

OPTICALLY ACTIVE O-ALKYL ALKYLsulPHINATES

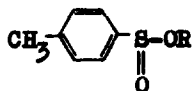
M. Mikołajczyk and J. Drabowicz

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,

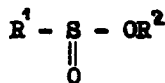
Department of Organic Sulphur Compounds, Łódź 40, Poland

(Received in UK 21 April 1972; accepted for publication 3 May 1972)

Optically active sulphinic esters having optically active alkoxy moieties (especially the menthoxy group) are the main source of optically active sulfoxides and occupy a central position in the study of organic sulphur stereochemistry¹. However, the synthesis of optically active sulphinic esters in which the sulphur atom is the sole chirality centre has received a very little attention. Optically active alkyl *p*-toluenesulphinates (I) were obtained in a very low state of optical purity for the first time by Phillips² in 1925 from (-)-menthyl *p*-toluenesulphinate by transesterification and then by Fava³ who carried out asymmetric oxidation of methyl *p*-toluenesulphinate with (+)-monoperoacetic acid.



(I), R=Me, Et, Buⁿ



(II), R¹ and R²= alkyl

Here we report that simple O-alkyl alkylsulphinates (II) can be readily resolved into optically active forms via β -cyclodextrin inclusion compounds. This resolution technique first introduced by Cramer⁴ was recently successfully applied to the resolution of O-alkyl alkylphosphonates⁵ and chiral sulfoxides⁶.

Since the sulphinates (II) are slowly hydrolysed by water^{*}, their

* we have also taken into account the fact that cyclodextrins act as hydrolysis catalysts⁷. Probably for this reason our attempt to resolve O-ethyl methylsulphinate was unsuccessful.

partial resolution was carried out according to the Benschop's procedure by mixing 5-6-molar excess of ester (II) with β -cyclodextrin in the presence of a small amount of water (2 ml). After 24 h the mixture was treated with ether and filtered to give the inclusion complex which was then decomposed in a methylene chloride-water mixture. The organic layer was washed with a 5% aqueous sodium carbonate solution in order to remove small acidic impurities. Then it was dried and on evaporation it gave optically active ester (II). The non-included sulphinate (II) having the opposite rotation sign was recovered from the ether filtrate. Optical rotations, optical purities and absolute configurations of the resolved sulphinates (II) are collected in the Table 1.

Table 1
Stereospecific inclusion of $R^1S(O)OR^2$ in β -CD

Sulphinate (II)		Non-included			Included			
R^1	R^2	$[\alpha]_{589}^a$ (°)	opt. pur. ^b (%)	abs. conf. ^b	$[\alpha]_{589}^a$ (°)	opt. pur. ^b (%)	abs. conf. ^b	Molar ratio ^c β CD:R
a	Me Pr ⁿ	- 0.25(15.0)	0.15	S	+ 2.38(3.3)	1.40	R	1:1
b	Me Pr ⁱ	+18.52(3.3)	7.80	R	-165.91(2.5)	70.20	S	1:1
c	Me Bu	- 1.34(11.3)	1.30	S	+ 10.10(4.9)	8.70	R	2:1
d	Me Bu ^t	+ 6.72(8.2)	4.10	R	- 19.90(1.0)	12.40	S	4:3
e	Me Cp ^d	- -	-	-	+ 1.10(10.4)	0.40	R	1:1
f	Me Np ^d	- 0.50(10.3)	0.40	S	+ 5.16(3.9)	4.20	R	1:1
g	Pr ⁱ Me	- 3.10(14.3)	0.95	S	+ 14.40(7.3)	4.20	R	1:1
h	Pr ⁱ Pr ⁱ	+ 0.66(10.3)	0.70	S	- 1.87(10.2)	2.10	R	1:1

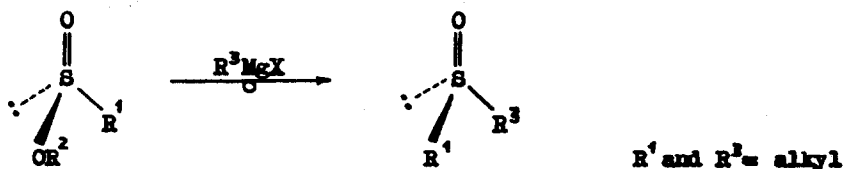
^a All rotation refer to solvent ethanol ^b See Table 2 for calculation of optical purities and determination of absolute configurations. ^c Based on elemental analyses ^d Cp = cyclopentyl; Np = neopentyl

The data in Table 1 show that the best resolution was achieved in the case of O-isopropyl methylsulphinate (IIb). The included ester (IIb) had $[\alpha]_D -165.91^\circ$ which corresponds to 70.2% of optical purity. The non-included residue had $[\alpha]_D +18.52^\circ$ (optical purity 7.8%). After four consecutive

inclusions its rotation increased to $[\alpha]_D +76.5^\circ$ (optical purity 32.5%). It is of interest that the highest stereospecific inclusion into β -cyclodextrin was observed by Benschop⁵ in the case of *O*-isopropyl methylphosphenate which has the structure very similar to that of ester (IIb).



Optical purities and absolute configurations of optically active sulphinates (II) obtained in the present work were determined chemically by means of their stereospecific conversion into known sulphoxides (methyl *n*-propyl sulphoxide⁸ and methyl iso-propyl sulphoxide⁹) assuming that the Grignard reaction proceeds with full inversion of configuration at the sulphur atom. The results of these determinations are shown in Table 2.



Considering our configurational assignments to sulphinates (II) it is noteworthy that the chirality at sulphur in all (-)-*O*-alkyl methylsulphinates is *S*. Further studies on the relation between the chirality at sulphur in sulphinates (II) and their rotation sign are in progress.

Table 2

Optical purities and absolute configurations of $R^1S(O)OR^2$, determined by stereospecific conversion into $R^1S(O)R^3$

Sulphinate (II)				Sulphoxide				
R^1	R^2	$[\alpha]_{589}^a$ (c)	abs. conf.	R^1	R^3	$[\alpha]_{589}^a$ (c)	opt. pur. (%)	abs. conf.
a Me	Pr^N	- 0.52(4.6)	S	Me	Pr^N	+ 0.44(10.2)	0.30	S
b Me	Pr^i	+47.20(3.3)	R	Me	Pr^N	-27.14(3.1)	20.70	R
c Me	Bu^i	- 1.34(11.3)	S	Me	Pr^N	+ 1.58(11.5)	1.30	S
d Me	Bu^t	+20.00(1.0)	R	Me	Pr^N	-16.24(10.5)	12.40	R
e Me	Cp^b	+ 0.99(10.4)	R	Me	Pr^N	- 0.33(5.0)	0.35	R
f Me	Np^b	- 1.60(4.5)	S	Me	Pr^N	+ 1.84(24.8)	1.30	S
g Pr^i	Me	- 3.10(14.3)	S	Pr^i	Me	- 1.40(19.2)	0.95	R
h Pr^i	Pr^i	+ 0.66(10.3)	S	Pr^i	Me	- 0.72(10.3)	0.45	R

^a All rotations refer to solvent ethanol ^b Cp = cyclopentyl; Np = neopentyl

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