SYNTHESIS OF 2-ALKYL-2-FORMYLTHIIRANES

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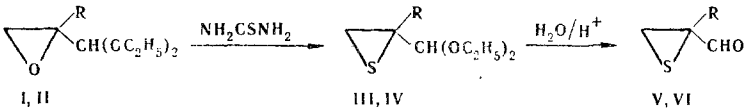
By means of the reaction of 2-alkyl-2-formyloxirane diethylacetals (I, II) with thiourea we obtained 2-alkyl-2-formylthiirane acetals (III, IV), the hydrolysis of which made it possible to obtain the corresponding 2-alkyl-2-formylthiiranes (V, VI) — a class of episulfides that has not been previously described in the literature. Considering the properties of their oxygen analogs, one might assume that these products will find wide application in organic synthesis.



I, III, V R = C_2H_5; II, IV, VI R = i-C_3H_7

EXPERIMENTAL

Diethylacetals III and IV. These compounds were synthesized by the reaction of 0.04 mole of acetals I and II and 0.05 mole of thiourea in 300 ml of methanol at 70°C for 8-9 h. Acetal III, with bp 89°C (11 mm) and n_D^{20} 1.4586, was obtained in 86% yield. Acetal IV, with bp 98°C (11 mm) and n_D^{20} 1.4600, was obtained in 82% yield.

2-Alkyl-2-formylthiiranes (V, VI). These compounds were formed by gentle refluxing of 0.05 mole of acetals III and IV in 15 ml of 7% phosphoric acid and 40 ml of dioxane for 40 min. After cooling and neutralization to give a weakly acidic medium, the reaction mixture was extracted with ether. Aldehyde V, with bp 50-51°C (10 mm) and n_D^{20} 1.4990, was obtained in 82% yield. Aldehyde VI, with bp 58-59°C (10 mm) and n_D^{20} 1.4910, was obtained in 83% yield.

The geminal protons of the thiirane ring of acetals III and IV show up in the PMR spectra in the form of two singlets at 2.15-2.25 ppm, whereas in the case of formylthiiranes V and VI they give two doublets with δ 2.46 and 2.58 and 2.37 and 2.58 ppm, respectively (J = 2.5 Hz). IR spectra (CCl_4): III and IV: 640 (C—S) and 1070-1120 cm^{-1} (C—O); V and VI: 600, 610 (C—S); 1710 cm^{-1} (C=O).

The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

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