Base-promoted Eliminations from Menthyl Arylsulphonates in Dimethyl Sulphoxide: A Correction

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THE observed tendency toward anti-elimination in highly dissociating solvents[1,2] and the effects of steric and torsional requirements on the mode of elimination[2,3] have led to a re-examination of base-promoted elimination from (—)-menthyl benzenesulphonate in dimethyl sulphoxide. Reaction of this ester with potassium t-butoxide at 20—25° has been reported to give nearly equal amounts of Δ^2- and Δ^3-menthenes.[4] Exclusive formation of 3-methylcyclohexene from *trans*-2-methylcyclohexyl tosylate under similar conditions in another study[5] seems to rule out an *E*1*cb* mechanism. Thus formation of Δ^3-menthene would require a *syn*-elimination, which was in fact postulated for eliminations from other substrates in dimethyl sulphoxide.[6]

Failure of *trans*-2-methylcyclohexyl tosylate to give any 1-methylcyclohexene and growing recognition of the importance of solvent and structural requirements have led to a re-examination of eliminations from the (—)-menthyl system. In the original study a total yield of 50% menthenes was obtained on distillation, but the isomeric ratio was determined indirectly, by racemization. A more rigorous examination, with direct analysis for the isomeric menthenes by g.l.c., has been carried out. A series of *p*-substituted (—)-menthyl benzenesulphonates was treated with potassium t-butoxide in dimethyl sulphoxide at 20—25° for 30 min. After addition of n-heptane the mixture was poured into cold water, separated, and the aqueous phase extracted with additional heptane. Combined organic phases were analyzed with a 12-m. column of 25% Carbowax 20M on 60/80 mesh Chromosorb P. At a column temperature of 160° authentic samples of Δ^2- and Δ^3-menthenes were clearly resolved.

In this study (—)-menthyl benzenesulphonate gave 62% Δ^2-menthene and no trace of Δ^3-menthene. Exclusive formation of the Δ^2-isomer was observed also with *para*-Me-, Br-, and Cl-substituents. The *p*-nitrobenzenesulphonate gave no menthenes with either potassium t-butoxide or sodium methoxide. While the source of error in the racemization has not been identified, it is clear that only Hofmann elimination occurs, presumably by an *anti*-route.

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[1] M. Pánková, J. Závada, and J. Sicher, *Chem. Comm.*, 1968, 1142; D. H. Froemsdorf, W. Dowd, and W. A. Gifford, *ibid.*, p. 449.
[2] J. Závada, M. Pánková, and J. Sicher, *Chem. Comm.*, 1968, p. 1145.
[3] J. L. Coke and M. P. Cooke, jun., *Tetrahedron Letters*, 1968, 2253.
[4] C. H. Snyder and A. R. Soto, *J. Org. Chem.*, 1964, **29**, 742.
[5] D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, 1965, **87**, 3983.
[6] C. H. Snyder and A. R. Soto, *J. Org. Chem.*, 1965, **30**, 673; *Tetrahedron Letters*, 1965, 3261.