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A BASE-INDUCED CARBANIONIC ELIMINATION REACTION OF PHENYLSULFONYLACETATES

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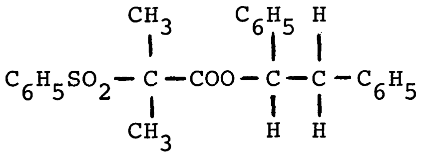
1,2-Diphenylethyl phenylsulfonylacetate underwent predominantly a syn β-elimination with potassium t-butoxide in t-butyl alcohol. A carbanion intermediate and a six-membered cyclic transition state are suggested.

It is well known that the pyrolytic elimination reactions of carboxylic esters at high temperatures proceed through cyclic transition states.[1,2] However, 2-phenylethyl phenylsulfonylacetate (I) was found to be subjected to elimination with a base to produce styrene and methyl phenyl sulfone, although (I) did not react on heating in diphenyl ether (260°C). In the present communication reactions of (I) and its derivatives were investigated in order to clarify the mechanism of this base-induced elimination reaction.

At an appropriate stage of the elimination reaction of (I) with an excess of potassim t-butoxide in absolute t-butyl alcohol under reflux, the reaction mixture was quenched by hydrochloric acid-d (DCl in D_2O). The NMR spectra of recovered (I) showed that the methylene hydrogen atoms α to the sulfonyl group were considerably displaced by deuterium atoms.[3] This observation suggests that (I) must be converted into its carbanion under the above conditions.

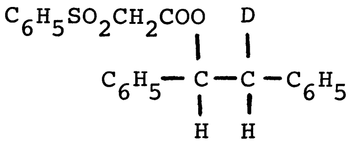
$$\underset{\text{(I)}}{C_6H_5SO_2CH_2COOCH_2CH_2C_6H_5} \xrightarrow{\text{Base}} CH_2{=}CHC_6H_5 + C_6H_5SO_2CH_3 + CO_2$$

Since 1,2-diphenylethyl 2-methyl-2-(phenylsulfonyl)propanoate (II) has no methylene hydrogens α to the sulfonyl group, it is unlikely to anticipate (II) to afford a carbanion similar to that of (I). Reaction of (II) with t-butoxide under the same condition was examined. A large amount of 1,2-diphenylethanol was produced (saponification), and a trace of stilbene (elimination) was detected (g.l.c.). This difference is clearly based on the fact that rapid formation of a carbanion intermediate occurs in the reaction of (I),[4] whereas not in the reaction of (II). From these findings it can be conclude that the carbanion α to the sulfonyl group plays an important role in the olefin-forming elimination reaction of (I).



$C_6H_5SO_2C(CH_3)_2COOCH(C_6H_5)CH_2C_6H_5$

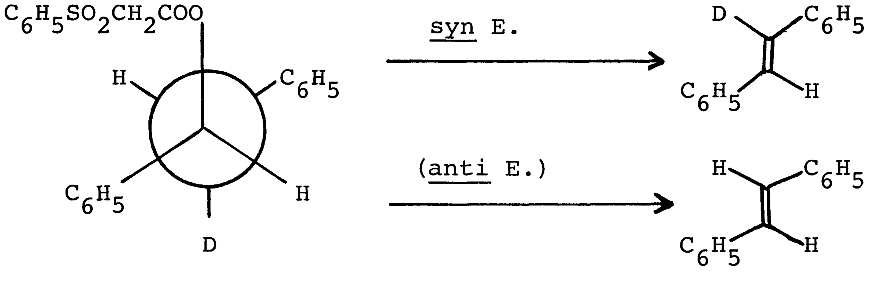
(II)



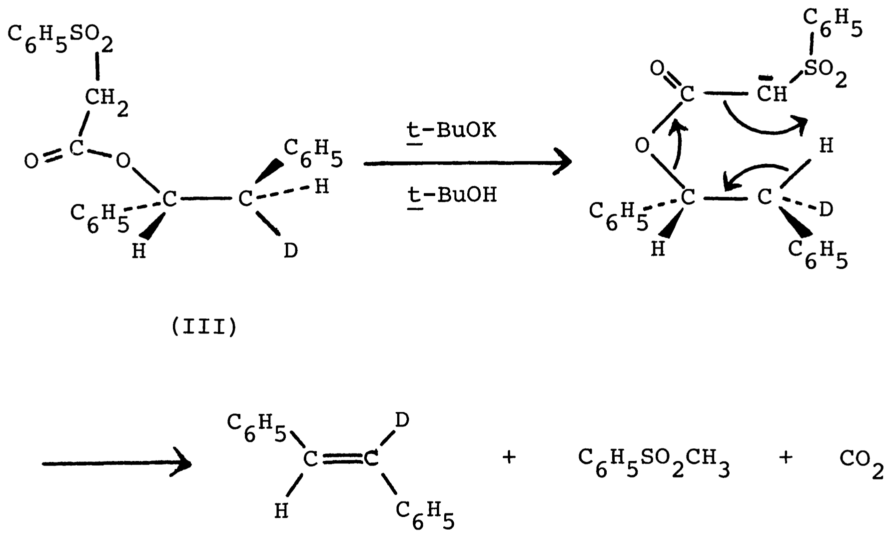
$C_6H_5SO_2CH_2COOCH(C_6H_5)CHDC_6H_5$

(III)

dl-erythro-2-Deuterio-1,2-diphenylethyl phenylsulfonylacetate (III) was treated with t-butoxide (20-fold excess to (III)) in absolute t-butyl alcohol under reflux to investigate the stereochemistry of this elimination. Under the condition employed, no isomerization of cis-stilbene to trans-stilbene was present as checked by g.l.c., and (III) was not converted into the threo-isomer as checked by NMR. Furthermore, recovered (III) from the reaction mixture was found to retain its deuterium atom, that is, no D-H exchange was present. From consideration of a stereo-model of (III), the most favorable conformation is suggested as is depicted (III-a). If the elimination were to occur in a syn fashion from (III-a), (III) should give trans-stilbene-d; while in an anti fashion, (III) should give trans-stilbene with no deuterium. The products of the reaction were carefully analyzed by g.l.c., NMR and mass spectrometry. No cis-stilbene was detected (g.l.c.), and it was found the deuterium content of trans-stilbene to be 80—90%.[5]



(III-a)



(III)

From the facts described above, it is concluded that a carbanion, namely a conjugate base of (III), is formed as an intermediate and this undergoes syn elimination through a six-membered cyclic transition state. A possible alternative may be a syn-E2 mechanism, however, it is unlikely to consider that syn concerted bimolecular elimination occurs in the present case. Previously, Curtin and Kellom reported similar results. They treated erythro-2-deuterio-1,2-diphenylethyl acetate with potassium amide in liquid ammonia, and obtained in fact trans-stilbene-d, however, no elimination was observed with potassium t-butoxide.6)

The elimination reaction described in the present paper resembles a so-called α',β-elimination reaction. Both reactions include the abstraction of hydrogen in the leaving groups and proceed through cyclic transition states. However, α',β-elimination is mainly a reaction of an 'onium salt with an organometallic compound and includes an ylid intermediate which leads inevitably to a five-membered transition state. It is interesting that a rare example of a base-induced cyclic elimination reaction was observed under the present conditions.

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References

1) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, (1959), p. 500.

2) P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.,* 86, 1557 (1964).

3) It was found that a quenching immediately after dissolving (I) into a solution of *t*-BuOK in *t*-BuOH gave rise to (I)-d with approximately 1.2 D atoms in the methylene α to the sulfonyl group. By quenchings at final stages of the reaction, (I)-d with 1.2 ± 0.2 D atoms was afforded.

4) Large excess of *t*-butoxide was required to proceed the elimination reaction of (I) smoothly. The reaction of (I) was followed spectrophotometrically and pseudo first order rate constant was determined to be 1.91×10^{-5} sec^{-1} at 60.0°C (concentration of (I), 5.00×10^{-3} mol/l). Pseudo first order rate constants showed a little dependence on initial concentration of (I) and detailed inspections of this relation suggested a possible intervention of a successive reaction. Details will be reported elsewhere.

5) The deuterium content was determined by mass spectrometry. Recently Donaghue et al. (*Org. Mass Spectrom.,* 2, 1061 (1969)) reported that hydrogen randomization preceded the formation of $M^{+\cdot}$-H· species from the stilbene molecular ion. The deuterium content was evaluated from intensities of the corresponding mass peaks using a method based on their observation.

6) D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.,* 75, 6011 (1953).

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