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Dedicated to Professor John C. Sheehan on the occasion of his sixty-fifth birthday.

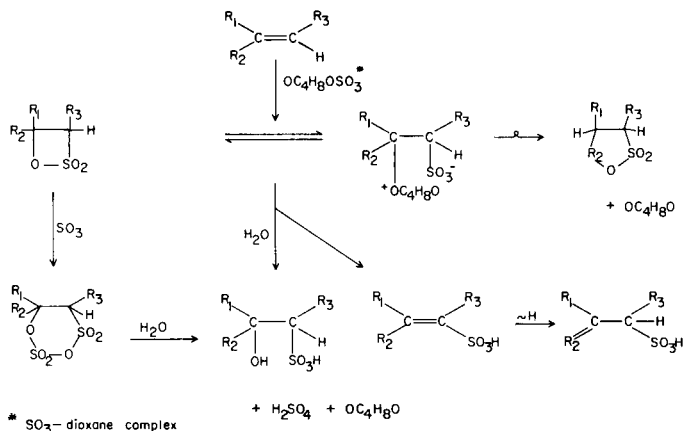
A six-membered ring carbyl sulfate rather than a four-membered β -sultone is suggested as the principal intermediate in liquid-phase sulfonations of olefins.

J. Heterocyclic Chem., 17, 1803 (1980).

Sir:

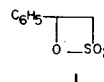
Although most classes of unsaturated compounds are easily sulfonated, the sulfonation reaction *per se* is very complicated and the study of its mechanistic aspects has been aggravated by the difficulty encountered in the analysis of the sulfonation reaction mixtures (1).

From the elaborate comprehensive work mainly of Bordwell (2-4) and of Suter (5), Truce (6) and their collaborators on sulfonation of alkylarylethylenes with sulfur trioxide-dioxane complex (2-6), it has been generally accepted that the mechanism of such sulfonations can be explained in terms of a four-membered ring β -sultone as the primary, dominant intermediate (2-3). All the various types of sulfonation products, which are dependent on the particular method of sulfonation employed and the specific reaction conditions (1-9), were claimed to be derived from this intermediate or an "equivalent" as illustrated in the following scheme (1-3).

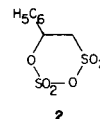


The above mechanistic patterns were "adopted" by industrial chemists and unquestionably applied to explain the mechanism and the spectrum of products obtained in sulfonations with sulfur trioxide to prepare surface-active agents from commercially available long chain olefins (1,7).

However, the claim for the intermediacy of a β -sultone in liquid-phase sulfonation of olefins was based, primarily, on two grounds: (a) the actual isolation of the claimed β -sultone intermediate **1** by sulfonation of styrene with sulfur trioxide at low temperature with the dioxane-sulfur trioxide complex in 1,2 dichloroethane (3); and (b) indirect evidence based on the analysis of the sulfonation reaction mixture after aqueous or basic hydrolysis, the essence of which was the determination of the unsaturated sulfonates by using the bromate-bromide titration method and the sulfate (sulfur trioxide originated)-gravimetrically (as barium sulfate) (2-4).



Based on both our own work (8) and a critical review of the work of others (2-6,11-15), we suggest that some of the conclusions of the earlier work (2-4) are questionable. Specifically, we claim that: (a) the isolated product for which structure **1** was assigned was, most probably the six-membered-ring carbyl sulfate **2**; and (b) the analytical methods used for determining the composition of the sulfonation mixtures (on which both the nature of the intermediates as well as the proposed mechanism of the sulfonation is based) are neither applicable nor valid under the conditions employed, particularly where a six-membered-ring carbyl sulfate of type **2** is present in the reaction mixture.



Nevertheless, the proved intermediacy of a six-membered-ring carbyl sulfate in liquid-phase sulfonation of olefins does not necessarily exclude the possibility of a β -sultone as a preliminary intermediate along the reaction coordinate, although this type of intermediate has yet to be characterized unequivocally.

The assignment of structure **1** to the isolated compound by Bordwell, *et al* (3), was based on: (a) neutralization equivalent (n.e.); and (b) boiling point elevation of methylene chloride solution. The value obtained for the n.e. (228) is 24% higher than the correct molecular weight for **1**. On the other hand, this value is only 13.5% lower than the correct molecular weight for **2** (264). At any rate, the neutralization value of carbyl sulfates is dependent on the method of titration, the solvent(s) used and the duration of the titration as was found by us in the case of the isolated and fully-characterized carbyl sulfate of 2,6-dichlorostyrene (**8a**). The boiling point elevation method gave a molecular weight of 215 (3), which is between the calculated molecular weight of **1** (184) and **2** (264).

Since carbyl sulfates are at least partially soluble in inert chlorinated solvents (3,8), as well as in other used solvents like dioxane, the "differential" method applied to the "post" hydrolyzed sulfonation mixture (after the separation of the organic layer) (3) is not valid for the elucidation of the actual composition of the sulfonation mixture proper. Furthermore, since the aqueous (and even the basic) hydrolysis of carbyl sulfates of type **2** is not instantaneous nor quantitative (4,8c) (but rather dependent on method, conditions, and time) (8c), the results of the "differential" method applied by Bordwell, *et al.* (2,3), were undoubtedly affected by the specific procedure of each individual experiment. If, in fact, as we claim, a carbyl sulfate of type **2** is the actual relatively stable intermediate in the liquid-phase sulfonations of olefins (4-6,8), rather than the elusive β -sultone (3), then the estimated sulfonation-mixture composition (and the derived mechanism and the nature of the intermediate) based on the methods used (2,3) is questionable. Moreover, although the presence of hydroxysulfonates does not affect the analytical results of the bromate-bromide method (2), the presence of either carbyl sulfates of type **2** or the sulfate-sulfonate salts (obtained on basic hydrolysis) does affect the results (8c).

Our claim for the intermediacy of carbyl sulfates in sulfonation of olefins is substantiated also by the following "positive" evidence.

1.

Six-membered-ring carbyl sulfates were obtained and actually isolated and/or characterized in many sulfonations of olefins regardless of whether: (a) sulfur trioxide itself or the sulfur trioxide-dioxane adduct served as the sulfonating agent (6,8); (b) a one to one or a two to one sulfur trioxide:olefin mole ratio was used (6); and (c) the addition of the olefin to the solution containing the sulfur trioxide or the reverse procedure (*i.e.*, adding the sulfur trioxide to a solution of the olefin) was employed-under comparable reaction conditions. The mechanism of

sultone formation in either the liquid-phase sulfonation of γ -branched-chain olefins (9) or in sulfur trioxide vapor-phase sulfonation of straight-chain olefins is beyond the scope of this communication.

2.

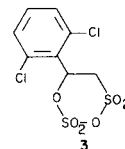
With the exception of one specific case (10), the only β -sultones isolated and unequivocally characterized to date, contain at least three halogens in their skeleton (1,11-13). More relevant to our case in hand is the fact that decreasing tendency towards β -sultone formation was found with a series of hydrofluoroolefins representing successive replacement of fluorine by hydrogen in tetrahydroethylenes (11). Simultaneously, the yields of the corresponding carbyl sulfates of the same series increased, respectively.

3.

The mechanism suggested for aromatic sulfonations with sulfur trioxide (1,14,15,16) can be considered to be analogous to the formation of carbyl sulfates in olefin sulfonations. In both cases two molecules of sulfur trioxide react with one molecule of the unsaturated compound being sulfonated.

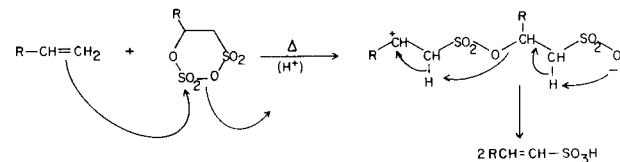
4.

Treatment of either the sulfonation reaction mixture of 2,6-dichlorostyrene or its carbyl sulfate **3** with wet acetonitrile, aqueous alkali, pyridine and piperidine, gave β -amidosulfonic acid and a mixture of sulfate and sulfonate salts respectively (8), analogously to the formation of sulfate and sulfonate salts obtained in a number of previous sulfonation studies (2,4,6). This observation supports the claim for a similar carbyl sulfate intermediate in all these liquid-phase sulfonation of olefins.



5.

Most of Bordwell's results can be easily accounted for by assuming the intermediacy of carbyl sulfate rather than that of β -sultone. For example, his finding that at elevated temperatures the unsaturated sulfonate is the major product can be explained as follows.



Conclusion.

The accumulated evidence critically discussed above

strongly suggests the intermediacy of carbyl sulfates rather than β -sulfones along the reaction coordinate of liquid-phase olefin sulfonations with sulfur-trioxide and/or its adducts. Also, some of the mechanistic aspects of these sulfonations can be understood in terms of this intermediate. Nevertheless, we are still short of understanding the entire mechanistic patterns involved. In view of the enormous significance of the sulfonation reaction (both theoretically and practical-economically), the time has probably come for new efforts in research and reinvestigation of this complex reaction.

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