

SYNTHESIS OF BIS-SULPHONIUM SALTS OF NAPHTHALENE DERIVATIVES

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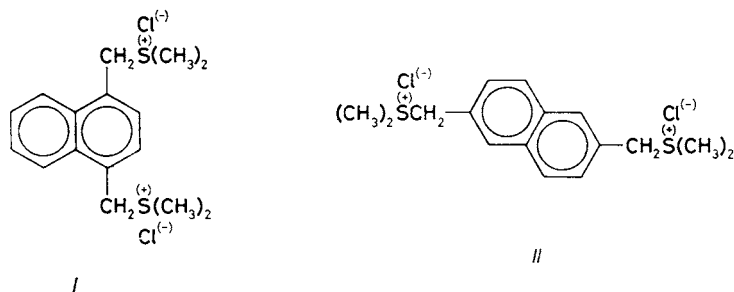
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Bis-sulphonium salts of naphthalene derivatives have been synthesized in good yields *via* the reaction of dimethyl sulphide with primary naphthyl halides under mild conditions.

There is increasing interest in the chemistry of sulphonium salts having a tricoordination sulphur atom attached to three carbon atoms, where the substituents may be alkyl, cycloalkyl, alkynyl, aryl or heteroaryl groups, or where the sulphur atom is part of a monocyclic or bicyclic system. Sulphonium salts become increasingly useful and important in organic synthesis since the demonstration in 1962 by Corey and Chaykovsky¹ of the easy preparation and highly selective methylene transfer capabilities of dimethylsulphonium methylide. Descriptions of some of the preparative methods were given by Goerdeler² and many references are to be found in the literature³⁻¹⁰.

In this work, 1,4-naphthalenedimethylenebis(dimethylsulphonium chloride) (*I*) and 2,6-naphthalenedimethylenebis(dimethylsulphonium chloride) (*II*) have been prepared by the reaction of 1,4-bis(chloromethyl)naphthalene and 2,6-bis(chloromethyl)naphthalene with dimethyl sulphide.



Prior to producing the naphthylsulphonium salts (*I* and *II*), the precursors chloromethylnaphthalene had to be synthesized. A mixture of 1,4- and 1,5-bis(chloromethyl)naphthalene had been obtained previously¹¹ by the chloromethylation of naphthalene. This reaction is based on the use of HCl and formaldehyde, which may

generate the carcinogens, chloromethyl methyl ether and bis(chloromethyl)ether¹². In the present report, a method was developed resulting in a good yield of the pure bis(chloromethyl)naphthalene. This involved the refluxing of dimethyl naphthalene with excess N-chlorosuccinimide in a carbon tetrachloride/benzene (2 : 1) solution with a trace of benzoyl peroxide as a radical initiator under nitrogen. The purity of the materials were confirmed by elemental analysis and ¹H NMR.

The synthesis of naphthylsulphonium salts (*I* and *II*) proceed *via* the reaction of primary naphthyl chlorides with dimethyl sulphide. It is well known, that dialkyl sulphides have sufficient nucleophilicity for reaction with primary benzyl halides^{6,13} to proceed under mild conditions, frequently simply by mixing the reagents at room temperature. Catalysts are often unnecessary although the reaction may be accelerated by the use of polar solvents as the transition state and product are more polar than the starting materials. Wessling and Zimmerman¹⁴ reported previously the synthesis of phenylsulphonium salts by the reaction of alkyl sulphide with benzyl halides in methanol. However, the synthesis of naphthylsulphonium salts by that method¹⁴ resulted in a low yield due to the poor solubility of naphthyl chlorides in methanol. In this work, both elevated temperature (50°C) and a mixture of methanol, acetone and water are employed in the synthesis of naphthylsulphonium salts.

The sulphonium salts *I* and *II* are relatively unstable and undergo some degradation within 24 to 48 h with the loss of dimethyl sulphide. However, their aqueous solutions are rather stable at room temperature indicating the aqueous stabilization of the pendant sulphonium ion group. Optimization of the procedure for the synthesis of these bis-sulphonium salts, has resulted in yields approaching 60–70% of a white hygroscopic crystalline powder with a clearly defined melting points. The title compounds serve as starting material for a large number of derivatives on the basis of the sulphonium ylides^{15–18} and conducting polymers^{19–20}.

EXPERIMENTAL

Melting points were determined on Mel-Temp apparatus and are uncorrected. ¹H NMR spectra were recorded on a Varian A-60 spectrometer and chemical shifts in parts *per* million were measured from internal tetramethylsilane. Microanalyses were performed by University of Massachusetts Microanalytical Laboratory.

1,4-Bis(chloromethyl)naphthalene

1,4-Dimethylnaphthalene (10 g, 64.1 mmol), N-chlorosuccinimide (25.67 g, 192.3 mmol), and benzoyl peroxide (0.4 g, 1.65 mmol) were dissolved in a mixture of carbon tetrachloride (300 ml) and benzene (150 ml) under nitrogen. The reaction mixture was refluxed at 85°C for 48 h. The mixture was cooled, filtered, and the succinimide was extracted with hot carbon tetrachloride. Some of the dichloride was soluble in carbon tetrachloride. The combined filtrate and extracts were evaporated and the residue was recrystallized from n-hexane to remove traces of mono-chlorinated and unchlorinated material. The dichloride was obtained as a white crystals (8.5 g, 59%), m.p. 132–135°C. ¹H NMR spectrum (CCl₄): δ 7.06–7.82 (bm, 6 H, ArH), 5.01 (s, 4 H,

2 CH₂Cl). For C₁₂H₁₀Cl₂ (225.9) calculated: 63.79% C, 4.46% H, 31.38% Cl; found: 63.78% C, 4.39% H, 31.82% Cl.

2,6-Bis(chloromethyl)naphthalene

The procedure was essentially the same as that described for the synthesis of 1,4-bis(chloromethyl)naphthalene, except that 2,6-dimethylnaphthalene (10 g, 64.1 mmol) was used instead of 1,4-dimethylnaphthalene. The crude product (10.5 g, 73%) was recrystallized from n-hexane and gave the dichloride as white crystalline powder, m.p. 140–143°C. ¹H NMR ((C²H₃)₂CO): δ 7.12–7.65 (bm, 6 H, ArH), 4.81 (s, 4 H, 2 CH₂Cl). For C₁₂H₁₀Cl₂ (225.9) calculated: 63.79% C, 4.46% H, 31.38% Cl; found: 63.67% C, 4.37% H, 31.90% Cl.

1,4-Naphthalenedimethylenebis(dimethylsulphonium chloride) (I)

Into a 250 ml round-bottom flask equipped with a magnetic stirrer 1,4-bis(chloromethyl)naphthalene (10 g, 44.4 mmol) was placed, and dimethyl sulphide (11.02 g, 177.7 mmol) in a mixture of methanol (45 ml) and acetone (45 ml) was added. The mixture was stirred at room temperature for 0.5 h followed by the addition of water (10 ml). The temperature was increased to 50°C for 20 h. The solvent was evaporated on a rotary evaporator and the product was treated with cold anhydrous acetone (800 ml) to give the bis-sulphonium salt as white hygroscopic powder (9.5 g, 61%), m.p. 155–158°C. For C₁₆H₂₂Cl₂S₂ (349.2) calculated: 55.03% C, 6.35% H, 20.24% Cl, 18.36% S; found: 55.39% C, 6.43% H, 20.49% Cl, 17.85% S.

2,6-Naphthalenedimethylenebis(dimethylsulphonium chloride) (II)

The synthesis of this sulphonium salt followed essentially the same procedure as was described for the synthesis of *I*, except that 2,6-bis(chloromethyl)naphthalene (10 g, 44.4 mmol) was used instead of 1,4-dichloride. The 2,6-bis(sulphonium chloride) was obtained as white hygroscopic product (11.5 g, 74%), m.p. 150–152°C. For C₁₆H₂₂Cl₂S₂ (349.2) calculated: 55.03% C, 6.35% H, 20.24% Cl, 18.36% S; found: 55.21% C, 6.49% H, 20.50% Cl, 17.19% S.

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