

## Nucleophilic Displacement by Hydrogen Carbonate Anion, and its Implications in the Oxidation of Alkyl Toluene-*p*-sulphonates with Dimethyl Sulphoxide–Sodium Hydrogen Carbonate<sup>1</sup>

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Hydrogen carbonate anion is shown to be a more effective nucleophile than dimethyl sulphoxide in reactions with *c*-3-hydroxy-2-methyl-4-*p*-tolylbornan-*r*-2-ylmethyl toluene-*p*-sulphonate (I) and with 3-hydroxy-2,2-dimethyl-3-phenylpropyl toluene-*p*-sulphonate (IX; R = Ts). The elements of carbon dioxide are retained in the product as a cyclic carbonate system.

OXIDATION of primary and secondary alkyl toluene-*p*-sulphonates by the dimethyl sulphoxide–sodium hydrogen carbonate procedure<sup>2</sup> is thought to utilise the hydrogen carbonate anion as a proton scavenger (Scheme I). Other roles for this anion are not considered presumably because it is thought to be an unlikely nucleophile to displace a primary toluene-*p*-sulphonate group in an S<sub>N</sub>2 reaction.<sup>3</sup>

We applied this procedure to the primary toluene-*p*-sulphonate (I),<sup>4</sup> hoping to obtain the corresponding

aldehyde. The product isolated in 78% yield from a reaction at 100° had  $\nu_{\max}$  1775 cm<sup>-1</sup>,  $\tau$  8.80 (3H, s), 7.70 (3H, s), 5.95 (2H, ABq, *J* 11 Hz), 6.0br (1H, s), and 2.9br (4H, s),† compatible only with the cyclic carbonate structure (II). This surprising observation was consistently reproducible, and the product (II) was identical (t.l.c., n.m.r. and i.r. data, m.p. and mixed m.p.) with that obtained from the diol (III) with phosgene–pyridine in toluene.

† In this paper, n.m.r. signals are mentioned only where diagnostic assignments can be made.

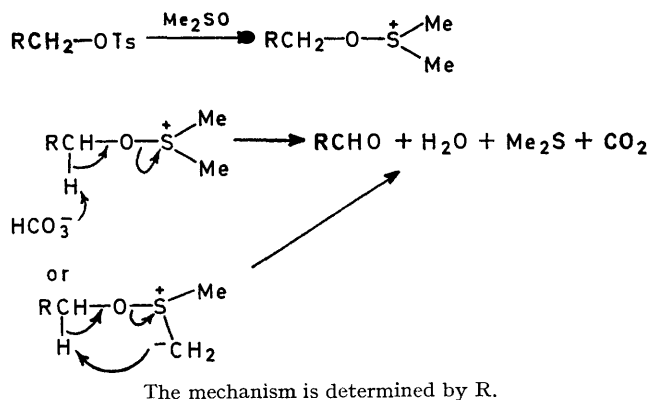
<sup>1</sup> N. Bosworth and P. D. Magnus, *J.C.S. Chem. Comm.*, 1972, 257.

<sup>2</sup> W. W. Epstein and F. W. Sweat, *Chem. Rev.*, 1967, **67**, 247.

<sup>3</sup> (a) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4113; (b) H. R. Nace and J. J. Monagle, *J. Org. Chem.*, 1959, **24**, 1792; (c) J. M. Tien and I. M. Hunsberger, *Chem. and Ind.*, 1959, **88**; (d) K. Torrsell, *Acta Chem. Scand.*, 1967, **21**, 1.

<sup>4</sup> N. Bosworth and P. D. Magnus, *J.C.S. Perkin I*, 1973, 76.

Two examples of similar displacements are known.\* Treatment of the glucose derivative (IV) with dimethyl



SCHEME 1

sulphoxide-potassium hydrogen carbonate at 20° gave the carbonate (V), whereas use of dimethyl sulphoxide-sodium hydrogen carbonate at 180° gave the anhydro-derivative (VI). Similarly, mannitol 1,6-ditosylate (VII), on treatment with dimethyl sulphoxide-potassium hydrogen carbonate at 20°, gave the bis-carbonate (VIII).<sup>5</sup> Both these experiments were carried out with the objective of preparing anhydro-sugars, and not to oxidise the primary toluene-*p*-sulphonate groups to aldehydes.

To study the reaction conditions and gain some insight into the mechanism of this reaction we used the more readily available substrate (IX; R = Ts).<sup>6</sup> The results of reactions with dimethyl sulphoxide-sodium hydrogen carbonate and a number of other systems designed to produce the carbonate (X) are given in the Table.

The formation of the cyclic carbonate (X) is favoured by high temperature (*ca.* 110°) and brief exposure to the reagents (NaHCO<sub>3</sub>-Me<sub>2</sub>SO). Presumably the decomposition of sodium hydrogen carbonate to sodium hydroxide and carbon dioxide causes hydrolysis of the carbonate (X) to the diol (IX; R = H).

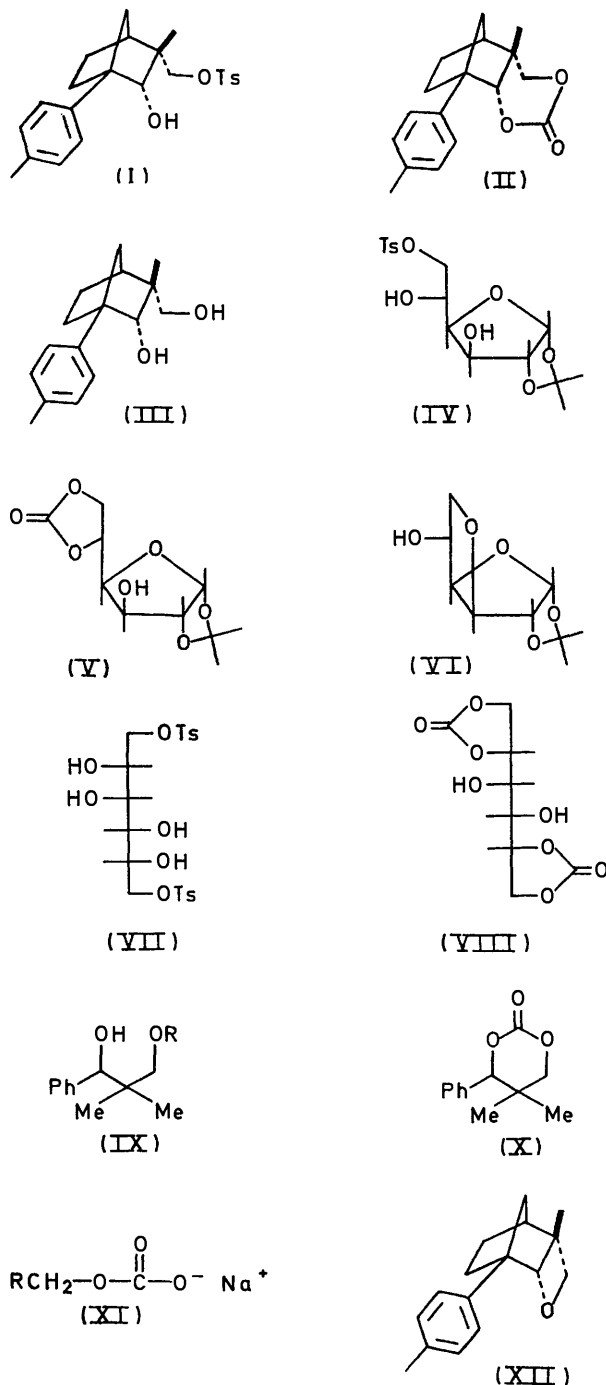
Dimethyl sulphoxide is known to accelerate displacement reactions. Indeed, in this solvent neopentyl halides<sup>7</sup> can be converted into nitriles without rearrangement, and dimethyl sulphoxide enhances the rate of bimolecular nucleophilic displacement of toluene-*p*-sulphonates by bromide ion.<sup>8</sup> The nucleophilic constant (*n*) for hydrogen carbonate anion (3·8) is almost identical with that of bromide anion (3·9).<sup>9</sup> The foregoing experiments demonstrate that for the particular substrates (I) and (IX; R = Ts) under the conditions used, hydrogen carbonate is a better nucleophile than dimethyl sulphoxide.

\* Dr. R. Gigg is thanked for bringing this to our attention.

<sup>5</sup> G. Hanisch and G. Henseke, *Chem. Ber.*, 1967, **100**, 3225.

<sup>6</sup> (a) F. Nerdel and U. Kretzschmar, *Annalen*, 1965, **688**, 61; (b) K. Kulka, O. Hansen, and R. Joseph (Fritzsche, Dodge, and Olcott, New York), personal communication.

We suggest two mechanisms which may account for these results (Scheme 2). The half-ester (A) is ideally constituted for elimination of water and formation of



the carbonate (II). Since oxidations with dimethyl sulphoxide-sodium hydrogen carbonate usually, in the absence of any functional group that can trap intermediates, give carbonyl compounds, it is possible that

<sup>7</sup> L. Friedman and H. Shechter, *J. Org. Chem.*, 1960, **25**, 877.

<sup>8</sup> J. Cason and J. S. Correia, *J. Org. Chem.*, 1961, **26**, 3645.

<sup>9</sup> C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 1956, **78**, 141.

(A) also reacts with dimethyl sulphoxide to give (B). Intermediates of type similar to (B) (without OH) are well known<sup>10</sup> and collapse to aldehydes, whereas in our particular system the intermediate is trapped as the

ester probably reacts with dimethyl sulphoxide to produce an intermediate that expels CO<sub>2</sub> and undergoes α-elimination to give an aldehyde (Scheme 3).

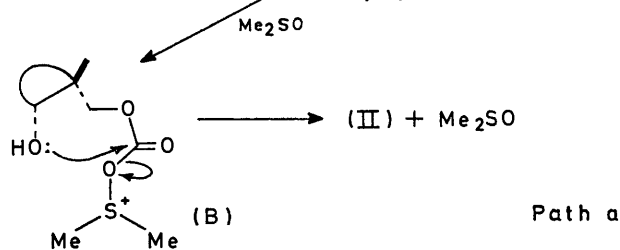
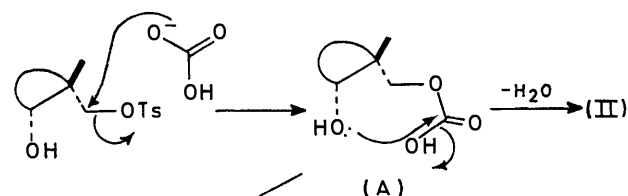
The alternative mechanism (Scheme 2, path b) is less

Substrate	Reaction conditions	Products *
(IX; R = Ts)	NaHCO <sub>3</sub> -Me <sub>2</sub> SO { 60–70° (3 h)	(IX; R = H)
	{ 110° (0.5 h)	(X) (50%)
	{ 110° (1 h)	(X) + (IX; R = H)
(IX; R = H)	KHCO <sub>3</sub> -Me <sub>2</sub> SO { r.t. † (3 days)	(IX; R = H)
	{ 60° (0.5 h)	(X) (ca. 60%)
	{ 110° (0.5 h)	(IX, R = H)
(IX; R = H)	K <sub>2</sub> CO <sub>3</sub> -Me <sub>2</sub> SO 100° (15 h)	(IX; R = H) + (X) (trace)
	EtO-CO <sub>2</sub> -Na <sup>+</sup> -Me <sub>2</sub> SO 100° (0.5 h)	(X) (44%)
(IX; R = H)	NaOH-CO <sub>2</sub> -Me <sub>2</sub> SO 100° (2 h)	Complex mixture; no (X)
	NaH-CO <sub>2</sub> -Me <sub>2</sub> SO 100° (2 h)	
	NaOH-CO <sub>2</sub> -Me <sub>2</sub> SO 100° (6 h)	

\* Yields refer to material isolated and recrystallised twice. † Room temperature.

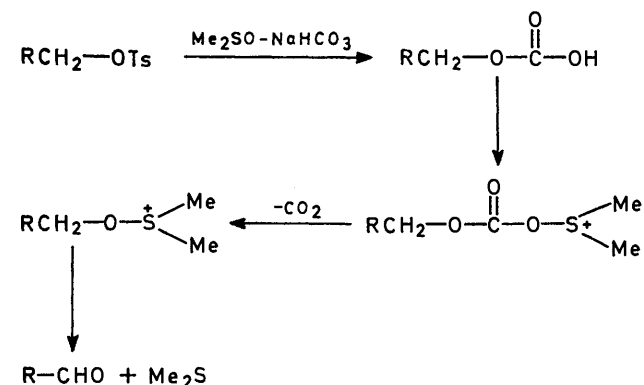
carbonate (II). Whether dimethyl sulphoxide is implicated or not (in these systems), there is no reason to suppose that hydrogen carbonate anion in dimethyl

attractive on the following grounds. Any concentration of alkoxide species might be expected to undergo intramolecular oxetan or 1,3-fragmentation reactions rather than intermolecular reaction with CO<sub>2</sub> (see later). Compounds of the type (XI) are usually made from treatment of an alcohol with sodium hydroxide-carbon



Path a  
Path b  
SCHEME 2

sulphoxide would not be a better nucleophile than dimethyl sulphoxide itself towards other primary toluene-*p*-sulphonates. We conclude that for a primary toluene-*p*-sulphonate, hydrogen carbonate is a better nucleophile than dimethyl sulphoxide. The initially formed half-



SCHEME 3

dioxide.<sup>11</sup> Application of these conditions to (IX; R = Ts) (see Table) gave no carbonate (X), and conditions that avoid the presence of sodium hydroxide also failed. The reaction with (IX; R = Ts) and sodium ethyl carbonate must take place with displacement at the toluene-*p*-sulphonate group first.

When the toluene-*p*-sulphonate (I) is treated with sodium hydrogen carbonate in dimethylformamide or tetrahydrothiophen dioxide the carbonate (II) is again formed (no other products are present). The reaction is slow (at least 24 h) compared with that in dimethyl sulphoxide (0.5 h). To eliminate the unlikely possibility that an oxetan (XII) is an intermediate, (I) was converted to the oxetan (XII) with potassium *t*-butoxide in *t*-butyl alcohol.<sup>4</sup> Exposure of (XII) to dimethyl sulphoxide-sodium hydrogen carbonate at 100–110° for 15 h gave no reaction.

Apart from Swain's<sup>9</sup> work, the nucleophile properties

<sup>10</sup> D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1964, 1855.

<sup>11</sup> (a) J. I. Jones, *Chem. and Ind.*, 1958, 228; (b) J. Thamsen, *Acta Chem. Scand.*, 1956, **10**, 1165; (c) A. Jensen, E. Jorgensen, and C. Faurholt, *ibid.*, 1952, **6**, 1036.

of hydrogen carbonate anion have not been reported previously.

#### EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were measured for Nujol mulls or thin films unless otherwise stated. N.m.r. spectra were recorded with Varian A60 and HA100 instruments for solutions in [<sup>2</sup>H]chloroform with tetramethylsilane as internal standard. All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction of b.p. 40—60°.

*Reaction of c-3-Hydroxy-2-methyl-4-p-tolylbornan-r-2-ylmethyl Toluene-p-sulphonate (I) with Sodium Hydrogen Carbonate-Dimethyl Sulphoxide.*—The hydroxy-tosylate (I) (50 mg) in dimethyl sulphoxide (1 ml) containing sodium hydrogen carbonate (40 mg) was heated at 100—110° for 0.5 h. The mixture was cooled, poured into ether, and washed with saturated aqueous sodium hydrogen carbonate and water. Evaporation of the dried (Na<sub>2</sub>SO<sub>4</sub>) ether layer gave 7-methyl-1-p-tolyl-3,5-dioxatricyclo[6.2.1.0<sup>2,7</sup>]undecan-4-

one (II) (78%), m.p. 104° (from benzene-light petroleum),  $[\alpha]_D^{28} + 87.6$  (c 0.7 in CHCl<sub>3</sub>) (Found: C, 74.9; H, 7.4. C<sub>17</sub>H<sub>20</sub>O<sub>3</sub> requires C, 75.0; H, 7.4%).

Treatment of the diol (III) (50 mg) in pyridine (1 ml) with phosgene in toluene (12% soln.; 2 equiv.) at 0° overnight, followed by work-up in the usual way, also gave the carbonate (II) (80%), m.p. 104°.

*Reactions of 3-Hydroxy-2,2-dimethyl-3-phenylpropyl Toluene-p-sulphonate<sup>6</sup> (IX; R = Ts) with Sodium Hydrogen Carbonate.*—*General procedure.* The tosylate (0.5 g) was heated in dimethyl sulphoxide (10 ml) containing an excess of sodium hydrogen carbonate (0.5 g) and the reaction was monitored by t.l.c. (see Table). 2,2-Dimethyl-1-phenylpropane-1,3-diyl carbonate (X) isolated in the usual way, had m.p. 105—106° (from light petroleum),  $\nu_{\max}$  1760 and 1720 cm<sup>-1</sup>,  $\tau$  9.04 (3H, s) 9.01 (3H, s), 5.83 (2H, ABq, J 11 Hz), 4.76 (1H, s), and 2.6br (5H, s) (Found: C, 69.6; H, 7.0. C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> requires C, 69.6; H, 6.8%).

The S.R.C. is thanked for studentships (to N. B. and R. M.).

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