

Acid-catalysed Formation of Naphthalenes from a β -Oxo-sulphoxide

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Summary Under mild conditions the β -oxo-sulphoxide (1) undergoes acid-catalysed rearrangement and cyclization to form naphthalenes.

β -OXO-SULPHOXIDES are known to be important intermediates in various organic syntheses^{1,2} and have been studied extensively.³ We report here the acid-catalysed formation of naphthalene derivatives from 3,4-dimethoxyphenethyl methylsulphinylmethyl ketone (1).

A solution of (1)† in ethyl acetate containing 1 equiv. of toluene-*p*-sulphonic acid was kept at room temperature. Ethyl acetate was evaporated off at 40°, and the residual oil was chromatographed on silica gel to give 2,3-dimethoxy-6-ethoxynaphthalene (2) [m.p. 144–146°; *m/e*, 232 (*M*⁺); λ_{\max} (EtOH), 318 and 332 nm], 2,3-dimethoxy-6-methylthionaphthalene (5) [m.p. 86–88°; *m/e*, 234 (*M*⁺); λ_{\max} (EtOH), 318 (shoulder), 330 and 340 nm], and 2,3-dimethoxy-6-hydroxynaphthalene (6) [*m/e*, 204 (*M*⁺); λ_{\max}

(EtOH), 320 and 333 nm; λ_{\max} (H⁺), 320 and 330 nm; λ_{\max} (OH⁻), 345 nm]. Structural assignments are based

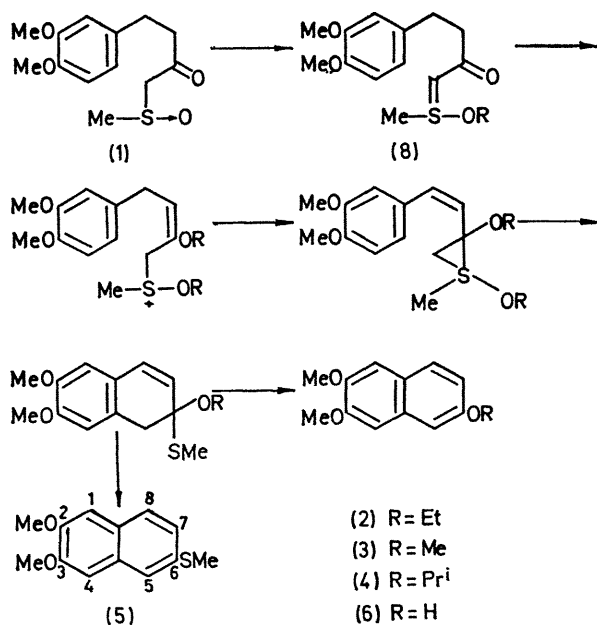
*Yields of naphthalenes obtained under various conditions**

	Naphthalene (%)				
	(2)	(3)	(4)	(5)	(6)
1	40			22	4
2		20		30	5
3			19.5	17	
4	36			24	5
5		23		55.5	14

* 1: TsOH (1 equiv.) in AcOEt, 36 h at room temperature, evaporated at 40°. 2: TsOH (1 equiv.) in AcOMe, 18 h. 3: TsOH (1 equiv.) in Me₂CHOH, 20 h. 4: MeSO₃H (1 equiv.) in EtOH, 20 h. 5: TsOH (0.5 equiv.), TsOMe (1 equiv.) in CH₂CH₂, 20 h.

mainly on n.m.r. and i.r. spectra. Chemical shifts [τ (CCl₄): (2) 2.55 (8-H), 3.10 (1-, 4-, 5-, 7-H); (5) 2.55 (8-H),

† Compound (1) was synthesised from ethyl 3,4-dimethoxyphenyl propionate and the dimsyl anion (MeSOCH₂⁻).



2-63 (5-H), 2-90 (7-H), and 3-15 (1,4-H)] and out of plane deformation bands [ν (Nujol): (2), 865 (isolated aromatic protons), and 855 cm^{-1} (two adjacent aromatic protons); (5), 870 (isolated aromatic protons), and 860 cm^{-1} (two adjacent aromatic protons)] of the aromatic protons show that these compounds are 2,3,6-trisubstituted naphthalenes.⁴ The structure of the thionaphthalene (5) was also confirmed by reduction with Raney nickel to 2,3-dimethoxynaphthalene (7).⁴ The reaction in methyl acetate, ethanol or propan-2-ol afforded the corresponding alkoxy-naphthalene.

Naphthalene formation probably occurs by O-alkylation of the sulphoxide (1) followed by acid-catalysed rearrangement and cyclization to the electron-donating aromatic nucleus as shown in the Scheme. An intermediate (8) [m/e , 298 (M^+), 105 [base peak, $\text{CH}=\text{S}(\text{Me})\text{OEt}$]; λ_{max} (EtOH), 286 nm; ν (Nujol), 1720 cm^{-1} ; τ (CCl_4), 3.23 (3H, aromatic), 5.25 (1H, vinyl)] was isolated and its spectral data suggest that because of the inductive effect of the alkoxy group (8) exists in the ylene and not the ylide form.⁵

Use of alkyl toluenesulphonate as an alkylating agent gave naphthalenes in >90% yield.

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⁴ A. Zweig, J. E. Lancaster, and M. T. Negia, *Tetrahedron*, 1967, **23**, 2577.

⁵ Cf. A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.