

HALOHYDRIN FORMATION IN DIMETHYL SULFOXIDE (1)

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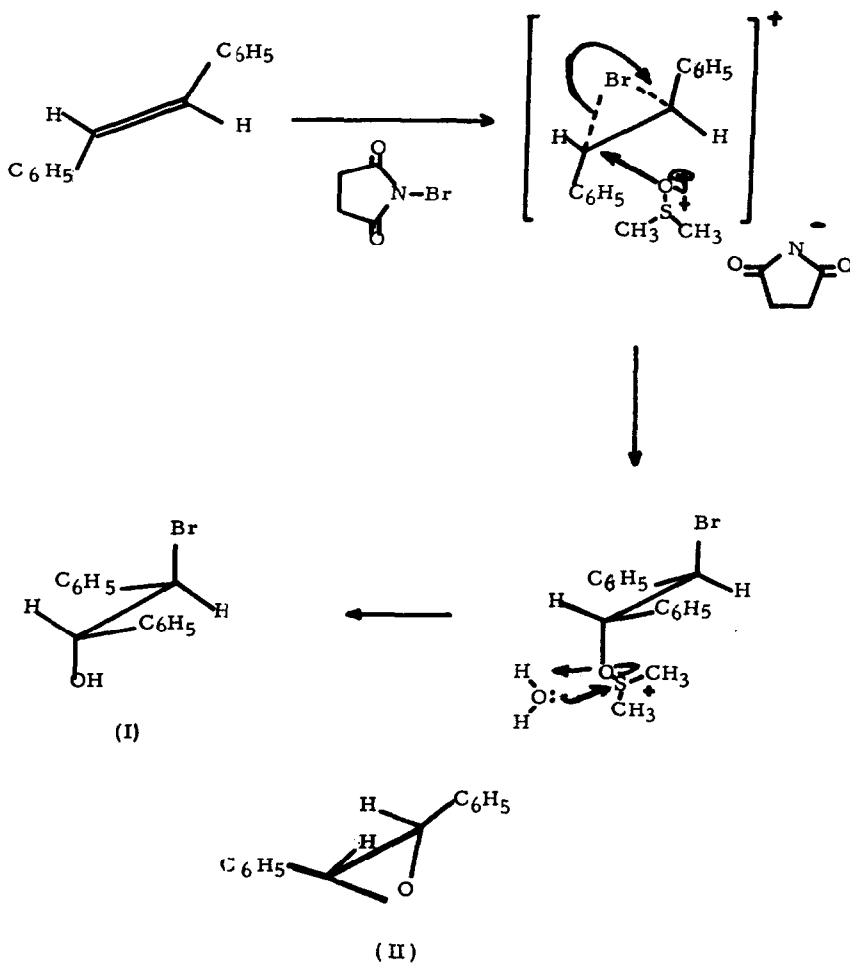
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Alkoxydimethylsulfonium salts have been shown to exist as intermediates in some solvolytic reactions in dimethyl sulfoxide (DMSO) (2). In addition, they appear to be the reactive species in the oxidation of alkyl halides in DMSO (3).

We wish to report that in the stereospecific formation of bromohydrins from olefins and N-bromosuccinimide (NBS) in DMSO containing small quantities of water (4) attack on the bromonium ion (5) is exclusively by DMSO.

Using trans-stilbene, the erythro-bromohydrin (I) (6) formed in DMSO containing a trace of water was converted, with potassium t-butoxide in t-butyl alcohol to the corresponding epoxide (II) (7). Mass spectrometric (8) examination of trans-stilbene epoxide (9) from bromohydrin formed (a) in the presence of 0-18 enriched water (10) and unenriched DMSO and (b) in the presence of unenriched water and 0-18 enriched DMSO (11) showed (12) that greater than 95% incorporation of 0-18 label could consistently be obtained from the 0-18 enriched DMSO and no incorporation resulted from the use of 0-18 enriched water.

The mechanism of bromohydrin formation depicted in Scheme A is consonant with this result although formation of a dimethyl sulfoxide-olefin complex (14) as a first step cannot yet be excluded.

SCHEME A

REFERENCES

1. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.
2. S. G. Smith and S. Winstein, Tetrahedron, 3, 317 (1958).
3. K. Torrsell, Tetrahedron Letters, 37, 4445 (1966).
4. D. R. Dalton, J. B. Hendrickson and D. G. Jones, Chemical Communications 17, 591 (1966).
5. L. P. Hammett, Physical Organic Chemistry, pp. 147 ff. McGraw-Hill, New York, 1940.
6. Exclusive formation of the erythro-bromohydrin has been reported elsewhere (4).
7. Conversion of trans-stilbene to the epoxide via the bromohydrin prepared in dioxane —0-18 enriched water with NBS showed no loss of label, indicating that the bromohydrin is converted to the epoxide with no exchange of oxygen.
8. Mass spectrometric examination of the bromohydrin was hindered by apparent recombination of fragments. Mass spectra were determined on a CEC 21-103 Mass Spectrometer with an inlet temperature of 350 at 70 volts. We gratefully acknowledge the assistance of Mr. M. Henry of Mobil Oil Corporation Laboratories, Paulsboro, New Jersey in the determination of the mass spectra.
9. H. E. Audier, J. F. Dupin, M. Fetizon and Hoppilliard, Tetrahedron Letters, 19, 2007 (1966).
10. Obtained as normalized 0-18 water of 10% enrichment from YEDA Research and Development Co., Ltd., Rehovoth, Israel.
11. Prepared by a modification of the method A. H. Fenselau and J. G. Moffatt, J. Am. Chem. Soc., 88, 1762 (1966).
12. The parent ion peak ratio (196/198) as well as the 105/107 ratio which presumably corresponds (9) to $C_6H_5CO^+$ were examined. Agreement was $\pm 0.5\%$ in each case after correction for a small and apparently spurious (13) peak at mass 198 present in all unenriched samples of trans-stilbene epoxide examined.
13. The nature of the ion represented by this peak is currently under examination.
14. C. D. Ritchie and A. L. Pratt, J. Am. Chem. Soc., 86, 1571 (1964).