An Improved Procedure for the Preparation of Bromohydrins

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THE preparation of bromohydrins has long been hampered by the limited solubility of olefins in water, necessitating, in many cases, the use of emulsions[1] or mixed solvent systems.[2]

We report a method, apparently of general utility, utilizing a single solvent system, which avoids the use of large quantities of water, precluding the above difficulties.

Olefins (Table) in dimethyl sulphoxide solvent, containing a small quantity of water have successfully been converted, in short reaction time, into the corresponding bromohydrin by the action of *N*-bromosuccinimide.

In a typical experiment, the olefin (10 mmoles) was permitted to dissolve in dry[3] dimethyl sulphoxide (50 ml.) and water (25 mmoles) added. Under a nitrogen atmosphere, *N*-bromosuccinimide (20 mmoles) was added with cooling (below 20°). After the time indicated, the reaction mixture was quenched in a large volume of water and the product removed by ether extraction.

We are currently examining other positive

Table

Olefin	Bromohydrin	Yield (%)	Time (min.)	m.p. or b.p./pressure (mm.)	Ref.
trans-Stilbene	*erythro*-2-Bromo-1,2-diphenylethanol	73	15	83·5—85	4
Indene	*trans*-2-Bromo-1-hydroxyindane	72	60	130—131·5	5
Cyclohexene	*trans*-2-Bromocyclohexanol	78	15	63—65/4 mm. n_D^{25} 1·5185	5
Styrene	2-Bromo-1-phenylethanol	73	15	110—111/2 mm. n_D^{25} 1·5768	5

halogen sources, the role played by the water initially added, and the mechanism of this reaction.

(*Received, July* 25*th*, 1966; *Com.* 536.)

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[1] W. F. Hanby and H. N. Rydon, *J. Chem. Soc.*, 1946, 114.

[2] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, 1958, **2**, 1.

[3] The dimethyl sulphoxide was Fisher Certified Reagent which had been dried over molecular sieve prior to use.

[4] H. O. House, *J. Amer. Chem. Soc.*, 1955, **77**, 3070.

[5] C. O. Guss and R. Rosenthall, *J. Amer. Chem. Soc.*, 1955, **77**, 2549.