An Unprecedented Nucleophilic Displacement by Bicarbonate Anion, and its Implications in the Oxidation of Alkyl Toluene-*p*-sulphonates with Dimethyl Sulphoxide–Sodium Bicarbonate

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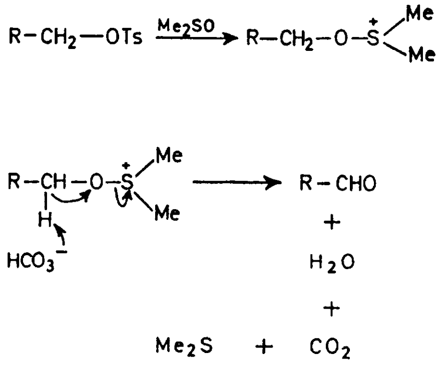
Summary Bicarbonate anion is shown to be a more effective nucleophile than Me_2SO when treated with the toluene-*p*-sulphonate (I); the elements of carbon dioxide are retained in the product as the cyclic carbonate (II).

Oxidation of primary and secondary alkyl toluene-*p*-sulphonates using the $Me_2SO–NaHCO_3$ procedure[1] is thought to utilise the bicarbonate anion as a proton scavenger (Scheme 1). The bicarbonate anion is not implicated in any other way, presumably because it is thought to be an unlikely nucleophile to displace a primary toluene-*p*-sulphonate group in an S_N2 reaction.[2,3]

We applied this procedure to the primary toluene-*p*-sulphonate (I),[4] hoping to obtain the corresponding aldehyde. Treatment of (I) with $Me_2SO–NaHCO_3$ at 100° gave a clean reaction. The product was isolated in 78% yield and had ν_{max} 1775 cm^{-1}, τ 8·80(3H, s), 7·70(3H, s), 5·95(2H, ABq, J 11Hz), 6·0(1H, bs), and 2·9(4H, bs).† These data are only compatible with the cyclic carbonate struc-



Scheme 1.

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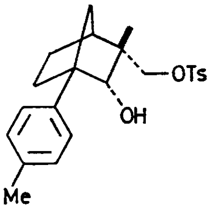
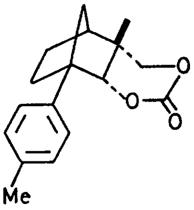
† Only signals where diagnostic assignments can be made are mentioned. This also refers to subsequent n.m.r. data.

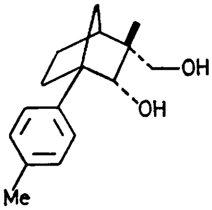
ture (II). This surprising experimental observation was consistently reproducible. To verify the structure of (II) the diol (III) was converted into the cyclic carbonate (II) with phosgene–pyridine in toluene. Comparison of their t.l.c., and n.m.r. spectra showed them to be identical.



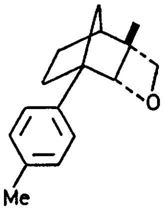
(I)



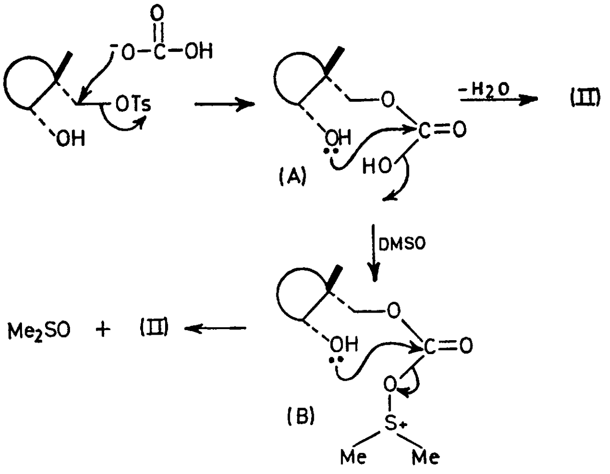
(II)



(III)

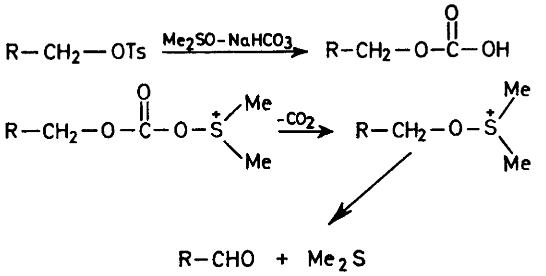


(IV)



Scheme 2.

Displacements in Me_2SO are known to be accelerated. Indeed, neopentyl halides[5] can be converted into nitriles without rearrangement, and Me_2SO enhances the rate of bimolecular nucleophilic displacement of toluene-*p*-sulphonates by bromide ion.[6] The nucleophilic constant (*n*) for bicarbonate anion (3·8) is almost identical to that of bromide anion (3·9).[7] The above experiment clearly demonstrates that for this particular substrate (I) under the Me_2SO–$NaHCO_3$ conditions, bicarbonate is a better nucleophile than Me_2SO. A possible mechanistic interpretation is outlined in Scheme 2. The half-ester (A) is ideally constituted for elimination of water and formation of the carbonate (II). Since Me_2SO–$NaHCO_3$ oxidation usually, in the absence of any functional group that can trap intermediates, gives carbonyl compounds, it is possible that (A) also reacts with Me_2SO to give (B). Intermediates of type similar to (B) (without OH) are well known[8] and collapse to an aldehyde, whereas in our particular system it is trapped as the carbonate (II). Whether Me_2SO is implicated or not (in this particular system), there is no reason to suppose that bicarbonate anion in Me_2SO would not be a better nucleophile than Me_2SO itself towards other primary toluene-*p*-sulphonates. Consequently one is lead to the conclusion that for a primary toluene-*p*-sulphonate, bicarbonate would be the better nucleophile than Me_2SO. The initially formed half-ester reacts with Me_2SO to produce an intermediate that expels CO_2 and α-eliminates to an aldehyde (Scheme 3).



Scheme 3.

When (I) is treated with sodium bicarbonate in dimethylformamide or sulpholane the carbonate (II) is formed, Scheme 2; (A) → (II), (no other products are present). The reaction is slow (at least 24 h) compared with Me_2SO as solvent (1 h). To eliminate the unlikely possibility that an oxetan (IV) is an intermediate, (I) was treated with Bu^tOK–Bu^tOH and the oxetan (IV), τ 8·72 (3H, s), 7·80(3H, s), 5·54(2H, ABq, *J*7Hz), 5·45(1H, s), 2·85(4H, s), was formed in quantitative yield. Exposure[7] of (IV) to Me_2SO–$NaHCO_3$ at 100° for 15 h gave no reaction.

To our knowledge this is the first example of a displacement of toluene-*p*-sulphonate by bicarbonate anion, where the elements of carbon dioxide have been retained in the product. Apart from Swains[6] work there is no reference to the nucleophilic properties of bicarbonate anion. It is difficult to avoid the conclusion that bicarbonate anion is an effective nucleophile in Me_2SO–$NaHCO_3$ oxidation since bicarbonate anion competes more successfully than Me_2SO for (I).

All new compounds gave satisfactory spectral and microanalytical data.

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