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Short Note

2-Methyl-7-(phenylsulfanylmethyl)naphthalene

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Abstract: A new sulfide, 2-methyl-7-(phenylsulfanylmethyl)naphthalene was synthesized and its MS, IR, ^{1}H NMR, ^{13}C NMR and DEPT-135 data are reported.

Keywords: phase-transfer catalysis; 2-methyl-7-(phenylsulfanylmethyl)naphthalene; naphthylmethyl phenyl sulfide

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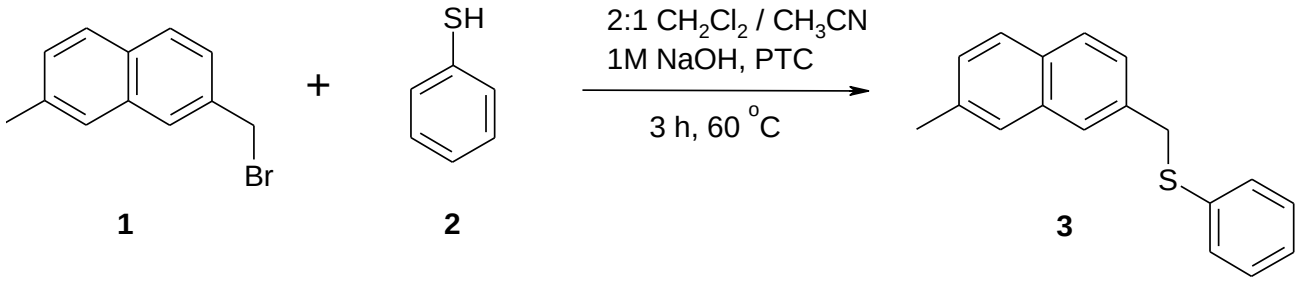
1. Introduction

In connection with our investigation of competitive mesolytic cleavages [1] of radical anions, we needed 2-methyl-7-(phenylsulfanylmethyl)naphthalene (**3**) as gas chromatography standard. The synthetic method of choice for this naphthylmethyl phenyl sulfide is reaction between naphthylmethyl halide and a corresponding thiophenoxide. From the various developed procedures [2–7] we have decided to utilize the phase-transfer variant used by Guthrie and Maslak [7] for preparation of the analogous ethers. The starting material for these derivatives was 2-bromomethyl-7-methylnaphthalene (**1**), which could be conveniently obtained by benzylic bromination of the commercially available 2,7-dimethylnaphthalene, using the procedure described by Buuhoi and co-workers [8]. We would like to report a convenient procedure for preparation of 2-methyl-7-(phenylsulfanylmethyl)naphthalene.

Scheme 1. Synthesis of 2-methyl-7-(phenylsulfanylmethyl)naphthalene.



1 **2** **3**

2. Experimental

2.1. General

All chemicals were obtained from commercial sources and were used without further purification. Melting points were determined using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on a Bruker 400 MHz instrument, using deuteriochloroform as solvent and tetramethylsilane as internal standard. The IR spectra were recorded on a Perkin Elmer Model 1600 instrument between sodium chloride plates in carbon tetrachloride. The number of hydrogens on each carbon was determined from ^{13}C NMR and DEPT-135 spectra. The mass spectra were recorded on a Kratos MS-25 RFA double-focusing mass spectrometer in electron impact (EI) mode. Gas chromatography was performed on a Varian 3700 instrument with packed column. The column was 1/8" in diameter and 50 cm in length packed with 5% OV-101 on supelcoport, purchased from Supelco. The carrier gas was helium (30 mL/min flow), the detection was accomplished with flame ionization and monitored with HP-3390A reporting integrator. TLC was carried out using Merck pre-coated plates (60 F_{254}, 250 μm).

2.2. 2-Methyl-7-(phenylsulfanylmethyl)naphthalene (**3**)

A mixture of 2-bromomethyl-7-methylnaphthalene (**1**) (0.200 g, 0.861 mmol), 2:1 (v/v) dichloromethane/acetonitrile (5 mL), 1M NaOH (5 mL), freshly distilled thiophenol (0.188 g, 1.71 mmol) and a drop of methyltricaprylammonium chloride (MTCAC) was vigorously stirred at 60 ℃ for 3 h under argon. The mixture was cooled to room temperature, the layers were separated and the organic layer was washed with 1M sodium hydroxide (2 × 10 mL), water (2 × 10 mL) and brine (1 × 10 mL). Drying over sodium sulfate and removal of the solvent *in vacuo* afforded a yellow solid. Recrystallization from ethanol yielded 0.121 g (54%) of **3** as white plates.

M.p. 89–91 °C.

R_f (20% dichloromethane in hexanes) = 0.26.

GC: R_t = 15.80 min (100 °C, 3 min, 8 °C/min to 280 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.58 (s, 1 H), 7.50 (s, 1 H), 7.38 (dd, *J* = 8.4 Hz, 1.7 Hz, 1 H), 7.34–7.29 (m, 2 H), 7.27 (dd, *J* = 8.4 Hz, 1.7 Hz, 1 H), 7.24–7.12 (m, 3 H), 4.24 (s, 2 H, Ar-C$\underline{H}_2$-SPh), 2.48 (s, 3 H, Ar-C$\underline{H}_3$).

^{13}C NMR (100 MHz): δ = 136.35 (C), 135.78 (C), 134.87 (C), 133.52 (C), 130.82 (C), 129.90 (CH), 128.83 (CH), 128.08 (CH), 127.99 (CH), 127.43 (CH), 126.78 (CH), 126.68 (CH), 126.35 (CH), 126.08 (CH) (*Ar*), 39.41 (Ar-$\underline{C}H_2$-SPh), 21.70 (Ar-$\underline{C}H_3$).

DEPT-135 NMR: δ = 129.90 (↑, CH), 128.83 (↑, CH), 128.08 (↑, CH), 127.99 (↑, CH), 127.43 (↑, CH), 126.78 (↑, CH), 126.68 (↑, CH), 126.35 (↑, CH), 126.08 (↑, CH) (*Ar*), 39.41 (↓, Ar-$\underline{C}H_2$-SPh), 21.70 (↑, Ar-$\underline{C}H_3$).

IR (CCl_4, cm^{-1}): 3055, 3022, 2924, 2861, 1638, 1610, 1585, 1515, 1480, 1439, 1383, 1336, 1230, 1078, 1025, 1012, 959, 902.

EI-MS (*m/z*, rel. intensity): 265 (M^+ + 1, 3%), 264 (M^+, 7%), 197 (3%), 157 (9%), 156 (9%), 155 (M^+ – SPh, 100%), 111 (14%).

3. Conclusion

The reaction of 2-bromomethyl-7-methylnaphthalene with thiophenol under phase-transfer catalytic conditions, in the presence of methyltricaprylammonium chloride (MTCAC) gave the desired product **3** in moderate yield. The structure of **3** was unambiguously determined by spectroscopic means (^{1}H NMR, ^{13}C NMR, DEPT-135 NMR, IR and MS). The reaction can be conveniently monitored by GC and/or TLC (20% dichloromethane in hexanes). The reaction was performed in degassed solution under argon atmosphere to avoid the oxidation of the thiophenol into diphenyl disulfide [9]. Diphenyl disulfide can pose a separation problem and can interfere with the mesolytic cleavage studies.

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