

The Deuterioxide-catalyzed Hydrogen Exchange of Dimethyl Sulphoxide. Preparation of Diperdeuteromethyl Sulphoxide, $(CD_3)_2SO$

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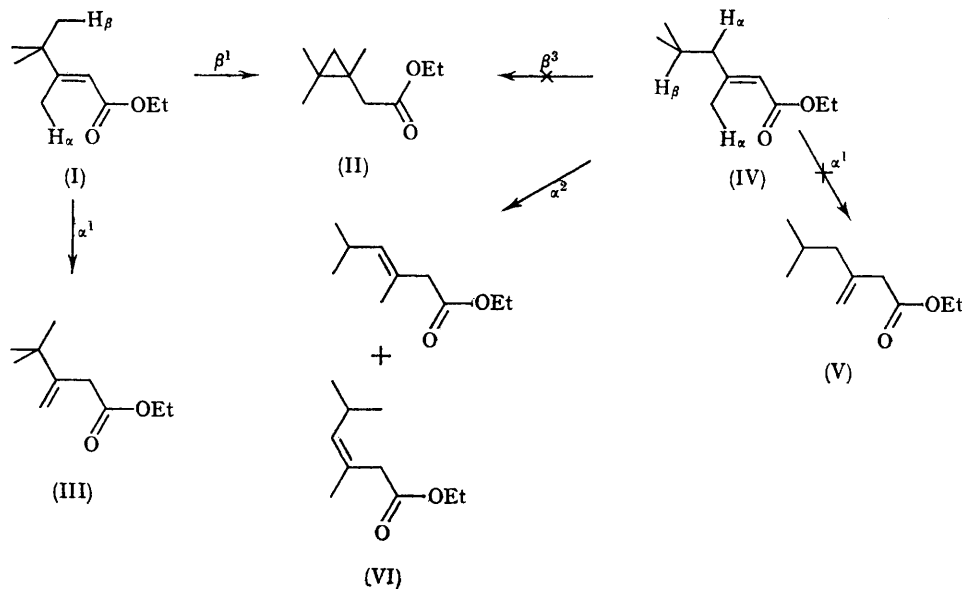
WE have observed that dimethyl sulphoxide (DMSO) undergoes hydrogen exchange in the presence of sodium deuterioxide under very mild conditions. Even at a deuterioxide concentration of 0.01M and at room temperature, a 10% D_2O —90% DMSO solution equilibrates hydrogen and deuterium within one hour. In a preliminary rate study, the rate of exchange was measured by following the appearance of OH absorption in the infrared spectrum (2.9μ). At a deuterioxide concentration of 0.002M in 10% D_2O —90%

DMSO by volume the initial (pseudo first order) rate constant is $2.3 \times 10^{-4} \text{ sec.}^{-1}$ at 28°C (ambient temperature). The rate increased linearly with deuterioxide-ion concentration over the range studied (0.001—0.003M). The rate of exchange also increased as the water content of the medium was decreased: at 0.001M-NaOD a change from 10% D_2O —90% DMSO to 5% D_2O —95% DMSO increased the rate about ten-fold.

This ready hydrogen exchange affords a convenient and inexpensive method for the preparation

is in an $n \rightarrow \pi^*$ excited triplet state. When methanol is employed in the irradiation of (I), formation of the $\beta\gamma$ -unsaturated ester (III) competes with the formation of the cyclopropyl

$\beta\beta$ -dimethylacrylate readily underwent isomerization to their $\beta\gamma$ -isomers. Similarly, ethyl 4-methylpent-2-enoate and ethyl 5-methylhex-2-enoate gave the corresponding $\beta\gamma$ -isomers while



ester (II). No solvent effects were discerned in the photochemistry of esters (IV) and (VII).

In contrast to the behaviour of the corresponding methyl ketones,² methyl crotonate and ethyl

ethyl 4,4-dimethylpent-2-enoate afforded ethyl (2,2-dimethylcyclopropyl)acetate. The ready accessibility of $\alpha\beta$ -unsaturated esters *via* the phosphonate Wittig reaction³ lends synthetic utility to these photochemical conversions.

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² N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1964, 1203.

³ W. S. Wadsworth, jun., and W. D. Emmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1733.