

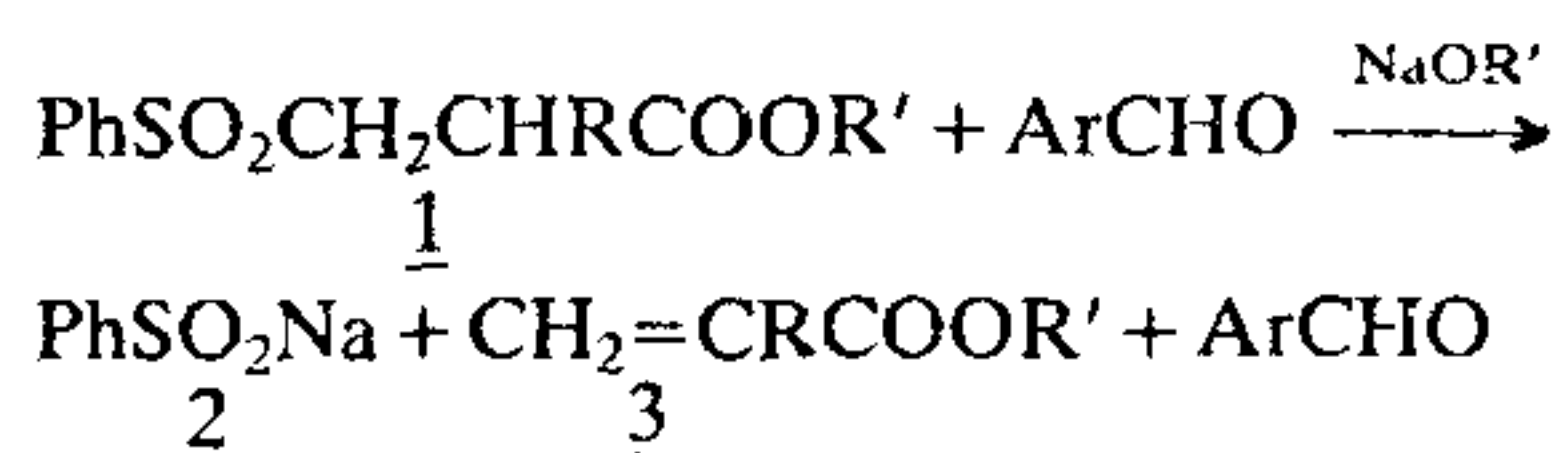
UNCONSIDERED ASPECTS OF MECHANISM OF REACTIONS OF SULPHONYLPROPIONATES

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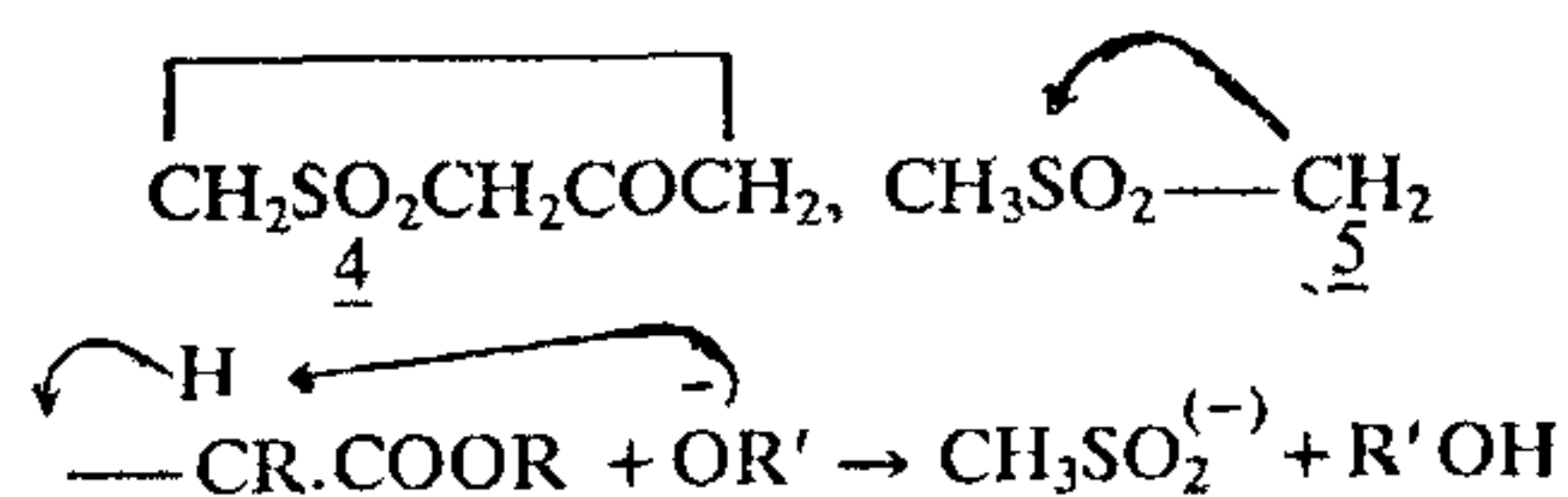
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EARLIER studies on ethyl β -phenylsulphonylpropionate (1:R = H, R' = Et) and methyl α -methyl- β -phenylsulphonylpropionate (1:R = R' = Me) were mainly concerned with their methods of preparation¹⁻⁴. The Claisen ester-aldehyde condensations were attempted on these, since Borsche⁵ had observed that PhCOCH₂CH₂COOEt, the ketonic analogue of (1:R = H, R' = Et) undergoes the sodium ethoxide catalysed claisen/Stobbe condensations with aldehydes, and such analogues exhibit analogies⁶ in their properties.

However, it was observed⁷ that (a) (1:R = H, R' = Et) did not condense with aldehydes but decomposed to benzenesulphinate (2) and ethyl acrylate (3:R = H, R' = Et) and (b) similar condensations of (1:R = R' = Me) under various experimental conditions gave only (2) and methyl methacrylate (3:R = R' = Me). Buckus⁸ observed somewhat similar decompositions on refluxing ArSO₂CH₂CH₂X (X = COOH, COOMe, COOEt, CONH₂, CN) with 10% KOH for 10 hours; the above reactions are at milder conditions.

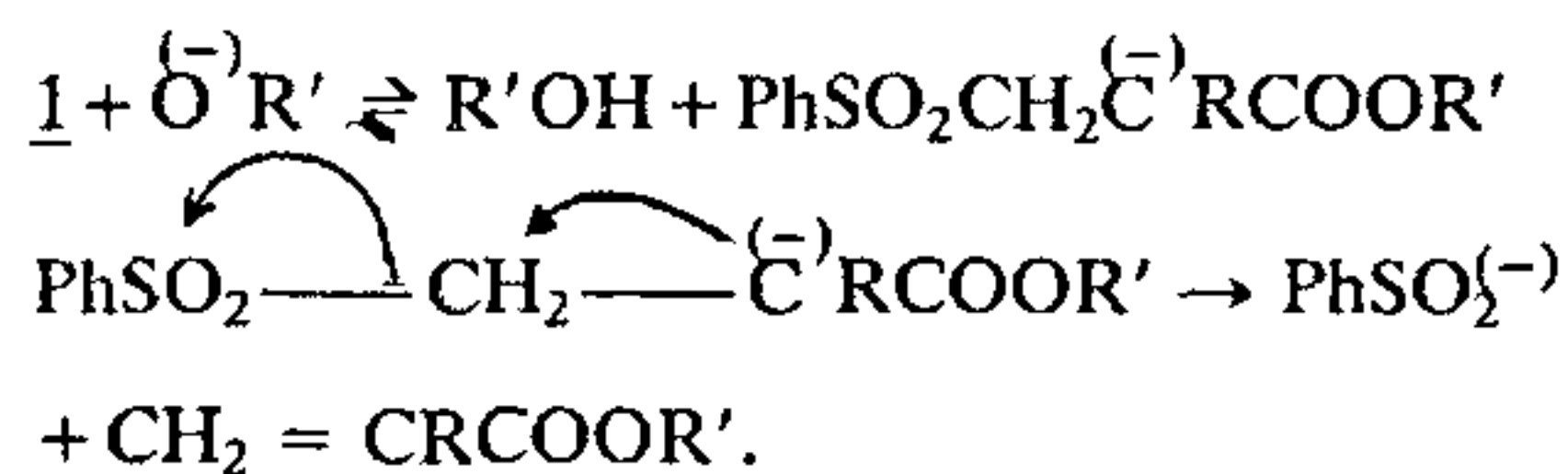


Truce and Knopse⁹ observed the decomposition of (5:R=H, R'=Et) to CH₃SO₂⁽⁻⁾ in the presence of NaOEt, instead of a desired cyclic product (4). They indicated a mechanism of E2 elimination type assuming the abstraction



of a proton α - to the ester instead of α - to the sulphone. However, this assumption is contrary to the ability of $-\text{SO}_2$ and $-\text{COOR}'$ to acidify the adjacent C-H bond¹⁰. Therefore the possible suggestion⁷ is that the $-\text{SO}_2$ (though stronger electron-withdrawing than $-\text{COOR}'$) exerts hindrance to the proton abstraction (by the base) due to the partial negative charges on the oxygen atoms of the $-\text{SO}_2$ greatly extending their effective radii in

blocking an incoming base anion; thus an E1cB mechanism would occur as



This suggestion is analogous to that given by Bordwell and Cooper¹¹ to explain the inertness of α -halosulphones (e.g. PhSO₂CH₂Cl) towards nucleophilic displacement of halogen.

An alternative suggestion⁷ could be that the formation of the sulphinate may be the driving force and this irreversibility directs the course of the reaction through the less acidic hydrogen by either E2 or the E1cB mechanism.

The author is grateful to Dr G. Bagavant, Department of Pharmaceutical Sciences, Nagpur University, Nagpur for helpful discussions.

18 November 1986; Revised 8 May 1987

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