SYNTHESIS OF ACROLEIN-1-D,-2-D AND -1,2-D_2 .

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In connection with some electronic absorption spectroscopic studies [1], a series of deuterioacroleins were synthesized.

Deuterated acroleins have previously been mentioned in the literature [2,3], but no experimental details were given for their syntheses. R. E. Partch [4] described an elegant method for the synthesis of aldehydes by lead tetraacetate oxidation of alcohols. However, the yields of acrolein obtained by us from the oxidation of allyl alcohol were never higher than 15%.

The aldol condensation of acetaldehyde and formaldehyde is often mentioned in the literature as a preparation of acrolein on a commercial scale [5,6,7]. It was found that this method, under improved experimental conditions, was suitable for the synthesis of the deuterated acroleins required for electronic absorption spectroscopic studies.

Experimental

Acrolein-1-D

An aqueous solution of formaldehyde was prepared by cracking at 60°-80° a mixture of paraformaldehyde (15 g) and phosphorus pentoxide (20 g) at 20 mm pressure [8] and by collecting the gaseous formaldehyde in 17 ml of water. This solution and freshly distilled acetaldehyde-1-D (1.1 g) were mixed and added dropwise from a separatory funnel over a period of 3 hr to a vertical Pyrex tube (24 inches long, 2 inches in diameter), packed with 10% lithium carbonate on silica gel (28-100 mesh) which was separated into three sections by glass wool. About one inch of glass beads was placed on top of the catalyst about three inches from the top of the tube. The tube was uniformly heated at 270° by means of a three-section furnace. The reaction products were collected in a trap cooled to -78° attached directly to the bottom of the reaction tube. The apparatus was swept out with nitrogen during addition of the aqueous solution and for 1 hr thereafter. The reaction products were distilled at room temperature on a vacuum line into a Stock trap cooled in liquid N_2 until about 5 ml of liquid had distilled over. This distillate was redistilled successively at 0° and -30° under reduced pressure into traps containing quinol as a stabilizer.

The acrolein obtained was over 97% pure (by N.M.R. and mass-analysis) and the yield was 0.73 g (52%).

Acrolein-2-D

The above procedure was repeated with a solution of formaldehyde in D_2O and freshly distilled acetaldehyde on a catalyst which had been treated with three portions of 15 ml of D_2O, twice at room temperature and once at 270°. The exchange of the protons on the α-carbon of the acetaldehyde was very much faster than its condensation with formaldehyde and, therefore, the acrolein obtained was 95.4% monodeuterated on the α-position.

Acrolein-1,2-D_2

This compound was prepared as described above from a solution of formaldehyde in D_2O and acetaldehyde-1-D. The acrolein obtained was 95.5% D_2 and 4.3% D.

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