J.C.S. Снем. Сомм., 1981

346

Reactions of a Triarylsulphonium Salt with Alkoxide Nucleophiles: Involvement of Radical Intermediates

By SUNG-KEE CHUNG* and KAZUMI SASAMOTO

(Department of Chemistry, Texas A & M University, College Station, Texas 77843)

Summary Tri-*p*-tolylsulphonium bromide reacts with sodium isopropoxide or potassium hydroxide to give toluene; solvent isotope labelling experiments clearly show involvement of the *p*-tolyl radical species rather than the corresponding anion in this reaction.

REACTIONS of sulphonium salts with a variety of nucleophilic species are of fundamental mechanistic interest.¹ It has previously been reported that triarylsulphonium salts react with a number of alkoxide species to produce the corresponding aryl alkyl ether and diaryl sulphide, together with varying amounts of aromatic hydrocarbon depending on the reaction conditions.^{2,3} McEwen has suggested that the hydrocarbon product arises *via* homolysis of the triarylsulphonium radical to diaryl sulphide and an aryl radical, which then abstracts a hydrogen atom from the alcohol solvent (Scheme 1).² On the other hand, Oae and

 $Ar \cdot + Solvent \longrightarrow Ar \cdot H$ (H-Atom transfer)

SCHEME 1.

Khim have proposed that, on the basis of a large solvent polarity effect, the same reaction is more likely to proceed *via* ionic pathways, involving the nucleophilic attack of the alkoxide ion on either the carbon or the sulphur centres (Scheme 2).³ Possible involvement of a benzyne intermediate in this type of reaction has been ruled out by product studies.^{2,3}

$$\begin{array}{c} \operatorname{Ar}_3{\rm S}^+ \, {\rm X}^- \, + \, \operatorname{OR}^- \longrightarrow \operatorname{Ar}_2{\rm S} \, + \, \operatorname{Ar}\text{-}\operatorname{OR} \\ & \downarrow^{\quad +} \\ & \longrightarrow \operatorname{Ar}_2{\rm S}\text{-}\operatorname{OR} \, + \, \operatorname{Ar}^- \\ \operatorname{Ar}^- \, + \, \operatorname{Solvent} \longrightarrow \operatorname{Ar}\text{-} \operatorname{H} \, (\operatorname{Proton} \, \operatorname{transfer}) \end{array}$$

SCHEME 2.

In order to differentiate between these two mechanistic possibilities, we examined the reaction by employing the solvent isotope labelling method as a mechanistic probe.⁴ Thus, reactions of tri-p-tolylsulphonium bromide with sodium isopropoxide and potassium hydroxide were carried out in a similar fashion to the literature procedure, but in various deuteriated solvents. The relative product ratios and the incorporations of deuterium isotope into the product are summarized in Tables 1 and 2, respectively.

If the tolyl anion is involved as the precursor to toluene, it is expected to incorporate a protic hydrogen of the solvent,

TABLE 1. Relative yields of products from reactions of tri-p-tolylsulphonium bromide.ª

	_			Product yield/%		
Run	Base/solvent	$T/^{\circ}C$	t/h	Toluene	Ether	Sulphideb
1	(CH ₃) ₂ CHONa/(CH ₃) ₂ CHOH	72	23	33	35	100
2	(CH ₃) ₂ CHONa/(CH ₃) ₂ CHOD ^c	72	23	35	45	100
3	$(CD_3)_2CDONa/(CD_3)_2CDOD^d$	72	23	17	55	100
4	$KOH/H_{2}O-C_{2}H_{5}OH$ (56:44)	85	20	12	(trace)	100
5	KOD ^e /D ₂ O–C ₂ H ₅ OD ^t	90	22	23	(trace)	100
6	$\mathrm{KOD}/\mathrm{D_2O-C_2D_5OD^g}$	90	22	17	(trace)	100

^a All the reactions were run under N₂. ^b The relative product yields were determined by g.c. analysis on a 5 ft, 10% FFAP on Anakrom-SD, 60/70 mesh column, and are uncorrected. ^c [²H₁]Propan-2-ol (>98 atom % D) from Aldrich. ^d [²H₈]Propan-2-ol (>99 atom % D) from Aldrich. ^d [²H₈]Propan-2-ol (>99 atom % D) from Aldrich. ^e Potassium deuterioxide (>98 atom % D) from Aldrich. ^f [²H₁]Ethanol (>99.5 atom % D) from Aldrich. ^g [²H₈]Ethanol (99 atom % D) from Merck.

while the tolyl radical intermediate should abstract the α -hydrogen of the alcoholic solvent. The maximum number of deuterium anions incorporated into toluene was found to be 6 in the reactions run in alcoholic solvents having α -D, while the maximum number of deuterium atoms incorporated was 5 in the product obtained from the solvents having α -H (Table 2). This observation, along with the

TABLE 2. Deuterium isotope distributions in toluene.⁸

Run	$^{2}H_{0}$	$^{2}H_{1}$	$^{2}H_{2}$	${}^{2}H_{3}$	${}^{2}\mathrm{H}_{4}$	${}^{2}H_{5}$	²Η ₆
2	9.3	20.7	33.9	$22 \cdot 8$	9.7	3.6	0
3	$7 \cdot 9$	15.1	26.9	27.3	18.0	$2 \cdot 6$	$2 \cdot 2$
5	7.4	21.3	38.5	$23 \cdot 2$	7.9	1.5	0
6	1.7	3.1	13.8	27.8	$33 \cdot 2$	10.2	10.2

^a Determined by mass spectral analysis of the molecular ion peaks on a Hewlett-Packard g.c./m.s. Data System, Model 5982-A, corrected for the amounts of natural abundances of M + 1 and M + 2 ions, and expressed as percentages.

overall pattern of the deuterium distribution in toluene, clearly indicates that the α -hydrogen of the solvent alcohol is abstracted by the intermediate to give toluene, and that the intermediate is most likely to be the p-tolyl radical species rather than the corresponding anion.

The multiple incorporation of the deuterium label into the products from the exchangeable positions of the alcoholic solvents has been determined to be a result of base-catalysed hydrogen exchange taking place primarily with the sulphonium salt. Careful n.m.r. and mass spectral analyses of the recovered tri-*p*-tolylsulphonium salt as well as of the di-p-tolyl sulphide product have shown relatively slow exchange at the two ortho-positions with respect to the sulphur substituents, and faster exchange at the methyl site. The regiospecific exchange at the ortho-position is also corroborated by the similar analyses performed on the triphenylsulphonium bromide system.5 The site-specific ortho-hydrogen exchange in the triarylsulphonium salts under basic conditions could best be explained in terms of the dipole stabilization of the corresponding carbanionic species.6

The exact mechanism of the radical formation in these reactions is not yet clear. It is possible that the radical intermediate is generated either from electron-transfer processes between the sulphonium salt and the alkoxide nucleophile or from the initial formation of a sulphurane species,⁷ followed by homolytic cleavage of the C-S bond.

This work was supported by grants from the Robert A. Welch Foundation and the National Institutes of Health.

(Received, 15th December 1980; Com. 1332.)

¹C. J. M. Stirling in 'Organic Chemistry of Sulphur,' ed. S. Oae, Plenum Press, New York, 1977. ² J. W. Kanpczyk and W. E. McEwen, J. Am. Chem. Soc., 1969, 91, 145; J. W. Knapczyk, C. C. Lai, W. E. McEwen, J. L. Calderon, and J. J. Lubinkowski, *ibid.*, 1975, 97, 1188.

³ S. Oac and Y. H. Khim, Bull. Chem. Soc. Jpn., 1969, 42, 3528.
⁴ A. I. Scott, J. B. Hansen, and S. K. Chung, J. Chem. Soc., Chem. Commun., 1980, 388; A. I. Scott, J. Kang, D. Dalton, and S. K. Chung, J. Am. Chem. Soc., 1978, 100, 3603; E. Konig, H. Musso and W.-I. Zahorszky, Angew. Chem., Int. Ed. Engl., 1972, 11, 45; G. A. Russell in 'Free Radicals,' ed. J. K. Kochi, Vol. 1, Wiley, New York, 1973.

S. K. Chung and K. Sasamoto, unpublished results.

⁶ H. W. Gschwend and H. R. Rodriguez, Org. React., 1979, 26, 1; P. Beak, G. R. Brubaker, and F. R. Farney, J. Am. Chem. Soc., 1976, 98, 3621; P. Beak and E. M. Monroe, J. Org. Chem., 1969, 34, 598; A. J. Anderson, J. Kitchin, and R. J. Stoodley, Tetrahedron Lett., 1973, 3379.

⁷ R. W. LaRochelle and B. M. Trost, J. Am. Chem. Soc., 1971, 93, 6077; B. M. Trost and H. C. Arndt, ibid., 1973, 95, 5288.