FOUR MEMBERED CYCLIC SULFONES FROM BEAZYLSULFONYL FLUORIDE, KETENE DIETHYLACETAL AND PHENYLLITHIUM

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It has recently been reported that benzylsulfonyl chloride reacts with triethylamine to give trans-stilbene¹ and in the presence of ketene diethylacetal to form an interesting four membered cyclic sulfone, 2-phenyl-3,3-diethoxythietane l,l-dioxide². These reactions have been formulated as involving the intermediacy of phenylsulfene, $C_{6H_5CH=SO_2}$. Benzylsulfonyl fluoride, however, does not react with triethylamine under a comparable reaction condition³.

We now wish to report on the formation of four membered cyclic sulfones from benzylsulfonyl fluoride, ketene diethylacetal and phenyllithium. The formation of four membered cyclic sulfones from a sulfonyl fluoride appears to be the first observation.

The reaction was carried out by adding phenyllithium to a stirred solution of benzylsulfonyl fluoride and ketene diethylacetal dissolved in anhydrous ether at $18-20^{\circ}$ under argon atmosphere. α -Benzylsulfonyl- α -benzenesulfonyl toluene (I), 2-phenyl-3,3-diethoxythietane l,l-dioxide (II) and 2-phenyl-3-etho. thiete l,l-dioxide (III) were obtained as products in 30.0%, 9.3% and 7.4% yields respectively.

 $C_{6H_{5}CH_{2}SO_{2}F} + CH_{2} = C(OC_{2H_{5}})_{2} + C_{6H_{5}Li} \xrightarrow{18-20^{\circ}}_{ether}$ $C_{6H_{5}CH} \begin{pmatrix} SO_{2}C_{6H_{5}} & CH_{2}-C(OC_{2H_{5}})_{2} & CH_{2}-C-OC_{2H_{5}} \\ I & I & I \\ SO_{2}CH_{2}C_{6H_{5}} & SO_{2}-CHC_{6H_{5}} & SO_{2}-C-C_{6H_{5}} \\ I & II & III & III \end{pmatrix}$

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The disulfone (I), m.p. $248-250^{\circ}$ (lit⁴ m.p. $248-250^{\circ}$), and the thietane sulfone derivative (II), m.p. $93.5-94^{\circ}$ (lit² m.p. $89-90^{\circ}$), were identified by comparison of their infrared spectra with those of authentic samples and mixed melting points with authentic samples. The structure of III, m.p. $132-133^{\circ}$ (lit⁵ m.p. $132-134^{\circ}$), was assigned on the basis of infrared and n.m.r. spectra, which proved to be identical with those reported. The elemental analysis was also in good agreement.

Since no appreciable reaction takes place between benzylsulfonyl fluoride and ketene diethylacetal under the present condition, the initial step for the formation of II and III may possibly be the formation of α -lithiobenzylsulfonyl fluoride (IV) and two paths are conceivable for the formation of II. A likely pathway appears to be cycloaddition of phenylsulfene, which results from B-elimination of lithium fluoride from IV.

An alternative path involves nucleophilic attack of IV on ketene diethylacetal.

$$\begin{array}{ccc} C_{6H5\overline{C}HSO_{2}F} & \xrightarrow{CH_{2}=C(OC_{2}H_{5})_{2}} & \overrightarrow{LiCH_{2}-C(OC_{2}H_{5})_{2}} & \xrightarrow{-LiF} & II \quad (2) \\ +Li & & FSO_{2}CHC_{6H_{5}} \end{array}$$

The simultaneous formation of the thiete sulfone derivative (III) is accounted for as resulting from the action of phenyllithium on II in the light of the result reported by Truce et al.⁵ that II is converted to III on treatment with sodium ethoxide in ethenol.

We previously reported the reaction between benzylsulfonyl fluoride and phenyllithium and observed the formation of trans-stilbene, the disulfone (I) and other products.^L The formation of trans-stilbene and the present finding that four membered cyclic sulfones were formed instead of trans-stilbene are suggestive of the existence of phenylsulfene intermediate in the interaction of benzylsulfonyl fluoride with phenyllithium. In addition, the present result presents a further information than described in the previous paper⁴ on the mechanism for the formation of I, which will be reported in a later paper.

References

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