REGIO- AND STEREOSPECIFIC SPLITTING OF THIOPHENE RING AND ITS USE IN A NEW SYNTHESIS OF δ-MERCAPTO-β,γ-ALKENE ACIDS

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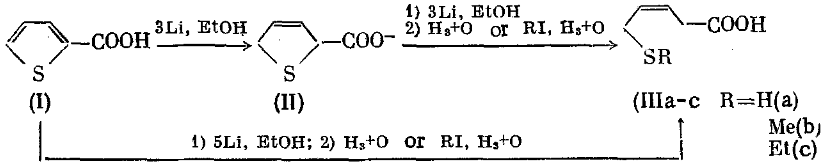
We have found that, in contrast to 2-alkylthiophenes, which undergo reductive splitting under the influence of lithium and alcohol in liquid NH_3, forming enthiolates [1], in 2-thiophenecarboxylic acid (I) under the same conditions, the thiophene ring is opened at the C–S bond in the α position to the substituent. Here, regiospecifically and stereospecifically, with high yield, 5-mercapto-cis-3-pentenoic acid (IIIa) is found. This acid has been isolated in pure form, and also in the form of the S-alkyl derivatives (IIIb and IIIc), obtained by the addition of the alkyl halide to the reaction mixture after reduction. The splitting of the C–S bond is preceded by the formation of the product of incomplete hydrogenation of the thiophene ring, 2,5-dihydrothiophene-2-carboxylic acid (II). This latter compound was detected in the reaction products when the quantity of lithium was 3 g-eq relative to (I). In turn, the acid (II), by the action of 3 g-eq of lithium, is smoothly converted to (IIIa)



By the indicated route, we obtain the following compounds [figures given represent the yield in %, bp in °C (p, torr), and n_D^{20}): (IIIa) 81, 82 (0.03), 1.5158; (IIIb) 74, 88 (0.02), 1.5120; (IIIc) 82, 97-98 (0.02), 1.5068. The structure of the compounds (III) was confirmed by data of elemental analysis and by the IR, NMR, and mass spectra.

An increase in the reaction temperature to room temperature leads to removal of the sulfur and the formation of the β,γ-unsaturated acid.

LITERATURE CITED

1. Ya. L. Gol'dfarb and E. P. Zakharov, Izv. Akad. Nauk SSSR, Ser. Khim., 1909 (1975).

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