Synthesis and Configuration of a Chiral Sulphimide and Sulphodiimide

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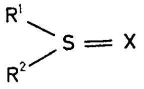
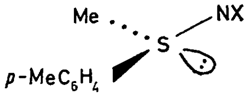
Summary (+)-*S*-Methyl-*S*-*p*-tolylsulphimide and (−)-*N*-*p*-toluenesulphonyl-*S*-methyl-*S*-*p*-tolylsulphodiimide are prepared and their chiralities established.

Sulphimides (**1a**), isoelectronic with sulphoxides (**1b**) and methylenesulphuranes (**1c**), are mostly reactive species, difficult to prepare and purify. However, we have found that *S*-methyl-*S*-*p*-tolylsulphimide (**1a**; R^1 = Me, R^2 = *p*-MeC_6H_4), m.p. 20°C, prepared in 70% yield *via* its mesitylenesulphonate† (m.p. 112 °C) in analogy with a recently described procedure,[1] is reasonably stable towards hydrolysis. Its salt, produced with (+)-α-bromo-π-camphorsulphonic acid afforded, after five recrystallizations from water, a single diastereoisomer,† m.p. 203—204 °C, $[\alpha]_D^{25}$ + 57° (*c* 1·0, H_2O), from which (*R*)-*S*-methyl-*S*-*p*-tolylsulphimide (**2a**),†[2] $[\alpha]_D^{25}$ + 59° (*c* 1·7, MeOH), was liberated, as shown from its quantitative conversion into enantiomerically homogeneous (*R*)-*N*-*p*-toluenesulphonyl-*S*-methyl-*S*-*p*-tolylsulphimide (**2b**), m.p. 124—125 °C, $[\alpha]_D^{25}$ + 267° (*c* 1·0, Me_2CO).[3] A chiral sulphimide (**1a**) has thus been produced.

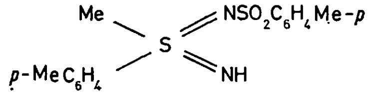


(1a) X = NH
(1b) X = O
(1c) X = CH_2

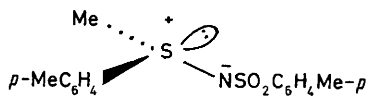


(2a) X = H
(2b) X = $SO_2C_6H_4Me$-*p*

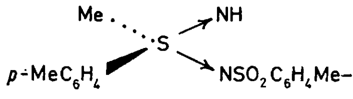
Conversion of racemic (**1a**; R^1 = Me, R^2 = *p*-MeC_6H_4), or its salts, into *N*-*p*-toluenesulphonyl-*S*-methyl-*S*-*p*-tolylsulphodiimide (**3**),† m.p. 142—143 °C, was carried out using chloramine-T in liquid ammonia, by a modification of a recently described procedure.[4] Analogously, (**2a**) gave the laevorotatory enantiomer of (**3**),† m.p. 105—108 °C, $[\alpha]_D^{25}$ −67° (*c* 2·0, Me_2CO). Treatment of the latter with HNO_2 ($MeOH-H_2O$; 25 °C; 25 min), followed by non-fractional work-up, yielded (*S*)-*N*-*p*-toluenesulphonyl-*S*-methyl-*S*-*p*-tolylsulphimide (**4**), m.p. 122–124 °C, $[\alpha]_D^{25}$ − 225° (*c* 1·0, Me_2CO), corresponding to an enantiomeric purity of 84%.



(3)



(4)



(5)

On the assumption, supported by analogy from sulphoximide cases,[3,5] that the conversion (**3**) → (**4**) proceeds with retention, (−)-(**3**) possesses the (*S*)-configuration (**5**). Sulphodiimides, of defined chirality, have thus become available for further studies. Attempts to resolve racemic *N*-*p*-toluenesulphonyl derivatives of alkyl, aralkyl, and dialkylsulphodiimides through salt formation with chiral sulphonic acids were unsuccessful.[6]

(*Received, 22nd July* 1975; *Com.* 835.)

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† Combustion analyses of these compounds gave values within 0·2% of theory.

[1] Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Letters*, 1972, 4137.

[2] (**2a**) possessed chiroptical properties [λ_{max} (EtOH) 230 nm; c.d. θ + 30,000 (vanishing on protonation $n \rightarrow \pi^*$)] similar to those of the corresponding sulphoxide [*R*-(**1b**), R^1 and R^2 = Me and *p*-MeC_6H_4]; see K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmonds, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, 1965, **87**, 1958.

[3] D. J. Cram, J. Day, D. R. Rayner, D. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, 1970, **92**, 7369.

[4] N. Furukawa, T. Omata, and S. Oae, *J.C.S. Chem. Comm.*, 1973, 590.

[5] B. W. Christensen, *J.C.S. Chem. Comm.*, 1971, 597.

[6] The resolution of *N*-*p*-toluenesulphonyl-*S*-ethyl-*S*-methylsulphodiimide by means of (+)-camphor-β-sulphonic acid has been reported; F. Müller-Kalben, Diplomarbeit, University of Bonn, 1969.