NOVEL POLYFUNCTIONAL SPIROHETEROCYCLICS BASED ON ACETYLENIC HYDROXYACIDS

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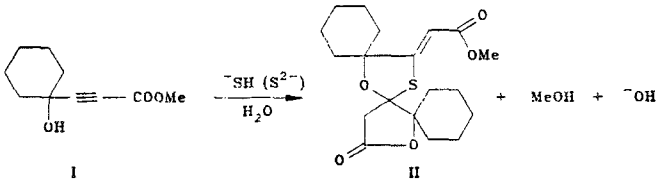
Esters of acetylenic hydroxyesters, such as type I, are easily obtained by the reactions of acetylenic alcohols with carbon monoxide [1]; they present several new opportunities for the construction of more complex heterocyclic systems.

For instance, the addition of sulfide ions to ester I in aqueous media under mild conditions (5-25°C) does not stop with the formation of the corresponding tetrasubstituted divinylsulfide, as reported previously [2], but rather proceeds unexpectedly to generate the novel polyfunctional heterocyclic system II.



I II

Apparently, one of the hydroxyl groups in the intermediate divinylsulfide adds crosswise to one of the double bonds, forming a 1,3-oxathiolane ring, whereas the second hydroxyl group reacts with the ester functional group to give a lactone ring. Thus, ester I, as well as various homologs with different substituents in the 4-position, generates isomerically pure cyclization products, in which the S—C=CHCO$_2$Me fragment is assigned the Z-configuration, based on the fact that reaction of propiolic acid under these conditions generates exclusively Z,Z-di(2-carboxyvinyl)sulfide [3].

18-Methoxycarbonylmethylene-7,11-dioxa-19-thiatrispiro[5.3.1.5.2]nonadecan-8-one (II). This was prepared from 2 mmoles of ester I and 1 mmole of Li_2S in 20 ml of H_2O (21-26°C, 4 h). Yield, 19%, mp 183°C. PMR spectrum (CCl_4), δ: 1.72 (10H, m), 3.02 (2H, d), 3.75 (3H, s), 5.74 ppm (1H, s). IR spectrum: 1190, 1600, 3070, 1690, 1780 cm^{-1}.

3-Methoxycarbonylmethylene-2,2,6,6-tetramethyl-1,7-dioxa-4-thiaspiro[4.4]nonan-8-one. This was prepared in an analogous manner from methyl-4-methyl-4-hydroxy-2-pentanoate; mp 157-158°C. PMR spectrum (CCl_4), δ: 1.43 (12H, s), 3.07 (2H, d), 3.76 (3H, s), 5.76 ppm (1H, s). IR spectrum: 1190, 1590, 3050, 1690, 1780 cm^{-1}.

Both cyclization products gave satisfactory elemental analyses.

LITERATURED CITED

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