Synthesis of Optically Active Sulphonium Salts from Optically Active Sulphoxides

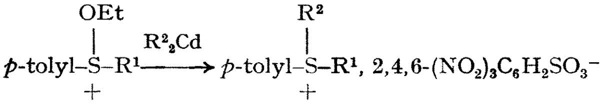
By KENNETH K. ANDERSEN†

(*Department of Organic Chemistry, Technical University of Denmark,* DK-2800 *Lyngby, Denmark*)

Summary Optically active sulphonium salts have been synthesized by treatment of ethoxy-sulphonium salts, derived from optically active sulphoxides, with alkyl-cadmium reagents.

WE report the synthesis of optically active sulphonium salts, formerly accessible only by resolution, from optically active sulphoxides. Ethylation of (*R*)-methyl *p*-tolyl sulphoxide, $[\alpha]^{25}_{D}$ + 145° (*c* 1·5, acetone) with triethyl-oxonium tetrafluoroborate in methylene chloride[1] followed by reaction for 3 h with ethereal Et_2Cd gave, after isolation as previously described,[2] (—)-ethyl methyl *p*-tolyl sulphonium bromide which was converted into (—)-ethyl methyl *p*-tolyl sulphonium 2,4,6-trinitrobenzenesulphonate [(—)-(I)], m.p. 199—200° (decomp.) $[\alpha]^{22}_{D}$ — 5·6° (*c* 0·4, acetone) (57%).‡

The structure of (—)-(I) was verified by i.r. (KBr): 1528 and 1349 (NO_2), 1247 (SO_3^-), and 806 cm^{-1} (*p*-substituted phenyl); and n.m.r.: δ [$(CD_3)_2SO$; Me_4Si] δ 1·18 (3H, *J* 7·1 Hz, *Me*CH$_2$), 2·43 (3H, s, Ar*Me*), 3·28 (3H, s, *Me*S$^+$), 3·64 (2H, m, C*H*$_2$S$^+$), 7·75 (4H, q, Ar*H*), and 8·87 (2H, s, Ar*H*) p.p.m. spectra. T.l.c. analysis revealed no contaminating sulphoxide. After several recrystallizations from aqueous acetone the rotation of (—)-(I) was $[\alpha]^{22}_{D}$ —8·0° while crystalline material obtained from the mother liquors was less leavorotatory. Therefore, (—)-(I), as obtained from the reaction, was partly racemic. Since the starting sulphoxide was optically pure and (—)-(I) is optically stable to the conditions of isolation and purification, racemization must have occurred in the reaction mixture.



$$p\text{-tolyl-}\overset{OEt}{\underset{+}{S}}\text{-R}^1 \xrightarrow{R^2_2Cd} p\text{-tolyl-}\overset{R^2}{\underset{+}{S}}\text{-R}^1,\ 2,4,6\text{-}(NO_2)_3C_6H_2SO_3^-$$

(I) R^1 = Me; R^2 = Et
(II) R^1 = Bu; R^2 = Me

Similarly, (+)-butyl methyl *p*-tolyl sulphonium 2,4,6-trinitrobenzenesulphonate, (+)-(II), $[\alpha]^{22}_{D}$ + 7·6° (*c* 0·3, acetone), m.p. 149—150°,‡ i.r (KBr): 1534 and 1346 (NO_2), 1242 (SO_3^-), and 806 cm^{-1} (*p*-substituted phenyl); n.m.r. [$(CD_3)_2SO$] δ 0·85 (3H, m, *Me*CH$_2$), 1·42 (4H, m, C*H*$_2$·C*H*$_2$), 2·43 (3H, s, Ar*Me*), 3·30 (3H, s, *Me*S$^+$), 3·65 (2H, m, C*H*$_2$S$^+$), 7·72 (4H, q, Ar*H*), and 8·80 (2H, s, Ar*H*) p.p.m., was obtained (74%) from the reaction of *O*-ethyl (*R*)-butyl *p*-tolyl sulphoxide, $[\alpha]^{22}_{D}$ +188° (*c* 1·1, acetone), with ethereal Me_2Cd during 40 h at room temperature. Racemic (II) was isolated upon repeated recrystallization of (+)-(II) from aqueous acetone while the crystals from the mother liquor showed an increased rotation. Apparently the longer reaction time (40 *vs.* 3 h) allowed more racemization to occur in the synthesis of (II) compared to (I), perhaps *via* reversible ylide formation in the basic mixture. Sulphonium ylides are known to racemize more rapidly than sulphonium salts by pyramidal inversion.[3]

Both (—)-(I) and (+)-(II) lost optical activity slowly in acetone solution at 40°; *e.g.*, $t_{\frac{1}{2}}$ (I) = *ca.* 26 h.

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† *Present address:* Department of Chemistry, University of New Hampshire, Durham, N. H. 03824.

‡ Carbon and hydrogen analyses were within 0·2% of theory.

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