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Synthesis of Methyl or Aryl Sulfonyl Hydroxy Biphenyls Catalyzed by Monoelectronic Transfer and Related Compounds

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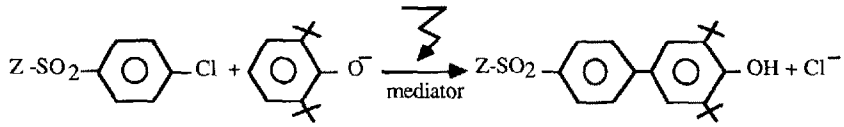
Key Words: liquid ammonia; $S_{RN}1$; electrosynthesis; sulfonyl hydroxy biphenyls.

Abstract: *Methyl or aryl sulfonyl hydroxy biphenyls could be electrosynthesized in liquid ammonia via a $S_{RN}1$ reaction, from chlorophenyl sulfones and 2,6-diterbutylphenoxide. Further transformations such as tertbutyl groups elimination, alkylation at the α carbon of the sulfone, or at the oxygen are described.*

Sulfonyl compounds are interesting intermediates in organic synthesis [1,2]. We have tried to synthesize methyl or aryl sulfonyl hydroxy biphenyls, which are interesting for non linear optics[3], starting from chlorophenylsulfones and 2,6-diterbutylphenoxide. The reaction involved is an electrochemically induced $S_{RN}1$ reaction [4a-d]:



Z = methyl, phenyl, 4-chlorophenyl.

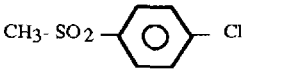
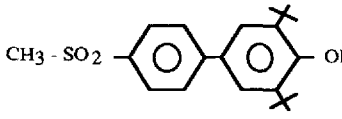
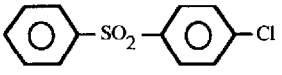
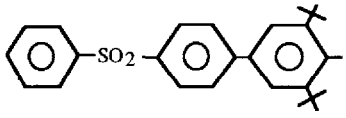
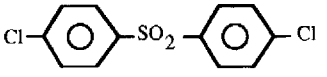
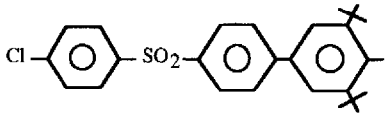
In the case of 4-chlorophenyl methyl sulfone as starting halide, related derivatives of the biphenyl sulfone were further synthesized.

1 Electrosynthesis of methyl or aryl sulfonyl hydroxy biphenyls.

The electrolyses were performed in a single-compartment cell containing 80 ml liquid ammonia at -40°C. 3 mmoles of the starting sulfone, 2 mmoles of mediator, 15 mmoles of 2,6-diterbutylphenol and the stoichiometric amount of potassium tertbutoxide were successively introduced into the cell. A constant current density of 1,5 $A.dm^{-2}$ was imposed between a platinum grid and a magnesium rod. When the reaction was over, ammonia was neutralized by ammonium chloride, and then evaporated. The organic phase was extracted with dichloromethane. The coupling product was separated by flash chromatography (silica gel, dichloromethane), and precipitated by adding pentane.

The results are gathered in Table 1.

Table 1. Electrosynthesis of Methyl or Aryl Sulfonyl Hydroxy Biphenyls.

Starting sulfone	Mediator	Product		Yield[(a)]
	4,4'-bipyridyl		I	90%
	4,4'-bipyridyl		II	90%
	quinoxaline	 [(b)]	III	90%

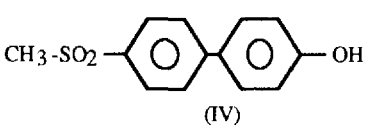
(a) isolated product yield in %.

(b) no disubstitution product is observed.

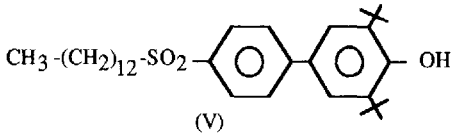
The rate constant of the coupling reaction, the key-step of the process, could be measured using perturbed redox catalysis[5]. Its rather high value ($k_2 = 8.10^9\ M^{-1}s^{-1}$) explains why the yield of preparative electrolysis is so high and the competitive reduction to phenyl sulfone remains limited to a negligible side reaction.

2 Synthesis of related compounds.

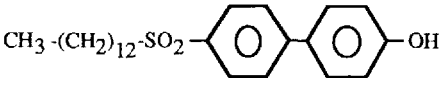
Starting from I, the following molecules were synthesized for possible mesomorphic applications:



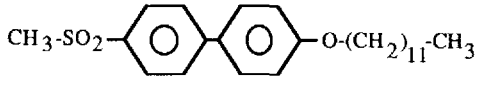
(IV)



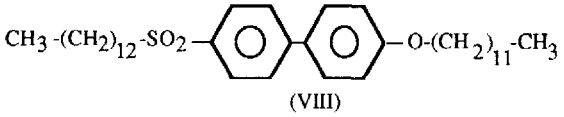
(V)



(VI)



(VII)



(VIII)

Three organic reactions are involved.

2a. Detertbutylation (I → IV), (V → VI)[6].

The starting material (I or V) was dissolved in freshly distilled toluene and reacted with 7 equivalents of aluminium chloride, stirring under nitrogen flow and heating at 50°C. After 1 hour, none of the starting material remainded; the reaction was worked up by the addition of water in excess. A precipitate formed between the aqueous and organic phases. This solid was filtered off, washed with water, extracted with dichloromethane, and crystallized from diethylether. The product (IV or VI) was obtained by column separation, eluting with methanol/dichloromethane (15/85, V/V).

2b. Addition of a chain next to the methyl sulfone (I → V, VII → VIII).

The sulfone was dissolved in the minimum of freshly distilled tetrahydrofuran in an atmosphere of nitrogen. At -78°C (dry ice in acetone), 2 equivalents of n-butyllithium (2,5 M in hexane) were added. The yellow reaction mixture was allowed to warm up to -40°C and 1.2 equivalent of n-bromododecane was introduced. The reaction was left to stir for 16 hours. The reaction mixture was hydrolyzed with diluted hydrochloric acid, extracted with dichloromethane. Separation of V or VIII from the other products was achieved by column elution with ethyl acetate/pentane (50/50, V/V).

2c. Alkoxylation of the phenolic moiety (IV → VII)[7].

The sulfone (IV) was dissolved in the minimum of dimethylformamide; 1 equivalent of potassium carbonate was added, together with 0.9 equivalent of n-bromododecane. The mixture was left to reflux for 20 hours at 80°C. The product (VII) was extracted with dichloromethane and crystallized from methanol.

We have electrosynthesized methyl or aryl sulfonyl hydroxy biphenyls with high yields in liquid ammonia, via a $S_{RN}1$ reaction. Alkyl chain substituted unsymmetrical biphenyl sulfones were further synthesized which could exhibit mesomorphic properties.

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8. Product analysis:

I m.p. 189°C; ^{1}H NMR (90 MHz, $CDCl_3$): 1.5 (s, 18H), 3.05 (s, 3H), 5.35 (s, 1 phenolic H), 7.45 (s, 2H), 7.8 and 8.0 (AA'BB', J_{app}=9 Hz, 4H); Anal. Calcd. for $C_{21}H_{28}O_3S$: C, 69.97; H, 7.83; O, 13.31; S, 8.89; Found: C, 69.86; H, 7.84.

II m.p. 234°C; ^{1}H NMR (90 MHz, $CDCl_3$): 1.5 (s, 18H), 5.4 (s, 1 phenolic H), 7.4 (s, 2H), 7.45 to 7.75(m, 5H), 7.85 to 8.15(m, 4H); Anal. Calcd. for $C_{26}H_{30}O_3S$: C, 73.90; H, 7.16; O, 11.36; S, 7.59; Found: C, 73.45; H, 7.12.

III m.p. 212°C; ^{1}H NMR (90 MHz, $CDCl_3$): 1.5 (s, 18H), 5.4 (s, 1 phenolic H), 7.4 (s, 2H), 7.5 and 7.95 (AA'BB', J_{app}=9 Hz, 4H), 7.7 and 8.0 (AA'BB', J_{app}=9 Hz, 4H); Anal. Calcd. for $C_{26}H_{29}O_3SCl$: C, 68.33; H, 6.42; O, 10.5; S, 7.01; Cl, 7.76; Found: C, 67.77; H, 6.25.

IV m.p. 206°C; ^{1}H NMR (90 MHz, acetone D_6): 3.1 (s, 3H), 6.9 and 7.55 (AA'BB', J_{app}=9 Hz, 4H), 7.8 and 7.95 (AA'BB', J_{app}=9 Hz, 4H), 8.7 (s, 1 phenolic H).

V m.p. 120°C; ^{1}H NMR (90 MHz, $CDCl_3$): 0.8 (m, 3H), 1.2 (s, 22H), 1.5 (s, 18H), 3.0 (m, 2H), 5.3 (s, 1 phenolic H), 7.35 (s, 2H), 7.7 and 7.9 (AA'BB', J_{app}=9 Hz, 4H).

VI m.p. 135°C; ^{1}H NMR (90 MHz, acetone D_6): 0.85 (m, 3H), 1.25 (s, 22H), 3.15 (m, 2H), 6.95 and 7.6 (AA'BB', J_{app}=9 Hz, 4H), 7.8 and 7.95 (AA'BB', J_{app}=9 Hz, 4H), 8.6 (s, 1 phenolic H).

VII m.p. 135°C; ^{1}H NMR (90 MHz, $CDCl_3$): 0.9 (m, 3H), 1.3 (br s, 20H), 3.1 (s, 3H), 4.0 (t, 2H), 7.0 and 7.6 (AA'BB', J_{app}=9 Hz, 4H), 7.7 and 8.0 (AA'BB', J_{app}=9 Hz, 4H); Anal. Calcd. for $C_{25}H_{36}SO_3$: C, 72.07; H, 8.71; O, 11.52; S, 7.69; Found: C, 71.96; H, 8.76.

VIII m.p. 115°C; ^{1}H NMR (90 MHz, $CDCl_3$): 0.85 (m, 6H), 1.2 (m, 42H), 3.1 (m, 2H), 4.0 (t, 2H), 7.0 and 7.55 (AA'BB', J_{app}=9 Hz, 4H), 7.7 and 7.95 (AA'BB', J_{app}=9 Hz, 4H); Anal. Calcd. for $C_{37}H_{60}SO_3$: C, 75.97; H, 10.34; O, 8.21; S, 5.48; Found: C, 75.87; H, 10.53.

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