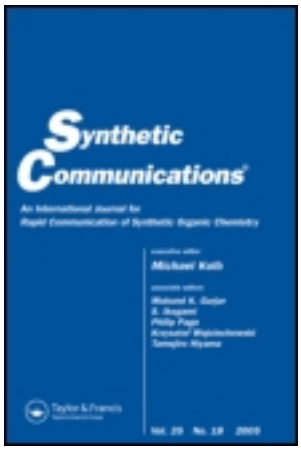

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THE EFFICIENT SYNTHESIS OF NEW SYDNONES CONTAINING FUSED RING

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THE EFFICIENT SYNTHESIS OF NEW SYDNONES CONTAINING FUSED RING

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ABSTRACT

Sydnones **2a–f** were prepared by the reaction of the corresponding sydnones **1a–f** with acetone in the presence of concentrate sulfuric acid or BF_3–Et_2O.

Key Words: Sydnone; Intramolecular Friedel–Crafts reaction; Acetone

Since their first syntheses sydnones have received much attention and have been reviewed by several authors.[1,2] Many of substituted sydnones and their derivatives have proved to possess valuable biological activity and their pharmacological activities in some instance were found high for practical purposes. So many sydnone compounds are known, but derivatives containing fused sydnone rings are less common[3,4] and their synthesis are difficult.[5,6] In an effort to prepare new fused ring sydnones we turned our attention to the preparation of 3-(3-hydroxylpropyl)sydnones and their intramolecular electrophilic aromatic substitution.

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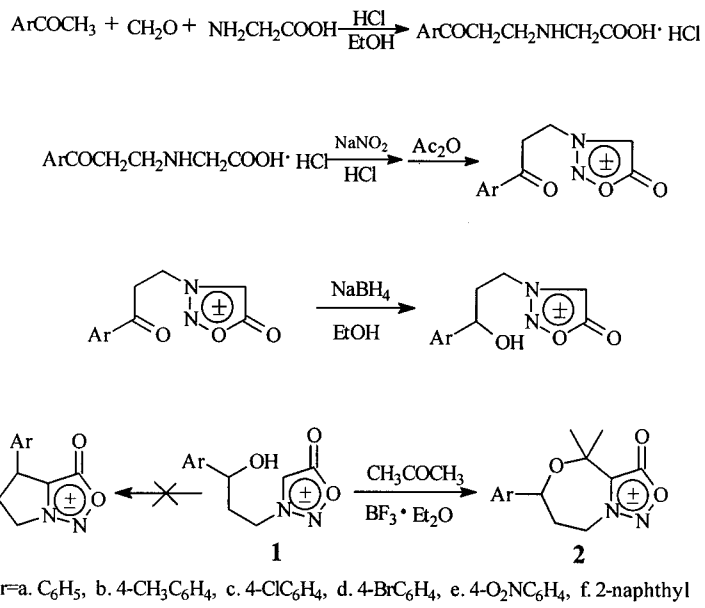
In our previous work, we reported that 3-(aroylethyl)sydnones[7] were reduced by sodium borohydride to produce 3-(3-aryl-3-hydroxylpropyl)sydnones.[8] We report here the preparation and identification of sydnones containing a seven-membered fused ring. Sydnones undergo a variety of reactions including electrophilic aromatic substitution (when unsubstituted at the 4-position), 1,3-dipolar cycloaddition (e.g. with alkynes) and acid induced cleavage, etc. As 3-(3-aryl-3-hydroxylpropyl)sydnones have a hydroxyl group in their side chains, they would undergo intramolecular Friedel–Crafts reaction. However the reaction did not take place under different conditions.

In the presence of H_2SO_4 or BF_3–Et_2O, 3-3-(aryl-3-hydroxylpropyl)-sydnones reacted with acetone to give sydnones containing a seven-membered fused ring. These compounds were identified on the basis of UV, IR, and ^{1}HNMR spectral data presented in Tables 1 and 2. The UV spectral data demonstrated that the sydnone ring was not decomposed. In the IR spectrum the very strong ring carbonyl stretching band falls in the range of 1750–1710 cm^{-1}, but the C–H of sydnone ring and the O–H stretching bands were absent. The proton NMR spectra of these compounds show the presence of two methyl groups as two singlets, but no characteristic singlet of the 4-proton on the sydnone ring at 6.5 ppm.

In summary, the procedure reported here represents an efficient synthetic entry to the fused-ring sydnones.



Ar=a. C_6H_5, b. 4-$CH_3C_6H_4$, c. 4-ClC_6H_4, d. 4-BrC_6H_4, e. 4-$O_2NC_6H_4$, f. 2-naphthyl

Table 1. Physical, Analytical, UV, and IR Data of Compounds **2a–g**

Compound	Yield (%)	M.P. (°C)	Elemental Analysis (calc.%) C H N	UV λ (nm, $\varepsilon \times 10^{-3}$)	IR (cm^{-1})
2a	85.7	176–178	64.82, 6.15, 11.08 (64.60, 6.20, 10.76)	296 (6.95) 207 (10.8)	1745
2b	80	175–176	66.06, 6.62, 10.49 (65.68, 6.61, 10.21)	298 (2.98) 207 (4.86)	1750
2c	82	161–162	57.24, 5.26, 9.78 (57.05, 5.13, 9.50)	299 (17.8) 220 (33.4)	1740
2d	79	169–170	50.02, 4.43, 8.41 (49.58, 4.46, 8.26)	295 (6.59) 220 (12.5)	1720
2e	60.3	218–220	55.33, 5.03, 13.48 (55.08, 4.95, 13.76)	274 (3.29) 208 (2.28)	1720
2f	67.2	142–143	69.38, 5.94, 9.01 (69.66, 5.85, 9.03)	286 (5.60) 224 (25.9)	1740

Table 2. ^{1}H NMR Spectral Data of Compounds **2a–g**

Compound	^{1}H NMR (ppm)
2a	7.37 (m, 5H, Ar-H), 4.85 (dd, 1H, CH-O), 4.75, 4.46 (2ddd, 2H, CH_2-Syd), 2.58, 2.30 (2m, 2H, CH_2), 1.69, 1.65 (2s, 6H, $2 \times CH_3$)
2b	7.25, 7.19 (2d, 4H, Ar-H), 4.82 (dd, 1H, CH-O), 4.75, 4.46 (2ddd, 2H, CH_2-Syd), 2.54, 2.35 (2m, 2H, CH_2), 2.357 (s, 3H, CH_3-Ar), 1.69, 1.63 (2s, 6H, $2 \times CH_3$)
2c	7.35, 7.30 (2d, 4H, Ar-H), 4.83 (dd, 1H, CH-O), 4.73, 4.47 (2ddd, 2H, CH_2-Syd), 2.56, 2.30 (2m, 2H, CH_2), 1.68, 1.65 (2s, 6H, $2 \times CH_3$)
2d	7.50, 7.25 (2d, 4H, Ar-H), 4.81 (dd, 1H, CH-O), 4.73, 4.47 (2ddd, 2H, CH_2-Syd), 2.56, 2.24 (2m, 2H, CH_2), 1.67, 1.64 (2s, 6H, $2 \times CH_3$)
2e	8.25, 7.56 (2d, 4H, Ar-H), 4.97 (dd, 1H, CH-O), 4.75, 4.51 (2ddd, 2H, CH_2-Syd), 2.66, 2.23 (2m, 2H, CH_2), 1.687 (s, 6H, $2 \times CH_3$)
2f	7.85, 7.47 (2m, 7H, Ar-H), 5.01 (dd, 1H, CH-O), 4.79, 4.49 (2ddd,2H,CH_2-Syd), 2.65, 2.37 (2m, 2H, CH_2), 1.73, 1.69 (2s, 6H, $2 \times CH_3$)

EXPERIMENTAL

^{1}H NMR spectra were obtained on an Advance 500 Bruker spectrometer in $CDCl_3$; chemical shifts are reported relative to TMS as an internal standard. Ultraviolet spectra were recorded on a Shimadzu UV-240 spectrophotometer in ethanol; Infrared spectra were obtained on a Hitachi 260-50 spectrophotometer as KBr discs; Microanalyses were performed on a Perkin-Elmer 240C CHN instrument. All melting points were determined with a Yanaco mp-500 melting point apparatus and are uncorrected.

Typical Procedure for Reduction of 3-Aroylethylsydnones by Using $NaBH_4$

To an ice-cooled EtOH solution (10 mL) containing 3-aroylethylsydnone (2 mmol), $NaBH_4$ (0.1 g, 2.6 mmol) was added. After being stirred at room temperature for 1 h, the resultant solution was poured into cold water (100 mL). The crude product was recrystallized from 95% ethanol yielding 3-Aroylethylsydnone **1a–f**.

The Synthesis of Sydnones **2a–f**, General Procedure

To a solution of 3-(3-aryl-3-hydroxylpropyl)sydnone **1** (2.5 mmol) in acetone (15 mL), concentrate H_2SO_4 (0.5 mL) or BF_3–Et_2O (1 mL) is added dropwise at 0°C and the stirring is continued for 24 h at r.t.. The mixture is poured into water (50 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer is dried over Na_2SO_4. The solvent is evaporated and the crude product is recrystallized from ethyl acetate/hexane to give colorless **2a–f.**

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