ADDITION OF HYDROGEN SULFIDE TO 1,5-DIPHENYLPENTA-1,4-DIYN-3-ONE

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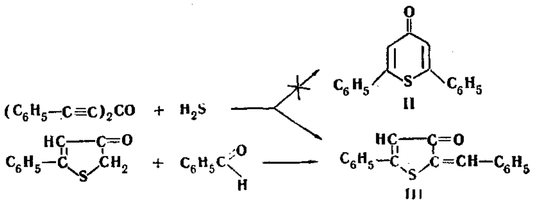
UDC 547.733'818:543.422

When α,α'-diacetylenic ketones are heated with alcoholic solutions of hydrogen sulfide in sealed tubes, 1-thia-γ-pyrones are formed [1]. One of us [2] has shown that the addition of H_2S to hepta-2,5-diyn-4-one in fact leads to 2,6-dimethyl-1-thia-γ-pyrone. However, the reaction takes place only in the presence of basic catalysts and is accompanied by spontaneous heating.

Under similar conditions, i.e., with the passage of hydrogen sulfide for 10 min into a solution of 1 g of 1,5-diphenylpenta-1,4-diyn-3-one (I) [3] in 10 ml of methanol containing 0.01 ml of triethylamine at 20-30°C, it is not 2,6-diphenyl-1-thia-γ-pyrone (II) that is formed, as described in the literature [1], but 2-benzylidene-3-oxo-5-phenyl-1,2,3-dihydrothiophene (III), with a yield of 57%. The structure of III was confirmed by its PMR spectra, which contained three signals with chemical shifts of 7.64, 7.40, and 6.6 ppm in an intensity ratio of 5 : 6 : 1. The central band in the spectrum, consisting of three components with chemical shifts of 7.43, 7.40, and 7.33 ppm is due to the superposition of the signals of the protons of one of the phenyl and one of the methine groups. If II were formed, then because of its symmetry two proton resonance signals corresponding to the two phenyl groups and two methine groups with an intensity ratio of 10 : 2 should be expected in the spectrogram.

This direction of the addition of hydrogen sulfide to I is confirmed by the independent synthesis of III which was effected by briefly heating 4-oxo-2-phenylthiophene [4] with benzaldehyde in ethanol in the presence of a drop of hydrochloric acid. After crystallization from ethanol, the materials obtained by the two methods had mp 143.4°C. A mixture of them melted without depression.



Their UV spectra (in ethanol, λ_{max} at 240, 281, 345, and 421 nm) and IR spectra were also identical.

LITERATURE CITED

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Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 8, p. 1146, August, 1970. Original article submitted December 30, 1969.