Oxidation Communications 37, No 4, 1132–1135 (*2014*)

Synthesis of organic compounds

CONVENIENT SYNTHESIS OF *para*-HALOSUBSTITUTED PHENYLSULPHANYL NAPHTHALENES

J. BOGDANOV

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, 5 Arhimedova Street, 1000 Skopje, FYR Macedonia
E-mail: *j_b_bogdanov@yahoo.com*

ABSTRACT

Two new sulphides, 2-{[(4-bromophenyl)sulphanyl]methyl}-7-methylnaphthalene and 2-{[(4-chlorophenyl)-sulphanyl]methyl}-7-methylnaphthalene were synthesised via nucleophilic substitution under phase-transfer conditions and their MS, ^{1}H NMR, ^{13}C NMR and ^{135}DEPT data are reported.

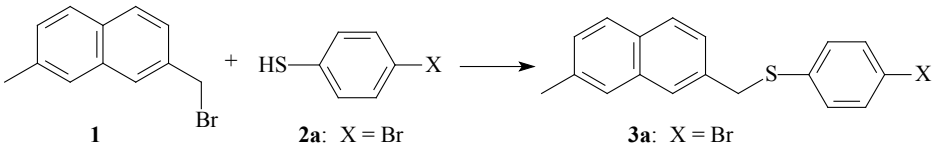
Keywords: phase-transfer catalysis, synthesis, 2-{[(4-bromophenyl)sulphanyl]methyl}-7-methylnaphthalene, 2-{[(4-chlorophenyl)-sulphanyl]methyl}-7-methylnaphthalene.

AIMS AND BACKGROUND

The new century has seen an increased interest in the synthesis and use of molecules possessing stereogenic sulphur center[1,2]. In the course of our work on chiral sulphoxides and asymmetric oxidation of sulphides, we needed the 2-{[(4-bromophenyl) sulphanyl]methyl}-7-methylnaphthalene (**3a**) and 2-{[(4-chlorophenyl)-sulphanyl] methyl}-7-methylnaphthalene (**3b**) as substrates. Chiral sulphoxides are quite important compounds as chiral auxiliaries and as pharmaceuticals[3], and their synthesis has attracted attention of many research groups. Especially appealing is their preparation by oxidation from prochiral sulphides[4–8].

There are many ways of preparing prochiral arylmethyl phenyl sulphides[9–13], and after trying several approaches we have found that the most convenient procedure employed the corresponding naphthylic bromide (**1**), and the corresponding thiophenol (**2**) and reaction under phase-transfer conditions (Scheme 1). 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[14].

Scheme 1



1 **2a**: X = Br **2b**: X = Cl **3a**: X = Br **3b**: X = Cl

Herein the synthesis of *para*-substituted phenyl naphthyl sulphides under phase-transfer conditions is presented.

EXPERIMENTAL

GENERAL

Dichloromethane, acetonitrile and methyltriphenylphosphonium bromide were obtained from Sigma-Aldrich. Acetonitrile, sodium sulphate and sodium hydroxide were obtained from Merck. 2-Bromomethyl-7-methylnaphthalene was prepared on a 10 mmol scale using literature method[13]. Melting points were determined using a Thomas-Hoover apparatus and were uncorrected. NMR spectra were recorded on a Bruker 400 MHz instrument using deuterated chloroform ($CDCl_3$) as solvent, with tetramethylsilane (TMS) as internal standard. The number of hydrogens on each carbon was determined from ^{13}C NMR and ^{135}DEPT spectra. The mass spectra were recorded on a Kratos MS-25 RFA double focusing mass spectrometer in electron impact (EI) mode. The IR spectrum was recorded on a Varian Excalibur 3100 Series FT-IR spectrometer using KBr pellet method. Thin layer chromatography (TLC) was carried out using Merck pre-coated plates (60 F_{254}, 250 μm).

SYNTHESIS

General procedure. A mixture of 2-bromomethyl-7-methylnaphthalene, **1**, (3.41 mmol), 3:1 (v/v) dichloromethane/acetonitrile (30 ml), 1 M NaOH (30 ml), 4-halothiophenol (0.064 g, 4.43 mmol) and methyltriphenylphosphonium bromide (MTPPB) (0.25 mmol) was lowered into an oil bath at 60°C and was vigorously stirred for 6 h under argon atmosphere. The mixture was cooled to room temperature, the layers were separated and the organic layer was washed with 1 M sodium hydroxide (2 × 5 ml), water (2 × 5 ml) and brine (1 × 5 ml). Drying over sodium sulphate and removal of solvent *in vacuo* afforded yellow solid, which was recrystallised from benzene/hexane (cooling at –20°C for 2 h).

2-{[(4-bromophenyl)sulphanyl]methyl}-7-methylnaphthalene **3a**. White powdery solid (62% yield), m.p. 98–100°C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.4 Hz, 1 H), 7.69 (d, J = 8.4 Hz, 1 H), 7.56 (s, 1 H), 7.51 (s, 1 H), 7.38–7.23 (m, 4 H), 7.15 (d, J = 8.3 Hz, 1 H), 4.21 (s, 2 H, Ar-CH_2-SPhBrp), 2.49 (s, 3 H, Ar-CH_3). ^{13}C NMR (100 MHz): δ = 136.35 (C), 135.82 (C), 134.83 (C), 133.88 (C), 132.27 (CH), 131.93

(CH), 131.26 (C), 128.64 (CH), 128.53 (CH), 127.87 (CH), 127.23 (CH), 127.10 (CH), 126.35 (CH), 120.75 (C) (*Ar*), 39.85 (Ar-CH_2-SPhBr*p*), 22.13 (Ar-CH_3). EI-MS (m/z, rel. intensity): 344 (M^+ + 2, 4.1%), 298 (M^+, 4%), 170 (11 %), 169 (9%), 161 (22%), 156 (16%), 155 (M^+ – SPhBr, 100%), 141 (10%).

2-{[(4-chlorophenyl)-sulphanyl]methyl}-7-methylnaphthalene **3b**. Off-white small plates (56% yield). m.p. 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.3 Hz, 1 H), 7.72 (d, J = 8.3 Hz, 1 H), 7.54 (s, 1 H), 7.50 (s, 1 H), 7.38–7.24 (m, 6 H), 7.08 (dd, J = 8.3 Hz, J = 1.5 Hz, 1 H), 4.20 (s, 2 H, Ar-CH_2-SPhCl*p*), 2.48 (s, 3 H, Ar-CH_3). ^{13}C NMR (100 MHz): δ = 135.90 (C), 134.64 (C), 134.48 (C), 133.45 (C), 132.44 (C), 131.43 (CH), 130.82 (C), 128.92 (CH), 128.19 (CH), 128.08 (CH), 127.44 (CH), 126.80 (CH), 126.66 (CH), 125.94 (CH) (*Ar*), 39.63 (Ar-CH_2-SPhCl*p*), 21.69 (Ar-CH_3). EI-MS (m/z, rel. intensity): 302 (M^+ + 4, 5%), 300 (M^+ + 2, 13%), 298 (M^+, 24%), 296 (23%), 261 (11%), 259 (7 %), 165 (12 %), 163 (27%), 161 (22%), 156 (16%), 155 (M^+ – SPhCl, 100%).

CONCLUSIONS

Reaction **1** with 4-halothiophenol under phase-transfer catalytic conditions, in the presence of methyltriphenylphosphonium bromide (MTPPB) gave the desired products **3a** and **3b**, respectively, in moderate yields (62 and 56%). It was found that for reproducible results it is best the reactions to be performed with degassed solutions under argon atmosphere to avoid the oxidation of the thiophenols to diaryldisulphides[9,15]. The structures of **3a** and **3b** were unambiguously determined by spectroscopic methods (^{1}H NMR, ^{13}C NMR, ^{135}DEPT NMR and MS). It is important for the obtained products to be free of diaryldisulphides because they can pose a separation problem and may interfere with the further oxidation studies to the corresponding sulphoxides.

ACKNOWLEDGEMENTS

The author is indebted to Dr. Alan Benesi for his help with the NMR data and to Dr. Pshemak Maslak for his helpful advices and suggestions.

REFERENCES

1. I. FERNANDEZ, N. KHIAR: Recent Developments in the Synthesis and Utilization of Chiral Sulfoxides. Chem Rev, **103**, 3651 (2003).
2. H. L. N. PELLISSIER: Use of Chiral Sulfoxides in Asymmetric Synthesis. Tetrahedron, **62**, 5559 (2006).
3. M. C. CARRENO: Applications of Sulfoxides to Asymmetric Synthesis of Biologically Active Compounds. Chem Rev, **95**, 1717 (1995).
4. J.-E. BÄCKVALL: Selective Oxidation of Amines and Sulfides. In: Selective Oxidation of Amines and Sulfides (Ed. J.-E. Bäckvall). Wiley-VCH Verlag GmbH & Co. KGaA, 2004. 193 p.
5. P. KOWALSKI, K. MITKA, K. OSSOWSKA, Z. KOLARSKA: Oxidation of Sulfides to Sulfoxides. Part 1: Oxidation Using Halogen Derivatives. Tetrahedron, **61**, 1933 (2005).

6. K. KACZOROWSKA, Z. KOLARSKA, K. MITKA, P. KOWALSKI: Oxidation of Sulfides to Sulfoxides. Part 2: Oxidation by Hydrogen Peroxide. Tetrahedron, **61**, 8315 (2005).
7. V. D. B. BONIFACIO: Enantioselective Sulfoxidation. Organic Chemistry Highlights (2005).
8. K. BHAGYALAKSHMI, H. HARI BABI, P. V. V. SATYANARAYANA: Kinetics and Mechanism of Oxidation of Some Monosubstituted Phenyl Methyl Sulphides by Cetyltrimethylammonium Dichromate. Oxid Commun, **36**, 338 (2013).
9. R. J. CREMLYN: An Introduction to Organosulfur Chemistry. Wiley, New York, 1996.
10. C. M. RAYNER: Synthesis of Thiols, Sulfides, Sulfoxides and Sulfones. Contemp Org Synth, **2**, 409 (1995).
11. J. M. YIN, C. A. PIDGEON: Simple and Efficient Method for Preparation of Unsymmetrical Sulfides. Tetrahedron Lett, **38**, 5953 (1997).
12. A. W. HERRIOTT, D. PICKER: Phase-transfer Synthesis of Sulfides and Dithioacetals. Synthesis, 447 (1975).
13. J. M. KHURANA, P. K. SAHOO: Chemoselective Alkylation of Thiols: A Detailed Investigation of Reactions of Thiols with Halides. Synth Commun, **22**, 1691 (1992).
14. N. P. BUUHOI, J. LECOCQ: Side-chain Bromination of Some Alkylnaphthalenes with N-bromo-succinimide. J Chem Soc, 830 (1946).
15. S. OAE: Organic Chemistry of Sulfur. Springer, Berlin, 1977.

Received 11 April 2014
Revised 15 May 2014