Synthesis of Olefins by Desulphuration of αβ-Unsaturated Phenyl Sulphones

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Summary Reductive cleavage of αβ-unsaturated phenyl sulphones with aluminium amalgam or $LiAlH_4$–$CuCl_2$ provides an attractive synthetic route to a variety of olefins in high yields.

RECENTLY we reported that 1,1-dimetal derivatives of alkyl and benzyl phenyl sulphones (I) obtained *via* Li–Mg exchange give good yields of αβ-unsaturated phenyl sulphones (II) on treatment with aldehydes or ketones.[1]

$$PhSO_2\text{–}\underset{\displaystyle M^2}{\overset{\displaystyle M^1}{\underset{|}{\overset{|}{C}}}}\text{–}R^1 + R^2C(O)R^3 \rightarrow PhSO_2(R^1)C{=}CR^2R^3$$

(I) (II)

M^1 = Li, M^2 = MgI, or $M^1 = M^2$ = Li or MgI; R^1 = H, or Ph

We now report that αβ-unsaturated phenyl sulphones (II) can be converted easily into the corresponding olefins (III) by reductive cleavage of the carbon–sulphur bond with aluminium amalgam. As shown in the Table olefins are

$$PhSO_2(R^1)C = CR^2R^3 \xrightarrow{Al\text{–}Hg} R^1CH = CR^2R^3$$

(II) (III)

produced in yields of *ca.* 85%. Products were identified either by direct comparison with authentic material or by n.m.r., i.r., and mass spectra and elemental analysis.

The reaction seems to be completely stereoselective; *Z*-1,2-diphenylvinyl phenyl sulphone and *Z*-2-*p*-chlorophenyl-1-phenylvinyl phenyl sulphone gave exclusively the corresponding *E*-isomers.

TABLE

$PhSO_2(R^1)C{=}CR^2R^3$			Yield (%)[a] of $R^1CH{=}CR^2R^3$
R^1	R^2	R^3	
H	Ph	Ph	90[b] 60[c]
Ph	Ph	H	90[b,d]
"	*p*-ClC_6H_4	H	90[b,d]
"	Ph	Ph	85[b] 65[c] 40[e]
"	Cholest-4-en-3-ylidene		80[b,f] 60[c,f]

[a] Yield of isolated, purified compounds. [b] From Al–Hg. [c] From $LiAlH_4$–$CuCl_2$. [d] *E*-isomer from *Z*-isomer. [e] From $LiAlH_4$. [f] Mixture of isomers.

The conversion of the former into (*E*)-1,2-diphenylethylene illustrates a typical procedure. Aluminium amalgam[2] (0·02 g. atom Al in 2% aqueous $HgCl_2$) was added to a solution of *Z*-1,2-diphenylvinyl phenyl sulphone (1 mmol) 10% aqueous tetrahydrofuran (50 ml) under argon. The mixture was refluxed for 3 h, and worked up, and the residue was chromatographed on silica gel.

Other reduction procedures give the same products but with smaller yields. Refluxing of 1,2,2-triphenylvinyl phenyl sulphone for 3 h with $LiAlH_4$ gives the expected 1,2,2-triphenylethylene in 40% yield. The use of a $LiAlH_4$–$CuCl_2$ (4:8) mixture[3] under the same conditions increases the yield to *ca.* 65%.

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