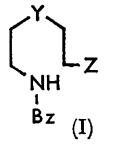
840. *Intramolecular Reactions of Amides. Part IV.*[1] *Promotion of Elimination by a β-Toluene-p-sulphonamido-group*

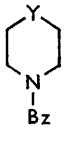
By A. Chambers and C. J. M. Stirling

Elimination rather than substitution predominates in reactions of β-toluene-*p*-sulphonamidoalkyl halides with ethanolic sodium ethoxide.

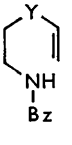
In Part III [1] it was reported that treatment of compounds of type (I) with sodium ethoxide under standardised conditions gave three types of product (II), (III), and (IV), derived, respectively, from cyclisation (internal substitution), β-elimination, and external substitution. The compounds (I; Y = NTs; Z = Cl, I, or OTs) gave negligible amounts of external substitution product (IV), but this was the major product from the compounds (I; Y = O or CH_2; Z = Cl, I, or OTs). A tentative explanation for this difference in behaviour was based upon adverse steric effects towards external substitution encountered in the preferred conformations of the sulphonamides. This suggestion has now been examined with simpler compounds and found to be unnecessary.



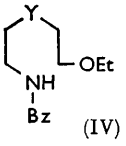
(I)



(II)



(III)



(IV)

$Ts \cdot NMe \cdot CH_2 \cdot CH_2Z$ (V)

$Ts \cdot NMe \cdot CH{:}CH_2$ (VI)

$[Ts = p\text{-}Me \cdot C_6H_4 \cdot SO_2]$

The series of compounds (V; Z = Cl, I, and OTs) was obtained from the alcohol (V; Z = OH). When these were individually treated with sodium ethoxide (0·05M-amide in ethanolic N-sodium ethoxide at 78°), the olefin (VI) was obtained from the chloride and

[1] Part III, C. J. M. Stirling, *J.*, 1962, 3676.

iodide in yields of 90 and 94%, respectively. Only traces of the ethoxy-compound (V; Z = OEt) were obtained. The toluene-*p*-sulphonate (V; Z = OTs) gave 31% of olefin and 57% of the ethoxy-derivative. It is thus clear that a β-toluene-*p*-sulphonamido-group favours elimination *versus* substitution to a much greater extent [1] than a β-alkoxy- or β-methylene group and that it is not necessary to invoke conformational effects to account for the observations reported in Part III. The lower proportion of elimination observed when the leaving group is toluene-*p*-sulphonyloxy is in accord with previous results [1] and with other observations.[2]

By contrast, *N*-2-chloroethylarenesulphonamides, $Ar{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2Cl$, yield arene-sulphonylaziridines under comparable conditions.[3,4] In certain circumstances, these aziridines subsequently give *N*-2-ethoxyethylarenesulphonamides but not, apparently, *N*-vinylsulphonamides.

Experimental

N-*Methyl*-N-2-*toluene*-p-*sulphonyloxyethyltoluene*-p-*sulphonamide*.—*N*-2-Hydroxyethyl-*N*-methyltoluene-*p*-sulphonamide [5] (14·5 g.), in dry pyridine (30 ml.) at 0°, was treated with toluene-*p*-sulphonyl chloride (13·3 g., 1·1 mol.). The mixture was set aside at 0° for 2 hr. and then at 20° for 15 hr.; it was then diluted with water and extracted with chloroform. The extracts were washed with ice-cold 2N-hydrochloric acid, dried, and evaporated. Crystallisation of the residue from ethanol gave the *ester* (72%), m. p. 81° (Found: C, 53·4; H, 5·5. $C_{17}H_{21}NO_5S_2$ requires C, 53·2; H, 5·5%).

The ester (3·66 g.) was kept with ethanolic N-sodium ethoxide (191 ml.) for 20 min. at 78°. The solution was added to acidified saturated brine in order to hydrolyse vinylsulphonamide, and after 48 hr. the mixture was extracted with chloroform. The extracts were evaporated, and the residue was dissolved in benzene and extracted with aqueous 2·5N-sodium hydroxide. Acidification of the alkaline extract and extraction with chloroform gave *N*-methyltoluene-*p*-sulphonamide (0·546 g., 31%), m. p. and mixed m. p. 72—74°. The benzene extracts were evaporated, and distillation of the residue gave N-2-*ethoxyethyl*-N-*methyltoluene*-p-*sulphonamide* (1·39 g., 57%), b. p. 134°/0·04 mm., $n_D^{18\cdot5}$ 1·5175, ν (C–O–C) 1110 cm.$^{-1}$ (Found: C, 56·4; H, 7·2. $C_{12}H_{19}NO_3S$ requires C, 56·0; H, 7·4%). This ether was recovered quantitatively when subjected separately to the reaction and working-up conditions.

N-2-*Iodoethyl*-N-*methyltoluene*-p-*sulphonamide*.—The preceding ester (3·5 g.) and sodium iodide (5 mol.) were refluxed in ethanol (30 ml.) for 6 hr. The mixture was diluted with water and the chloroform extracts were washed with aqueous sodium thiosulphate. Evaporation of the extracts gave the *iodide* (2·82 g., 91%), m. p. 88° (from ethanol) (Found: C, 35·4; H, 3·85. $C_{10}H_{14}INO_2S$ requires C, 35·4; H, 4·2%). The iodide (6·835 g.) was treated with ethanolic N-sodium ethoxide (20 mol.) as for the toluene-*p*-sulphonate. The products were *N*-methyltoluene-*p*-sulphonamide (94%), m. p. and mixed m. p. 77—78°, together with the ethoxy-compound (0·6%), b. p. 126—128°/0·25 mm., n_D^{18} 1·5222 (infrared spectrum identical with that of an authentic specimen).

In a second experiment, the reaction mixture was diluted with neutral brine and extraction was with benzene. Evaporation of the extracts gave *N*-methyl-*N*-vinyltoluene-*p*-sulphonamide (99%), m. p. 42—47° raised to 55° (from ethanol) (Found: C, 56·7; H, 6·1. Calc. for $C_{10}H_{13}NO_2S$: C, 56·8; H, 6·3%) (lit.,[6] m. p. 56—56·5°). Acid hydrolysis [1] of the sulphonamide gave *N*methyltoluene-*p*-sulphonamide, m. p. and mixed m. p. 76°.

N-2-*Chloroethyl*-N-*methyltoluene*-p-*sulphonamide*.—The above toluene-*p*-sulphonate (5·9 g.) was refluxed for 40 hr. with lithium chloride (10 mol.) in a mixture of butanone (20 ml.) and t-butyl alcohol (4 ml.). Dilution with water and extraction with chloroform gave the *chloride* (3·66 g., 96%), m. p. 71° (from ethanol) (Found: C, 48·2; H, 5·55. $C_{10}H_{14}ClNO_2S$ requires C, 48·5; H, 5·7%).

The chloride (3·562 g.) was kept with ethanolic N-sodium ethoxide for 70 min. as before. The neutral fraction gave recovered chloride (8·5%), m. p. and mixed m. p. 66—70°, together

[2] C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2532.
[3] R. Adams and T. L. Cairns, *J. Amer. Chem. Soc.*, 1939, **61**, 2464.
[4] F. L. Scott and E. Flynn, *Tetrahedron Letters*, 1964, 1675.
[5] K. H. Slotta and R. Behnisch, *J. prakt. Chem.*, 1932, **135**, 225.
[6] F. W. Stacey, J. C. Sauer, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1959, **81**, 987.

with the ethoxy-compound (0·85%), b. p. 77—80°/0·2 mm., n_D^{19} 1·5241. The acidic product was *N*-methyltoluene-*p*-sulphonamide (90% based on the chloride reacted), m. p. and mixed m. p. 76—78°.

This work was carried out during the tenure by one of us (A. C.) of a postgraduate studentship awarded by the Northern Ireland Ministry of Education.

THE QUEEN'S UNIVERSITY, BELFAST. [*Received, December 29th,* 1964.]