The Reaction of 2-(3-Sydnonyl)phenylmethanol with Sulfonyl Chlorides. A One Pot Conversion to the Chloro Congener

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The interesting transformation of 2-(3-sydnonylphenylmethanol (**1**) to its chloro congener **2**, in moderate to good yield using sulfonyl chlorides, is described. A mechanism for the transformation is suggested.

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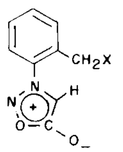
For another study the chloro sydnone **2** was required. Its synthesis from the sydnone alcohol **1** [1] by standard methods (*viz.* with hydrochloric acid, phosphorus pentachloride, or thionyl chloride) proved to be surprisingly difficult (complex mixtures were obtained in all cases). This may be attributable in part to the susceptibility of the sydnone ring to both acidic conditions [2] and reaction with thionyl chloride [3]. Additionally, the reactivity of the alcohol function towards electrophiles may be diminished by the electron-withdrawing effect of the sydnone ring [2], thus allowing competitive reactions to occur.

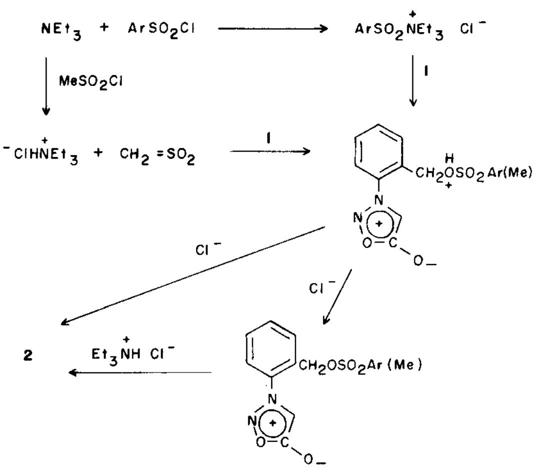


1, X = OH
2, X = Cl
3, X = $OSO_2C_6H_4Me-4$
4, X = $^{+}NC_5H_5\ Cl^{-}$
5, X = OSO_2Ph
6, X = OSO_2Me

To circumvent this problem the preparation of **2** from **1** in a two step process *via* the tosylate **3** was attempted. Reaction of **1** with *p*-toluenesulfonyl chloride (1.1 equivalents) in pyridine at room temperature overnight (standard conditions for tosylation) [4], and subsequent quenching with water, gave no tosylate **3** or starting material **1**. No organic species could be extracted from the aqueous layer, presumably due to the formation of a pyridinium salt **4** (perhaps formed by reaction of excess pyridine with **3**). No attempt was made to verify this assumption, however, the reaction conditions were modified to minimize this difficulty. Accordingly, the alcohol (**1**) was treated with *p*-toluenesulfonyl chloride (1.1 equivalents) and triethylamine (1.1 equivalents) in dichloromethane at room temperature. After stirring overnight the mixture was "worked-up" to afford a colorless, crystalline solid (47-68% yield, from 5 runs) identified as the chlorosydnone **2**. Similar results were obtained with benzenesulfonyl chloride (61% yield) and methanesulfonyl chloride (73% yield). To the best of our knowledge this is the first transformation of an alcohol to its chloro congener with sulfonyl chlorides, cleanly, under such mild conditions, and in satisfactory yield. The preparation of allyl chlorides from allyl alcohols with tosyl chloride in pyridine at 80° has been reported [5]. Additionally, methanesulfonyl chloride in pyridine has been used to effect the transformation in low (at room temperature or below) [6] to moderate (at 100°) [7] yield. Clearly the present process offers significant advantages where base and temperature sensitivity are problems. "Work-up" is convenient and product yields are good (especially with methanesulfonyl chloride). The generality of the reaction is not yet known but clarifying studies are currently underway.

The structure of **2** was verified from its satisfactory analytical and spectral data. The mass spectrum gave a molecular ion at 210/212 and a fragmentation pattern typical for the sydnone ring, *viz.* loss of consecutively 30 (-NO) then 28 (-CO) [8]. The infrared spectrum displayed a strong ν C=O absorption band at 1747 cm^{-1}, and a sharp ν C-H band at 3145 cm^{-1}, assigned to the sydnone ring carbonyl and C-H rspectively [2], and the ^1H pmr spectrum showed a singlet at δ 4.0 for the methylene protons, a singlet at δ 6.3 for the sydnone ring proton, and a multiplet centered on δ 7.6 for the four aryl ring protons.

The mechanism was at first thought to involve formation of **2** *via* reaction of the initially formed tosylate **3** with the hydrochloric acid used in "work-up". This theory was discounted by repetition of the experiment and washing instead with aqueous hydrobromic acid; the chloro compound was again obtained. Participation by dichloromethane was also discounted by the successful utilization of acetone as solvent. Replacement of triethylamine by an equimolar quantity of pyridine also afforded **2**. In the absence of triethylamine, **1** and tosyl chloride did not react, thus negating a mechanism whereby the tosylate **3** is formed initially by reaction of **1** with tosyl chloride without participation by triethylamine. From these data the most appealing mechanism is one where triethylamine and the sulfonyl chloride react to form an intermediate salt (with mesyl chloride a sulfene may be formed [9]) which is then attacked by the sydnone alcohol **1**. Subsequent conversion to **2** may then involve direct displacement by Cl or a two step process involving proton abstraction and subsequent slow reaction with triethylammonium chloride (formed *in situ*) (Scheme 1). Apparent support for the latter postulate was afforded by the isolation of mesylate **6** from **1** and methanesulfonyl chloride/triethylamine after reaction for five minutes (no **6** could be observed after overnight reaction). However, shorter reaction times did not provide the corresponding sulfonate esters **3** and **5** from reaction of **1** with tosyl chloride or benzenesulfonyl chloride, respectively; only **2** and unreacted **1** were isolated. The difference is probably attributable to the greater reactivity of methanesulfonyl chloride.



It remains to be seen whether or not the reaction is a facet of the properties of the sydnone ring. However, this notwithstanding, a useful synthetic tool for further study of the unique mesoionic sydnones has been developed.

EXPERIMENTAL

3-(2-Chloromethylphenyl)sydnone (**2**).

To a solution of the sydnone alcohol **1**, 1.00 g (5.20 mmoles) and triethylamine, 0.54 g (5.34 mmoles) in 15 ml of dichloromethane was added the sulfonyl chloride (5.40 mmoles) with stirring. After 16 hours at room temperature the dichloromethane solution was washed successively with 10% hydrochloric acid (2 × 15 ml), water (20 ml), 5% sodium carbonate (2 × 15 ml), water (10 ml) and saturated sodium chloride solution (20 ml). Drying (sodium sulfate) and evaporation of the solvent *in vacuo* afforded a reddish oil which crystallized on standing. Recrystallization from dichloromethane/petroleum ether gave **2** as colorless plates, 0.63-0.80 g (58-73%); ir 3145, 3060, 1747, 1200, 940, 780, 730 cm^{-1}; 60 MHz pmr (deuteriochloroform): δ 4.6 (s, 2H, CH_2), 6.3 (s, 1H, CH) and 7.6 (m, 4H, aromatic H); ms: m/e (relative intensity) 212 (M^+, 3.86), 210 (M^+, 6.77), 182 (3.14), 180 (9.4), 154 (31.98), 152 (100), 127 (18.92), 125 (59.26), 117 (59.37), 116 (54.41), 90 (31.58), 89 (56.31).

Anal. Calcd. for $C_9H_7ClN_2O_2$: C, 51.31; H, 3.35; N, 13.30. Found: C, 51.14; H,3.57; N, 13.56.

2-(3-Sydnonyl)benzylmethane Sulfonate (**6**).

To a solution of the sydnone alcohol **1**, 1.00 g (5.20 mmoles) in triethylamine, 0.60 g (5.94 mmoles) and 15 ml of dichloromethane was added methanesulfonyl chloride, 0.68 g (5.94 mmoles) dropwise with stirring. After 5 minutes, "work-up" was effected as previously described except that the reddish oil obtained was chromatographed on silica gel. Elution with dichloromethane gave 0.2 g of **2** (18%). The mesylate **6** was eluted with dichloromethane/acetone (3:1) and isolated as a colorless crystalline solid, 0.4 g (28%), mp 119-121°; ir (potassium bromide): 3140, 3018, 2925, 1735, 1347, 1175, 1000, 980, 850, 770 cm^{-1}; 60 MHz pmr (deuteriochloroform): δ 3.1 (s, 3H, CH_3), 5.3 (s, 2H, CH_2), 6.95 (s, 1H, CH), 7.7 (m, 4H, aromatic H); ms: m/e (relative intensity) 270 (M^+, 3.74), 240 (0.30), 212 (18.61), 117 (50), 116 (100), 90 (24), 89 (37).

Anal. Calcd. for $C_{10}H_{10}N_2O_5S$: C, 44.45; H, 3.73; N, 10.37. Found: C, 44.23; H, 3.60; N, 9.98.

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