

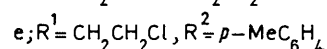
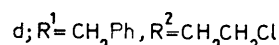
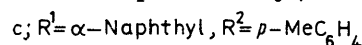
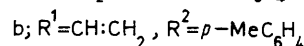
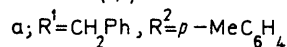
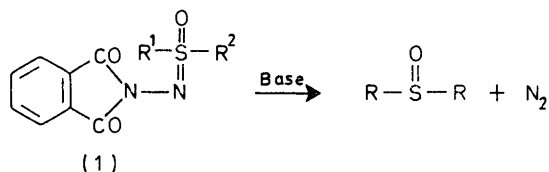
Stereochemistry and Reactivity in Interconversions of Three- and Four-co-ordinate Imino-derivatives of Sulphur †

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Optically pure sulphoxides have been converted into *N*-phthalimidodisulphoximides by treatment with *N*-aminophthalimide and lead tetra-acetate. Sulphoxides are regenerated in high yields and optical purities on treatment with sodium ethoxide or hydrazine in ethanol and it is suggested that each step in these two-step cycles occurs with retention of configuration at sulphur. No attack occurs at the carbon-carbon double bond in formation of the sulphoximide from *p*-tolyl vinyl sulphoxide.

Reactions of *S*-vinyl- and of *S*- β -substituted-ethyl-sulphimides have been briefly investigated in a qualitative evaluation of the activating effects of the sulphonylimino-sulphur group on elimination and addition reactions.

THE reactivity and stereochemistry of simple imino-derivatives of sulphur has been widely investigated.¹ Much attention has been focused on the interchange of ligands at sulphur and rather less on the effect of imino-sulphur groups on reactivity at more distant molecular sites. In this paper we report on two aspects of imino-sulphur chemistry: first, the stereochemistry of formation of *N*-phthalimidodisulphoximides (1) from optically active sulphoxides and the subsequent regeneration of the sulphoxides; and secondly, the effect of the three-co-ordinate imino-sulphur group in sulphimides on the reactivity of leaving groups situated β to it and upon the electrophilic reactivity of an adjacent carbon-carbon double bond.



Sulphoximides.—Several methods are available for the conversion of sulphoxides into sulphoximides. These include treatment with a sulphonyl azide and copper,² with hydrazoic acid,³ and with a sulphonamide together with lead tetra-acetate and a mild base such as triethylamine.⁴ A particularly simple procedure has been reported by Rees and his collaborators⁵ which involves treatment of the sulphoxide with *N*-aminophthalimide

† Part of this work has been reported in a preliminary communication: S. Colonna and C. J. M. Stirling, *Chem. Comm.*, 1971, 1591.

¹ T. R. Williams, R. E. Booms, and D. J. Cram, *J. Amer. Chem. Soc.*, 1971, **93**, 7338.

² D. J. Cram, J. Day, D. R. Rayner, D. M. von Schrittz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, 1970, **91**, 7369.

³ R. Fusco, and A. Tenconi, *Chimica e Industria*, 1965, **1**, 61.

and lead tetra-acetate in dichloromethane; a synthesis which probably involves nitrene intermediates.⁶ We have now applied this procedure to a number of sulphoxides including three optically active compounds; the results are in the Table; yields are excellent and the sulphoximides obtained from the active sulphoxides are themselves optically active. Particularly interesting in this respect is the conversion of optically active *p*-tolyl vinyl sulphoxide⁷ into the $\alpha\beta$ -unsaturated sulphoximide (1b). No competing reactions were observed which could have been associated with the carbon-carbon double bond which, in this case, is susceptible to electrophilic,⁷ nucleophilic,⁸ and radical⁹ addition. Nitrene addition is a familiar reaction type for alkenes.¹⁰

The *N*-phthalimidodisulphoximides (e.g. *S*-*p*-tolyl-*S*-vinyl-) were stable to concentrated sulphuric acid for short periods (ca. 30 min) at room temperature; conditions in which *N*-*p*-tolylsulphonylsulphoximides are readily hydrolysed² to the simple sulphoximides. With longer reaction times, however, decomposition occurred. Treatment of the *N*-phthalimidodisulphoximides with sodium ethoxide or with hydrazine in ethanol, however, regenerated the sulphoxide with concurrent formation, in the case of sodium ethoxide, of the half-ester of phthalic acid. In the case of the *S*-vinylsulphoximide, the adduct with ethanol, 2-ethoxyethyl *p*-tolyl sulphoxide, was isolated as the regeneration product. When optically active sulphoximides were used, the sulphoxides were obtained in good yield and with high optical purity (Table). These observations established that both formation of the sulphoximides from the sulphoxides and their regeneration occurs with high stereospecificity. Clearly, in this two-reaction cycle, both reactions occur with retention or both with inversion of configuration. We favour double retention in the cycle; Cram and his co-workers,² have shown that treatment of methyl *p*-tolyl sulphoxide with toluene-*p*-sulphonyl

⁴ T. Ohashi, K. Matsunaga, M. Okalbara, and S. Koniori, *Synthesis*, 1971, **96**, and references cited.

⁵ C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1972, 77.

⁶ D. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1230.

⁷ D. J. Abbott and C. J. M. Stirling, *Chem. Comm.*, 1971, 472.

⁸ D. J. Abbott, S. Colonna, and C. J. M. Stirling, *Chem. Comm.*, 1971, 471.

⁹ C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957.

¹⁰ H. Kwart and A. A. Khan, *J. Amer. Chem. Soc.*, 1967, **89**, 1951.

Reaction of N-Phthalimidodisulphoximides with Bases.—(a) *With sodium ethoxide in ethanol.* Sodium ethoxide (0.15 mol) was added to a stirred solution of the sulphoximide (1c) (0.01 mol) in ethanol (100 ml). The mixture was stirred for 4 h, poured into water, acidified with dilute sulphuric acid, and extracted with chloroform. The organic layer was washed with water and evaporated. The residue, on treatment with ether–light petroleum (b.p. 40–60°) gave, after filtration, (–)- α -naphthyl *p*-tolyl sulphoxide (96%), m.p. and mixed m.p. 135–136°, $[\alpha]_D^{25}$ –398° (*c* 1, acetone) (lit.,¹⁴ –414°). Evaporation of the filtrate yielded monoethyl phthalate (80%) as an oil whose spectral properties (i.r., n.m.r.) were identical with those of an authentic sample.¹⁸

The reaction was repeated in a two-necked flask attached to a vacuum line. The solution of the sulphoximide in ethanol was degassed by freeze–thaw cycles and oxygen was admitted at 1 atm. with a levelling bulb. Degassed ethanolic sodium ethoxide was added by syringe through a serum cap and after 4 h, samples of the gas space were removed by syringe and shaken in a gas burette with alkaline pyrogallol. The yield of nitrogen calculated from seven determinations was $100 \pm 2\%$. It was confirmed that the products of the reaction under oxygen were as obtained from reactions under air.

Separate experiments showed that had hydrazine been liberated in the reactions, even in small amounts, it could have been isolated as the *NN*-dibenzoyl derivative by addition of benzoyl chloride and triethylamine to the reaction mixture. None was detected in this way.

(b) *With hydrazine and ethanol.* Hydrazine hydrate (0.04 mol) was added to a stirred suspension of the sulphoximide (1c) (0.001 mol) in ethanol (10 ml). After 30 min at 40°, the mixture was diluted with ether (100 ml), water was added, and the organic layer separated, dried, and evaporated to give α -naphthyl *p*-tolyl sulphoxide (80%), m.p. and mixed m.p. 135°, $[\alpha]_D^{25}$ –398° (*c* 1, acetone).

Reactions with the other sulphoximides were carried out similarly.

Preparation of Sulphimides.—2-Chloroethyl *p*-tolyl sulphide (0.01 mol) in ethanol (20 ml) was added dropwise, with stirring, to chloramine τ (0.015 mol) in ethanol (100 ml). After 20 h, water (100 ml) was added to precipitate *S*-2-chloroethyl-*S*-*p*-tolyl-*N*-*p*-tolylsulphonylsulph-

imide (2b) (60%), m.p. 125° (from ethanol) (Found: C, 54.1; H, 5.3; N, 4.1. $C_{16}H_{18}ClNO_2S_2$ requires C, 54.0; H, 5.1; N, 3.9%).

S-Benzyl-*S*-2-chloroethyl-*N*-*p*-tolylsulphonylsulphimide (2a) (67%), m.p. 135° (from ethanol) was obtained in a similar way (lit.,¹⁹ m.p. 133–134°).

Elimination Reactions with S-2-Halogenoethylsulphimides.—The *S*-*p*-tolylsulphimide (2b) (1.4 g) in toluene (170 ml) was treated with triethylamine (0.3 g). After 24 h at 25°, the mixture was kept at 50° for 30 h and the precipitate of triethylammonium hydrochloride was filtered off. Evaporation of the solvent gave *S*-*p*-tolyl-*S*-vinyl-*N*-*p*-tolylsulphonylsulphimide (3b) (87%), m.p. 129° (from methanol) (Found: C, 60.1; H, 5.2; N, 4.4. $C_{16}H_{17}NO_2S_2$ requires C, 60.2; H, 5.3; N, 4.4%).

S-Benzyl-*S*-vinyl-*N*-*p*-tolylsulphonylsulphimide (75%), m.p. 127°, was similarly obtained (Found: C, 59.8; H, 5.3; N, 4.3. $C_{16}H_{17}NO_2S_2$ requires C, 60.2; H, 5.3; N, 4.4%).

*Formation of S- β -Substituted-ethyl-*S*-*p*-tolyl-*N*-*p*-tolylsulphonylsulphimides.*—(a) The *S*-vinylsulphimide (3b) (0.01 mol) in ethanol (60 ml) was treated with ethanolic sodium ethoxide (0.03 mol). After 24 h, the mixture was poured into acidified saturated brine and extracted with chloroform. Evaporation of the extract gave *S*-2-ethoxyethyl-*S*-*p*-tolyl-*N*-*p*-tolylsulphonylsulphimide (100%), m.p. 114° (from ethanol) (Found: C, 59.3; H, 6.4; N, 3.9. $C_{18}H_{23}NO_3S_2$ requires C, 59.2; H, 6.3; N, 3.8%).

(b) The *S*-2-chloroethylsulphimide (2b) (0.01 mol) in ethanol (60 ml) was treated with piperidine (0.05 mol). After 6 h at 50°, the mixture was evaporated and extraction of the residue with ether gave *S*-2-piperidinoethyl-*S*-*p*-tolyl-*N*-*p*-tolylsulphonylsulphimide (4b) which readily formed an unstable carbonate (Found: C, 56.1; H, 5.7; N, 6.1. $C_{22}H_{30}N_2O_2S_2$ requires C, 56.5; H, 6.4; N, 6.0%). This product was converted into the *picrate* (98%), m.p. 128° (from ethanol) (Found: C, 50.1; H, 5.0; N, 11.8. $C_{20}H_{25}N_4O_8S$ requires C, 50.0; H, 5.2; N, 11.6%).

The same product (4b) was obtained in quantitative yield by direct addition of piperidine to the *S*-vinylsulphimide (3b).

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¹⁸ K. von Auwers and A. Heinze, *Ber.*, 1919, **52**, 600.

¹⁹ T. P. Dawson, *J. Amer. Chem. Soc.*, 1947, **69**, 968.