

Absolute Configuration of Methylethylpropylsulphonium Ion

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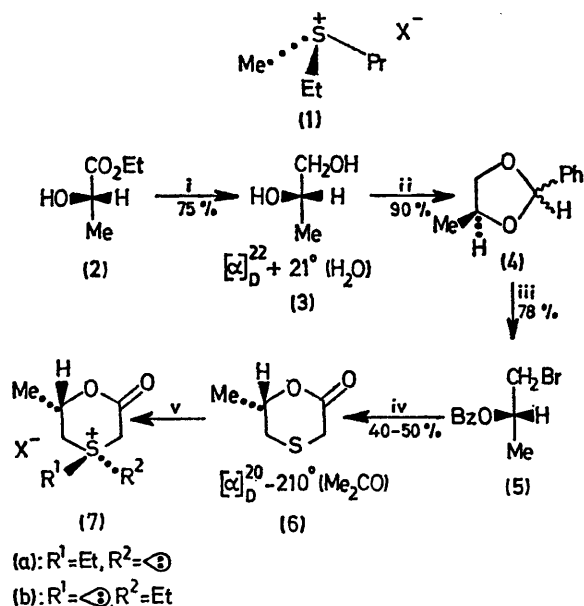
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Summary The absolute configuration of methylethylpropylsulphonium ion has been established by chemical correlation with lactic acid through an intermediate, stereochemically identified by X-ray analysis.

CHIRAL trialkylsulphonium ions, first prepared 75 years ago,¹ have remained configurationally unidentified. We report

the absolute configuration of methylethylpropylsulphonium ion (1), the simplest representative of its class, which supplements the recent allocation of specified chirality to dialkylarylsulphonium salts.²

S-Ethylation of (*S*)- β -thia- δ -caprolactone (6),[†] produced from (*S*)-ethyl lactate (2), $[\alpha]_D^{20} - 11.2^\circ$ (neat), through the unexceptional sequence (2) \rightarrow (3)³ \rightarrow (4)⁴ \rightarrow (5)⁵ \rightarrow (6)⁶ (Scheme 1), afforded a ca. 1:1 mixture of the diastereomeric sulphonium salts (7a) and (7b), $[X^- = \text{TNBS}^-$ (2,4,6-trinitrobenzenesulphonate)]. One of these, obtained in pure

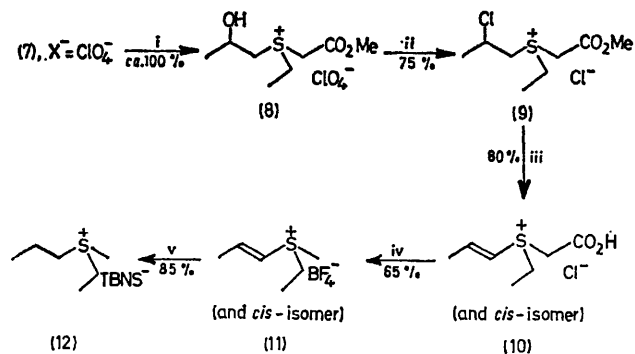


SCHEME 1. Reagents: i, LiAlH₄, THF; ii, PhCHO, TsOH, C₆H₆; iii, *N*-bromosuccinimide, CCl₄, BaCO₃, *hν*, heat; iv, (a) HS-CH₂CO₂H, NaOMe, MeOH, (b) HCl, (c) IR 120/H⁺-resin; v, Et₃O⁺BF₄⁻, CH₂Cl₂.

[†] Throughout this study, ¹H n.m.r. spectra served to confirm the proposed structures and establish the composition of mixtures.

[‡] Combustion analyses of these compounds were within 0.2% of theory.

[§] Corrected for a small (+0.09°) residual rotation, surviving total racemization of (12) in MeCN at 65°.



SCHEME 2. Reagents: i, (a) NaOMe, MeOH (9 min), (b) HCl; ii, (a) ClO₄⁻ \rightarrow Cl⁻, (b) SOCl₂, MeNO₂; iii, (a) NaOH (2 min), (b) HCl; iv, (a) Cl⁻ \rightarrow BF₄⁻, (b) Bu₃N, Me₂CO, heat, (c) HCl; v, (a) H₂, Pd-C, MeOH, 122 atm, (b) H⁺ TNBS⁻.

form by several recrystallizations, $[\alpha]_D^{20} - 63.4^\circ$ (c 2.5, MeCN), was converted, as its perchlorate, under carefully selected conditions, into the trialkylsulphonium salt, (12),[‡] $[\alpha]_D^{20} + 1.18 \pm 0.02^\circ$ (c 18.1, MeCN),[§] through the sequence (7) \rightarrow (12) (Scheme 2). A specimen of (+)-(12), produced

by resolution of the racemate with α -bromo- π -camphor-sulphonic acid, followed by anion exchange, had $[\alpha]_D^{20} + 1.06 \pm 0.02^\circ$ (c 20.1, MeCN).

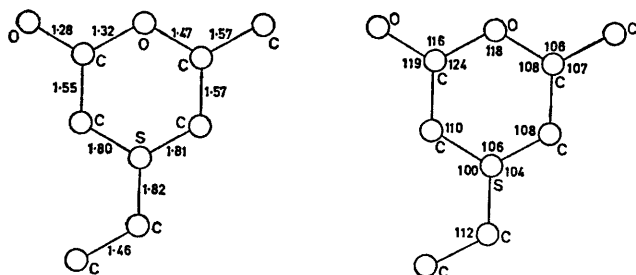


FIGURE 1. Bond distances and angles in compound (7).

Model studies, performed on pure, racemic specimens of (7a) and (7b),[‡] showed that the reactions (7) \rightarrow (8) and (8) \rightarrow (9), though accompanied by a certain equilibration of diastereoisomers, proceeded with predominantly unchanged configuration around sulphur. The probability of the reaction (9) \rightarrow (10) being accompanied by a major change in sulphur chirality is considered negligible under the conditions employed. Hence, the absolute configuration of (12) follows from that of the diastereomer of (7) employed in the correlation. Since extensive ^1H and ^{13}C n.m.r. studies did not permit unequivocal establishment of the latter, recourse was taken to single-crystal X -ray analysis, performed on the tetrafluoroborate of the appropriate racemic sulphonium salt.

X -Ray data were recorded on a Picker Facs 1 diffractometer using $\text{Cu-K}\alpha$ radiation. *Crystal data*: compound (7), $\text{C}_7\text{H}_{18}\text{O}_2\text{S}^+\text{BF}_4^-$, space group $P2_1/c$, $a = 6.908$, $b = 11.344$,

$c = 16.811 \text{ \AA}$; $\beta = 123.19^\circ$. 795 Reflections with $2\theta < 100^\circ$ ($> 4\sigma$ above background) were used in the structure determination. The structure was solved using sulphur as the heavy atom. The least-squares refinement proceeded

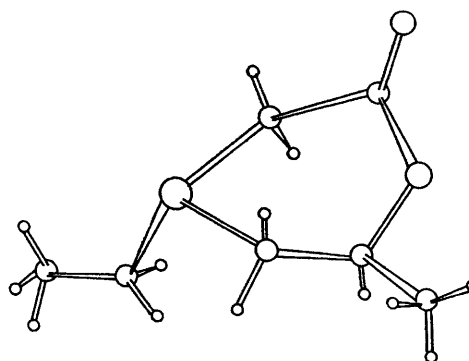


FIGURE 2. Spatial drawing of the sulphonium ion in compound (7a).

normally for the sulphonium ion whereas the anisotropic thermal parameters of the tetrafluoroborate ion shifted to large values. This indicates that disorder may exist. Thus the bond distances and angles of the sulphonium ion are normal (Figure 1) whereas the B-F distances vary between 1.22–1.49 \AA . At this stage the R -value is 0.13.

From the established *trans*-configuration (7a) (see Figure 2) follows the (*S*)-configuration for (+)-methyleneethylpropylsulphonium 2,4,6-trinitrobenzenesulphonate (1, $\text{X}^- = \text{TNBS}^-$).

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