Asymmetric Oxidation of Bivalent Organic Sulphur Compounds. Absolute Configuration of Thiolsulphinate and Sulphinate Esters obtained by Stereoselective Oxidation of Disulphides and Sulphenate Esters

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OXIDATION of organic sulphides by asymmetric per-acids generally leads to mildly stereoselective synthesis of sulphoxides.[1] The direction of asymmetric induction has been widely discussed and is still controversial.[2] More recently two reports have appeared simultaneously from our[3] and Kice's[4] laboratories dealing with the stereoselective oxidation of aryl disulphides with (+)-monopercamphoric acid to give the optically active aryl arenethiolsulphinates.

Here we report that this stereoselective oxidation can be extended to other bivalent sulphur compounds, *i.e.*, sulphenic esters and sulphenamides yield optically active sulphinate esters and sulphinamides, respectively. We also give the absolute configuration and optical yield of the thiolsulphinate and sulphinate esters thus obtained.

p-*Tolyl toluene*-p-*thiolsulphinate*. *p*-Tolyl disulphide was oxidized with (+)-monopercamphoric acid at 0° in $CHCl_3$ to give *p*-tolyl toluene-*p*-thiolsulphinate. The crude material had m.p. 89—92°, $[\alpha]_D^{25}$ +4·4 (*c* 2, chloroform). After crystallization, m.p. 105—106° $[\alpha]_D^{25}$ $+7{\cdot}6$ (*c* 2, chloroform). Treatment of the latter with benzylmagnesium chloride in ether[5] gave benzyl *p*-tolyl sulphoxide (40% yield) m.p. 140—142°, $[\alpha]_D^{25}$ $-3{\cdot}6$ (*c* 2, acetone). From the work of Stirling, the sulphoxide is deduced to have the (*S*)-configuration and an optical purity of 1·4%.[6] Since the Grignard reaction is highly stereospecific and occurs with inversion of the configuration,[7] then the (±)-thiolsulphinate has the (*R*)-configuration and an optical purity of 1·4%. This result conforms with the rule given by Montanari *et al.*[1c] for phenylalkyl sulphides, providing SAr and Ar are regarded as the "small" and "large" group respectively, which appears reasonable. The minimum optical yield in the asymmetric oxidation of the disulphide, calculated from the rotation of the raw thiolsulphinate, is 1%.

*Methyl toluene-*p*-sulphinate.* Methyl toluene-*p*-sulphenate,[8] b.p. 70—72°/0·6 mm., was oxidized in chloroform at −25° to give methyltoluene-*p*-sulphinate $[\alpha]_D^{25}$ $+2{\cdot}16$ (c 6·94, chloroform); after distillation, $[\alpha]_D^{25}$ $+2{\cdot}33$ (*c* 8·13, chloroform) b.p. 82°/0·07 torr. (lit.,[9] b.p. 68°/0·001 torr). Treatment of the sulphinate ester $[\alpha]_D^{25}$ $+2{\cdot}16$ with benzylmagnesium chloride in ether gave *p*-tolyl benzyl sulphoxide $[\alpha]_D^{25}$ $-5{\cdot}5$ (*c* 2·8, acetone), corresponding to an optical purity of 2·2%. This value also sets the lower limit of stereoselectivity in the asymmetric oxidation of the sulphenate ester and establishes that the absolute configuration of the resulting methyltoluene-*p*-sulphinate is (*R*).[6] This conforms with the Montanari rule [1c] if, as is reasonable, the *p*-tolyl group is bulkier than the methoxyl one.

*Toluene-*p*-sulphino-piperidide.* Toluene-*p*-sulphenopiperidide,[10] b.p. 110—112°/0·07 mm., was oxidized in chloroform at −20°. The resulting toluene-*p*-sulphinopiperidide (m.p. 64—65°) had $[\alpha]_D^{25}$ $-1{\cdot}14$ (*c* 8, chloroform). Treatment of the latter with benzylmagnesium chloride did not afford any appreciable yield of sulphoxide and therefore the correlation of configuration could not be established through the usual route.

An attempt to determine the correlation was made with the (±)-methyl toluene-*p*-sulphinate ester, which was heated under reflux with piperidine in heptane for 3 hr. From the evaporated reaction mixture, the toluene-*p*-sulphinopiperidide was obtained in 50% yield. This however, was optically inactive. Apparently the reaction conditions induce racemization either of the starting ester or the amide product. Other routes are being investigated to establish the absolute configuration.

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