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THE REDUCTIVE CLEAVAGE OF CARBON-CARBON BOND OF CIS-1,2-DIPHENYLETHYLENE EPISULFONE BY METAL HYDRIDES

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We have reported the stereospecific formation[1] and the decomposition[2] by bases and acids of cis-1,2-diphenylethylene episulfone (I).

In the present paper, we report the reduction of the episulfone by such reducing agents as sodium borohydride, lithium borohydride and lithium aluminum hydride, and describe the effect of solvents on the reduction reaction. The results are summarized in TABLE 1.

The formation of dibenzylsulfone (III) is noteworthy since this new type of reduction[3] involves the cleavage of the C-C bond rather than cleavage of the originally weaker C-S bond.

The reduction mechanism appears to be as represented in SCHEME 1.

In this mechanism, we assume the four centered transition state II, because if aluminum hydride ion or borohydride ion would attack in a manner similar to epoxide reduction (S_N2 back side attack), SCHEME 2, to give II', the C-S bond is likely to cleave resulting in the formation of the sulfinic acid salt, IV.

TABLE 1

	Metal Hydrides (II)	(II)/(I)	Solvents	(°C) Temp.	Products (mole %)		
					Dibenzyl sulfone	*cis*-Stilbene	*trans*-Stilbene
1a	$NaBH_4$	2 : 1	THF	15	33.1	66.1	0
1b	$NaBH_4$	2 : 1	MeOH	15	0	85.1	0
2	$LiBH_4$	2 : 1	THF	15	51.0	40.0	0
3a	$LiAlH_4$	2 : 1	THF	15	0	88.6	0
3b	$LiAlH_4$	2 : 1	THF	70	3.5	77.2	0
3c	$LiAlH_4$	2 : 1	Et_2O	15	9.0	65.4	trace
4	NaH	2 : 1	THF	15	0	100	0
5	LiH	2 : 1	THF	15	0	100	0

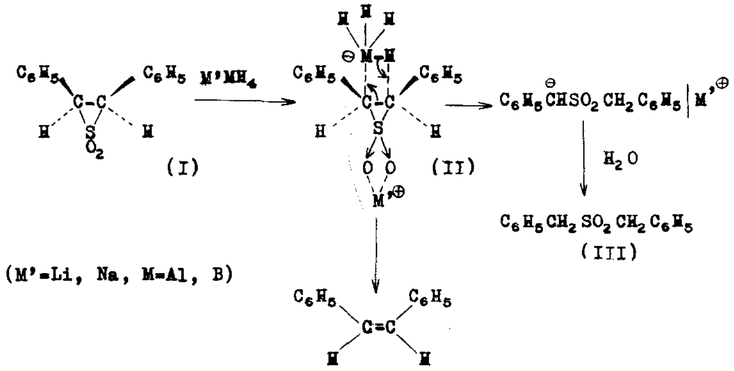
Undoubtedly, this reaction occurs by the nucleophilic attack of $BH_4^{\ominus}$ or $AlH_4^{\ominus}$ on the α-carbons, where the electron densities may be considerably lower.

It was previously reported that *cis*-stilbene is formed by the interaction of metal cations with the oxygen atoms of the sulfone group.[2]

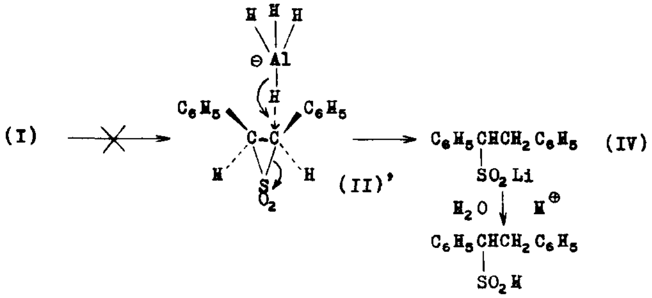
The difference between lithium aluminum hydride and lithium borohydride (or sodium borohydride) as reducing agents is particularly remarkable. Thus no dibenzylsulfone (III) was formed when lithium aluminum hydride in THF at 15°C was used, while, under the same conditions, the borohydride did give (III).

As there is no difference between metal cations, lithium and sodium (Exps. 1a, 2), the above result suggests that aluminum hydride ion may be more strongly solvated in THF than the borohydride ion, which inhibits the attack of aluminum hydride ion on the α-carbon atoms of (I).

SCHEME 1



SCHEME 2



This suggestion is supported by comparison of the results of lithium aluminum hydride in THF and ether (Exps. 3a and 3c). In ether, aluminum hydride is less solvated and has some ability for reduction.

This is in accordance with the solvent effects reported by E. L. Eliel et al.[4] Thus, in methanol, Exp. 1b, (I) could not be reduced by sodium borohydride, due to the greater solvation by methanol.[4]

Also, the small effect of reaction temperature observed in Exp. 3b can be interpreted in terms of a lower degree of solvation at the higher temperature.[5]

References

1. N. Tokura, T. Nagai and S. Matsumura, J. Org. Chem., 31 349 (1966).
2. S. Matsumura, T. Nagai and N. Tokura, Bull. Chem. Soc., Japan., to be published.
3. R. Breslow et al, [R. Breslow, T. Fischer, A. Krebs, R. A. Peterson and J. Posner, J. Am. Chem. Soc., 87 1320 (1965).] reported that dibenzyl ketone was obtained by the catalytic hydrogenation of diphenyl-cyclopropenone.
4. H. Haubenstock and E. L. Eliel, J. Am. Chem. Soc., 84 2368 (1962).
5. P. T. Lansbury and R. E. McLeay, J. Org. Chem., 28 1940 (1963).