish to report a very facile and convenient synthesis of organic sulfonyl fluorides employing crown ether catalysis.

Organic sulfonyl fluorides are of interest owing to their insecticidal, germicidal,[1,2] and enzyme inhibitory properties.[3-5] There are many methods available for their preparation, most of which involve halogen exchange (i.e., conversion of the corresponding sulfonyl chloride to the sulfonyl fluoride). One of the original sulfonyl fluoride preparations requires boiling the sulfonyl chloride with an aqueous solution of potassium fluoride.[6,7] This procedure results in only moderate yields (46–83%) and will not work for water-sensitive compounds. Other syntheses include (1) refluxing the corresponding sulfonyl chloride and potassium fluoride in a cosolvent system (e.g., dioxane/water) (70% yield), (2) reacting anhydrous hydrogen fluoride with the sulfonic anhydride (90–95%),[8] (3) addition of sodium nitrite to a solution of the corresponding sulfonamide in anhydrous hydrogen fluoride (53–78%),[9] and (4) heating the sulfonyl chloride with sodium fluoride suspended in tetramethylenesulfone, acetonitrile, or dimethylformamide (62–72%).[3,10]

A recently reported synthesis of sulfonyl fluorides involved conversion of the sulfonyl chloride using a dialkylaminosulfur trifluoride compound as the fluorine/chlorine exchange reagent (72–79%).[11] The reagent, however, must be prepared in two low-yield steps from a secondary amine, trimethylsilyl chloride, and sulfur tetrafluoride.[12]

In recent years, solid–liquid phase-transfer catalysis involving crown ethers has gained widespread use as a tool in organic synthesis.[13] The nucleophilic enhancement of anions by crown ethers in aprotic solvents is well known. The use of 18-crown-6 ether[14] to catalyze fluorine/halogen exchange with a wide variety of substrates has also been documented;[15] however, to the best of the authors' knowledge, no mention has been made in the literature of a crown ether catalyzed fluoride exchange reaction with organic sulfonyl chlorides.

The reaction is conducted by stirring the sulfonyl chloride and excess potassium fluoride at room temperature in acetonitrile solution or neat in the presence of 18-crown-6 ether catalyst. Representative sulfonyl fluorides have been prepared by this method in very high yield (see Table I).

$$RSO_2Cl \xrightarrow[KF,\ CH_3CN,\ RT]{\text{18-crown-6 ether}} RSO_2F + KCl$$

The reaction mixture is heterogeneous at all times, but the appearance of the solid phase changes as the reaction progresses. The reaction is exothermic, and controlled addition is sometimes necessary. The 18-crown-6 ether is catalytic (see Table I); however, the reaction will proceed in the absence of catalyst at a slower rate. All conversions are complete within 4 h and are essentially quantitative, making isolation and purification remarkably simple. Water washing easily separates the sulfonyl fluoride product from the salts. It was found that liquid sulfonyl chlorides make excellent solvents for this phase-transfer catalyzed reaction. These conversions were run neat with the potassium fluoride being phase transferred into the coreactant. For solid sulfonyl chloride reactants, acetonitrile appeared to be the solvent of choice, although other aprotic solvents may work equally well.[17]

Dansyl chloride is of importance as a fluorescent probe, but has a poor shelf life owing to its water sensitivity. This preparation allows one to prepare dansyl fluoride (**7**), which is quite stable and has the same fluorescent probe properties.[5] The

Table I. 18-Crown-6-Ether Catalyzed Conversion of Sulfonyl Chlorides to Sulfonyl Fluorides

Registry no.		Product[a]	Equiv of KF	Solvent	Mp/bp, °C	% yield[b]	Concn of crown, mol %[c]
5558-25-8	1	Methanesulfonyl fluoride	1.2		123–124	84[d]	~0.6
329-98-6	2	α-Toluenesulfonyl fluoride	2.0	CH_3CN	91–92	89	~2.0
368-43-4	3	Benzenesulfonyl fluoride	1.2		84 (8 mmHg)	92.5	~0.7
455-16-3	4	*p*-Toluenesulfonyl fluoride	2.0	CH_3CN	42.5–43.5	100	~1.0
498-83-9	5	*p*-Bromobenzenesulfonyl fluoride	2.0	CH_3CN	64–65	100	~1.0
329-20-4	6	*p*-Acetamidobenzenesulfonyl fluoride	2.0	CH_3CN	175–177	96	~1.0
34523-28-9	7	5-Dimethyl-amino-1-naphthalenesulfonyl fluoride (dansyl fluoride)	2.0	CH_3CN	48–50	100	~3.0

[a] In all cases, conversion to product was quantitative. All spectral data (IR, NMR) are consistent with the assigned structure of the isolated product. [b] Represents isolated yield. [c] In all cases, the 18-crown-6 ether was used as its acetonitrile complex. NMR analysis of the complex indicates a 2:1 ratio of acetonitrile to 18-crown-6 ether. This has been confirmed by an x-ray diffraction study.[16] [d] Yield is not optimized.

conversion can be visually monitored as the orange dansyl chloride converts to the yellow dansyl fluoride.

The mild reaction conditions, excellent yields, simple isolation and purification of products, and scalability[18] are advantages of this procedure over prior arts that require energy input, sophisticated equipment, and expensive, noncommercially available reagents.

Experimental Section

Reactions were carried out in Pyrex equipment. Sulfonyl chlorides were commercially available (Eastman Kodak Co.). Potassium fluoride was commercially available (MCB) in anhydrous form and was not dried prior to use. 18-Crown-6 ether was prepared according to a known literature procedure.[19]

Preparation of *p*-Acetamidobenzenesulfonyl Fluoride (6). Acetonitrile Method. To a mixture of *p*-acetamidobenzenesulfonyl chloride (117.0 g, 0.5 mol) and potassium fluoride (58.0 g, 1.0 mol) in 200 mL of acetonitrile was added a solution of 18-crown-6 ether/acetonitrile complex (5 g) in 100 mL of acetonitrile at room temperature (20 °C). The reaction mixture was allowed to stir overnight. It was then drowned out in 5 volumes of water. The off-white solid was collected, washed with water, and dried to provide 105.0 g of *p*-acetamidobenzenesulfonyl fluoride, mp 175–177 °C, 96% yield.

Preparation of Benzenesulfonyl Fluoride (3). Neat Method. To a solution of 18-crown-6 ether/acetonitrile complex (5 g) and benzenesulfonyl chloride (340 g, 1.93 mol) was added portionwise potassium fluoride (130 g, 2.24 mol). The reaction mixture was allowed to stir overnight after completion of the exothermic addition. One liter of water was then added, and the organic layer was separated, dried over anhydrous magnesium sulfate, and vacuum distilled to give 285.0 g of benzenesulfonyl fluoride, bp 84–85 °C (8 mmHg), 92.5% yield.

Registry No.—1 chloride derivative, 124-63-0; 2 chloride derivative, 1939-99-7; 3 chloride derivative, 98-09-9; 4 chloride derivative, 98-59-9; 5 chloride derivative, 98-58-8; 6 chloride derivative, 121-60-8; 7 chloride derivative, 605-65-2.

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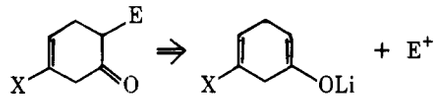
Communications

α′-Functionalization of β,γ-Unsaturated Cyclohexenones. Utilization of Silyl Enol Ethers Produced from the Lithium/Ammonia Reduction of Silyl Aryl Ethers

Summary: Lithium/ammonia reduction of isopropyldimethyl- and *tert*-butyldimethylsilyl aryl ethers provides a high-yield synthesis of 1,4-dihydroaryl silyl ethers which may be regiospecifically elaborated to nonconjugated ketones.

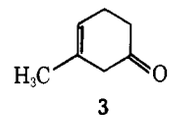
Sir: We have been faced with the need for a general method for synthesis of nonconjugated enones of the type **1a,b.** Analysis of this problem suggested that one conceptually simple solution might be via the reaction of enolate **2a,b** with an electrophilic species, E^+.



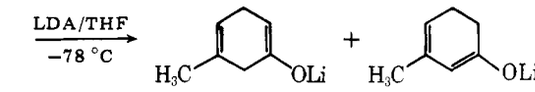
1a, X = CH_3 2a, X = CH_3
b, X = OCH_3 b, X = OCH_3

Attempts to generate enolate **2a** by addition of ketone **3** to a solution of lithium diisopropyl amide (LDA) were precluded by preferential formation of conjugated enolate **4**.[1]

Since it has been established that silyl enol ethers can be regiospecifically functionalized under kinetic conditions either directly, by electrophilic substitution reactions,[2] or via prior conversion to an enolate,[3,4] it was felt that a similar expedient with dihydroaryl silyl ethers such as **6a–c** might provide an efficient synthesis for the desired class of nonconjugated enones.

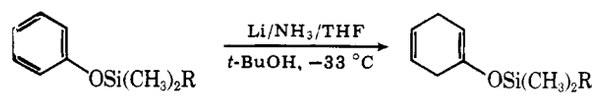


3



2a (~20%) **4** (~80%)

Preparation of the requisite dihydroaryl silyl ethers can be conveniently achieved by lithium/ammonia reduction of the corresponding *tert*-butyldimethylsilyl or isopropyldimethylsilyl phenyl ethers **5a–b**[5] under carefully controlled conditions[6] (see Chart I). The corresponding trimethylsilyl aryl ether **5c** is hydrolytically unstable to the reaction conditions and provides only a very poor yield of dihydroaryl isomer **6c.**



5a, R = $C(CH_3)_3$
b, R = $CH(CH_3)_2$
c, R = CH_3

6a–c

The dihydroaryl silyl ethers **6–15** serve as excellent substrates for further functionalization; for example, reaction of isopropyldimethylsilyl enol ether of **7b** with methyllithium[3,13] cleanly generates enolate **2a** as demonstrated by reaction with acetic anhydride (inverse addition) to produce oxygen and carbon acylated products **16**[8,9] and **17**[8,9,14] which are uncontaminated by products which would have resulted from eno-