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# THE MECHANISM OF OLEFIN FORMATION FROM BENZYLIC SULFOXIDES USING PHENYLLITHIUM

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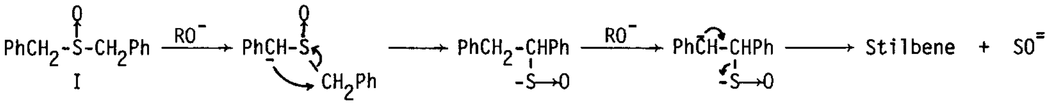
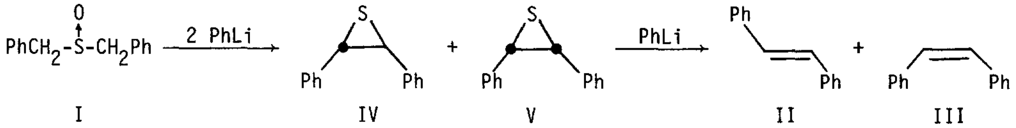
Benzylsulfoxide (I)[1] has been reported to react with potassium *t*-butoxide in dimethyl sulfoxide or dimethylformamide to give stilbene in moderate yield.[2] The mechanism proposed for this reaction is given as follows:



We have studied the formation of olefins from benzylic sulfoxides using phenyllithium. The course of this reaction has been found to differ markedly from that suggested for the potassium base.

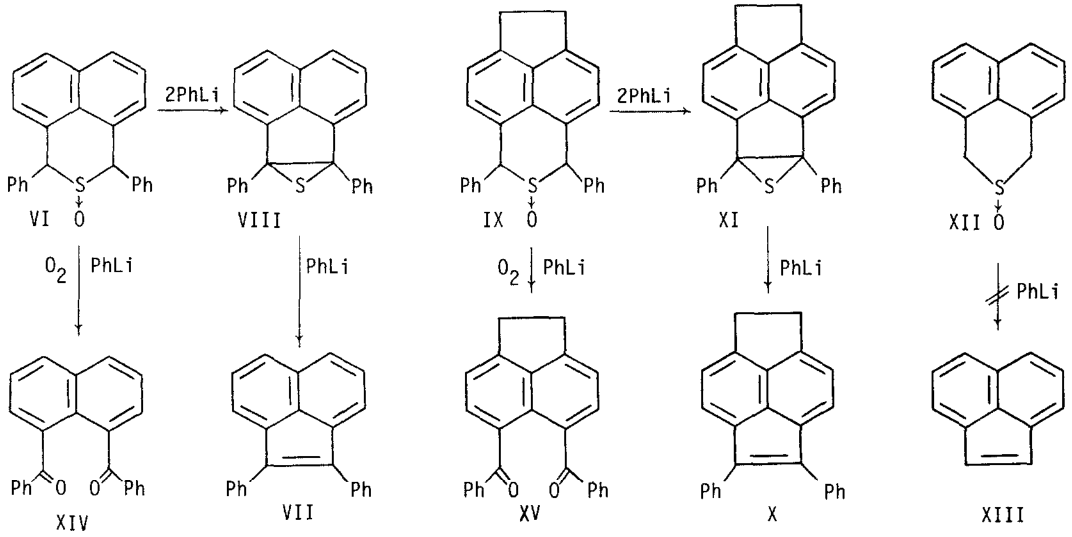
When I was treated briefly with excess phenyllithium in benzene at room temperature a 6:1 mixture of *trans* and *cis*-stilbene was formed in 85% yield. It was found that at least three moles of base were required to effect complete reaction. A deficiency of phenyllithium gave a mixture of products which was found to contain approximately 50% *trans*-stilbene (II), 8% *cis*-stilbene (III), 15% *trans*-stilbene episulfide (IV),[3] 5% *cis*-stilbene episulfide (V)[3] and 10%

unreacted starting material.[4] No incorporation of phenyllithium into products arising from I were observed indicating the reaction is intramolecular. Reaction of episulfides IV and V with phenyllithium under identical conditions gave rise stereoselectively to stilbenes II and III.[5]

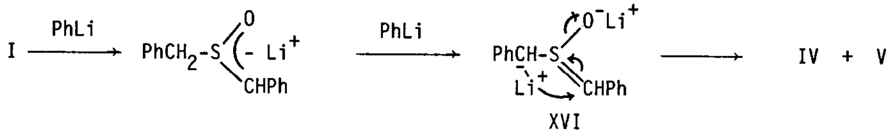


Similar reactions have been observed for other sulfoxides. Excess phenyllithium rapidly and quantitatively converted sulfoxide VI[6] into 1,2-diphenylacenaphthylene (VII).[7] When less than three moles of base were used, episulfide VIII[6] was formed in 30% yield along with VII. Identical behavior was found for sulfoxide IX[8] which gave the hydrocarbon X[9] in 95% yield. No attempt was made to isolate the corresponding episulfide XI in this case. Sulfoxide XII gave only polymer and not acenaphthylene (XIII). Acenaphthylene is stable under these conditions.

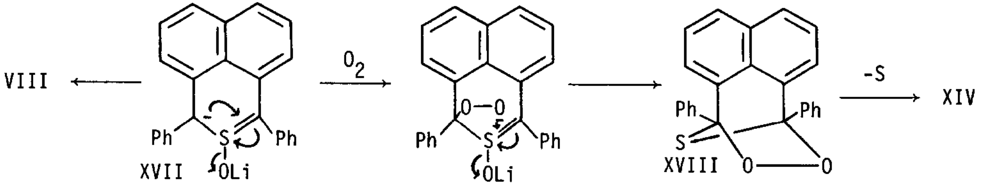
We have also studied the effect of oxygen on these reactions. Sulfoxide VI when treated with phenyllithium in the presence of oxygen gave 1,8-dibenzoylnaphthalene (XIV)[10] in 40% yield along with hydrocarbon VII. The same results were obtained for sulfoxide IX which gave the diketone XV.[11] Control experiments have shown that diketone XIV does not arise from either the hydrocarbon VII or the episulfide VIII under these conditions. Oxygen interception in the reaction of sulfoxide I could not be determined since stilbene gave rise to the same product mixture.



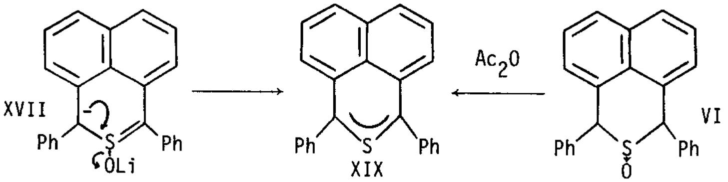
The formation of IV and V from sulfoxide I seems best accounted for by assuming the reaction to proceed through the dianion XVI. Collapse of XVI with overall loss of the elements of lithium oxide would give rise to IV and V.



The same mechanism can be written for the transformation VI to VIII. The formation of XIV from VI may be rationalized by assuming oxygen interception of the dianion XVII followed by cyclization to the peroxide XVIII. Loss of sulfur from the peroxide would give the diketone.[12]



An alternative pathway for the reaction of VI and IX with phenyllithium should be considered. It has been reported that sulfoxide VI on treatment with acetic anhydride gives rise to the transient heterocycle XIX.[6] Both the episulfide VIII and the diketone XIV have been shown to arise from XIX. It appears possible that the heterocycle XIX also may be formed from the dianion XVII. Thus far we have not been able to distinguish between these two possible modes of reaction. A comparable reaction path for sulfoxide I does not appear likely as I has been shown not to form a sulfur species analogous to XIX under a variety of conditions.[13]



That the mechanism of reaction for sulfoxides with phenyllithium has been found to differ from that of potassium *t*-butoxide is not surprising. The difference in cations employed as well as the greater base strenght of phenyllithium may well account for this observation.

It should be pointed out that the conversion of sulfoxides to olefins as described here is of some synthetic utility. Olefin formation from benzylic sulfides and sulfones has been described.[14] These reactions usually do not give good yields and are not as stereoselective.

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3. R. Ketchem and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).
4. Reaction mixtures were conveniently analyzed by nmr since compounds I through V all show sharp singlet resonance for the non-aromatic protons.
5. For other examples of this reaction see R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **26**, 3467 (1961), and references cited therein.
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8. The preparation of this sulfoxide will be reported shortly.
9. H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25**, 356 (1960).
10. W. Schlenk and J. Holtz, *Ber.*, **50**, 268 (1917).
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12. This reaction could occur either thermally or by sulfur displacement with phenyllithium.
13. Private communication from A. H. Lerit.
14. R. M. Dodson, P. P. Schlangen and E. L. Mutsch, Chem. Commun., 352 (1965), and references cited therein.