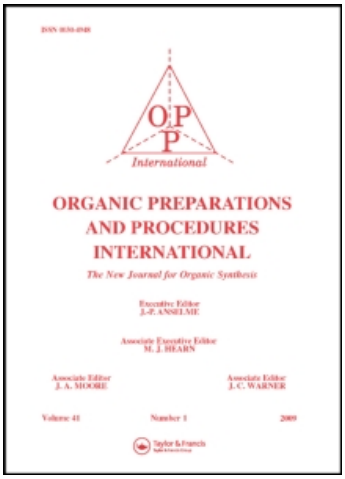

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PREPARATION OF 1-ETHYNYL-7-METHOXYNAPHTHALENE

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PREPARATION OF 1-ETHYNYL-7-METHOXYNAPHTHALENE

Submitted by (07/21/88) Jane A. Moore, James W. Roche, Philippe Prince, Richard D. Gandour* and Frank R. Fronczek

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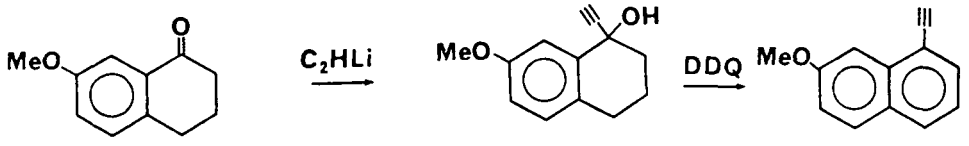
As an entry into 1,7-disubstituted naphthalenes, we report a simple two-step synthesis of 1-ethynyl-7-methoxynaphthalene (1) starting from 7-methoxy-1-tetralone (2).



2 **3** **1**

Treatment of 2 with monolithium acetylide[1] produced 1-ethynyl-7-methoxy-1,2,3,4-tetrahydro-1-naphthol (3) in 97% yield, which was converted into 1 in 73% yield by treatment with DDQ.[2] The overall yield from 2 to 1 was 70%.

EXPERIMENTAL SECTION

Tetrahydrofuran was distilled from Na-K under nitrogen. Acetylene (Liquid Carbonic, welding grade) was passed through a -78° trap, bubbled through two sulfuric acid traps, and scrubbed through a lime tower. Butyllithium (Aldrich) was titrated as described.[3] 7-Methoxy-1-tetralone (Aldrich) was vacuum distilled and recrystallized from petroleum ether. Glassware was stored at 125° for 12 hrs and assembled hot while being flushed with argon. Benzene was distilled and stored over 4 A molecular sieves. DDQ (Lancaster) was recrystallized from chloroform/dichloromethane.

^1H and ^{13}C NMR data were determined on a Bruker 400 Mhz using deuterated chloroform as the solvent and TMS as the internal standard. Chemical shifts and coupling constants were calculated by best fit to peak positions using the Bruker PANIC (1981) program on a Bruker ASPECT 2000 computer. Melting points were measured using an Electrothermal melting point apparatus and were uncorrected. IR spectra were obtained on a Perkin Elmer 283B spectrophotometer. Mass spectra were determined by a Hewlett-Packard 5985A spectrometer. Elemental analyses were carried out by Desert Analytics of Tucson, Arizona.

1-Ethynyl-1,2,3,4-tetrahydro-7-methoxy-1-naphthol (3).- Acetylene was bubbled for 15 min into THF (200 mL) and the system was cooled to -78° and flushed with argon. Butyllithium (46 mL of 2.4 M in hexanes, 110 mmol) was added dropwise while maintaining the temperature below -70°. Acetylene was bubbled through the system for 10 min. Compound 2 (6.06 g, 34 mmol) in 40 mL of THF was added slowly, and the mixture was stirred for 1 hr. The solution was warmed to room temperature over a period of 2 hrs, and water (40 mL) was added . The

aqueous phase was extracted with 3 x 20 mL of DCM. The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. A bulb-to-bulb distillation of the residue yielded 6.66 g (97%) of a colorless solid, which was pure by ^1H NMR. A small sample was recrystallized from methanol/water for analytical purposes, mp. 70.5-71.5°. ^1H NMR ($CDCl_3$): δ 7.29 (d, 1H, C8, J = 2.65 Hz), 7.00 (d, 1H, C5, J = 8.35 Hz), 6.80 (dd, 1H, C6, J = 8.35 and 2.65 Hz), 3.80 (s, 3H, CH_3O-), 2.74 (m, 2H, C4), 2.58 (s, 1H, C-H), 2.28 (s, 1H, -OH), 2.18 (m, 2H, C2), 1.95 (m, 2H, C3). ^{13}C NMR ($CDCl_3$): δ 158.2 (C7), 139.5 (C8a), 130.2 (C5), 128.1 (C4a), 115.2 (C6), 111.8 (C8), 88.0 (-C≡), 72.4 (≡C-H), 67.9 (C1), 55.4 (-OCH_3), 38.9 (C2), 28.3 (C4), 19.2 (C3). IR (CCl_4): 3600 (s), 3100 (s). Mass spec., m/e (relative intensity): 202 (M+, 47.4), 184 (100), 169 (32.7), 131 (41.7), 115 (30.6), 103 (30.8).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93. Found: C, 77.09; H, 7.01

1-Ethynyl-7-methoxynaphthalene (1).- To 3 (1.01 g, 5 mmol) dissolved in 10 mL of benzene was added DDQ (1.2 g, 5.05 mmol) in 40 mL of benzene. The mixture was heated to reflux for 1 hr. More DDQ (1.2 g, 5.05 mmol) in 25 mL of benzene was added . After 1 hr of reflux the mixture was quenched by 20 mL of 0.5 M $NaHSO_3$ solution. After filtration the aqueous layer was extracted by 3 x 20 mL of ethyl acetate. The organic phases were combined and washed with 3 x 40 mL of 5% NaOH, saturated $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and concentrated. Distillation on Kugelrohr apparatus yielded 0.66 g (72.5 %) of a colorless solid, which was pure by ^1H NMR. A small sample was recrystallized from methanol/water for analytical purposes, mp. 51-51.5°. ^1H NMR ($CDCl_3$): δ 7.76 (d, 1H, J = 7.59 Hz, C2), 7.72 (d, 1H, J = 8.90 Hz, C5), 7.70 (d, 1H, J = 7.70 Hz, C4), 7.63 (d, 1H, J = 1.52 Hz, C8), 7.26 (dd, 1H, J = 7.70 and 7.59 Hz, C3), 7.17 (dd, 1H, J = 8.90 and 1.52 Hz, C6), 3.95 (s, 3H, -OCH_3), 3.47 (s, 1H, ≡C-H). ^{13}C NMR ($CDCl_3$): δ 158.7 (C7), 134.9 (C8a), 131.7 (C4), 129.8 (C5), 129.0 (C2), 128.6 (C4a), 122.8 (C3), 119.3 (C6), 118.3 (C1), 104.2 (C8), 82.1 (-C≡), 81.8 (≡C-H), 55.3 (-OCH_3). IR (CCl_4): 3200 (s), 700-850 (b). Mass spec., m/e (relative intensity): 182 (M+, 94.7), 139 (100). The structure of the product was ultimately confirmed by single crystal X-ray analysis. Crystal structure parameters:[4] monoclinic, $P2_1/c$, Z = 4, a = 10.325(2), b = 6.420(3), c = 15.534(3), β = 94.52(2), R (obs. data) = 0.115, Obs. data = 808.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.71; H, 5.49. Found: C, 85.79; H, 5.30

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4. X-Ray crystallographic experimental details and crystal structure parameters are available from the authors on request.

REDUCTION OF SULFONYL CHLORIDES WITH SODIUM CYANOBOROHYDRIDE

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The increasing utilization of sodium cyanoborohydride to specific synthetic problems coupled with its selectivity and stability in acidic media,[1] prompted us to use it for the reduction

$$RSO_2Cl \xrightarrow{NaBH_3CN} RSSR$$

of sulfonyl chlorides to the corresponding disulfides. This successful reduction is to be contrasted to the reduction with lithium aluminum hydride[2] or sodium borohydride[3] which gives thiols or sulfinic acids at lower temperatures. Most reductions of sulfonyl chlorides with $NaBH_3CN$ can be performed in refluxing dioxane; in some cases, hexamethylphosphoramide (HMPA) was the solvent of choice, even though the formation of some N,N-dimethylsulfonamides resulting from the decomposition of HMPA by the sulfonyl chlorides could not be avoided.

Aromatic disulfides were obtained in satisfactory yields, while benzylsulfonyl chloride was reduced in only 45% yields. Although trialkylamine-trichlorosilane system[4] or $Mo(CO)_6$ in tetramethylurea[5] are known to reduce sulfonyl chlorides to the symmetric disulfides, the chemoselectivity, the stability of sodium cyanoborohydride as well as the simple experimental procedure, recommend the present method as an alternative synthetic tool.

EXPERIMENTAL SECTION

Diphenyl Disulfide (1). Typical Procedure.- To a solution of 176 mg (1 mmol) of benzenesulfonyl chloride in 2 mL of dried dioxane, was added 252 mg (4 mmol) of sodium cyanoborohydride in portions over a 10 min period; the mixture was then stirred under reflux for 20 hrs and cooled to room temperature. After dilution with water and extraction with chloroform, the extract was dried over anhydrous magnesium sulfate and the chloroform was evaporated. The residue was recrystallized from ethanol to give 85 mg (78%) of diphenyl disulfide as colorless needles. Other sulfonyl chlorides (runs 2,3,4 and 9) were reduced similarly.