SYNTHESIS OF 2-BENZOYL(THENOYL)BENZO-1,4-THIAZINES

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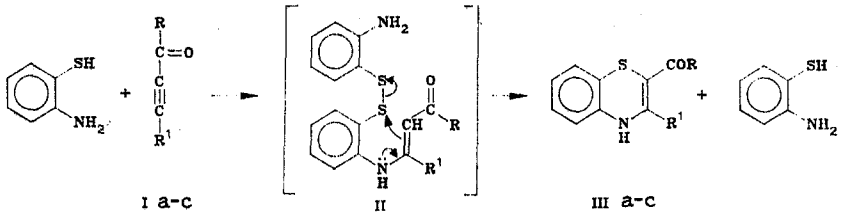
Reaction of o-aminothiophenol with acetylenic ketones in methanol or glacial acetic acid affords benzo-1,5-thiazepines [1]. Similar compounds have been obtained by reacting o-aminothiophenol with chalcone [2]. The reaction of terminal α-acetylenic ketones with o-aminothiophenol in the presence of triethylamine yields 2-acylmethyl-4,5-benzothiazolines and 3-acylvinyl-2-acylmethyl-4,5-benzothiazolines [3].

We have found that the reaction of α-acetylenic ketones (Ia-c) with o-aminothiophenol in equimolar proportions in DMSO at 145-150°C gives 2-benzoyl(thenoyl)benzo-1,4-thiazines (IIIa-c).



I a-c II III a-c

I, III a R = Ph, b, e R = C_4H_3S; a, b R^1 = H, c R^1 = Ph

By analogy with the findings reported in [4], it is assumed that under the reaction conditions the o-aminothiophenol is readily oxidized to bis(o-aminophenyl)disulfide which reacts with the acetylenic ketone (Ia-c) to give the intermediates (II). Intramolecular cyclization of the latter with fission of the S—S bond on heating leads to the formation of the benzo-1,4-thiazines IIIa-c.

(IIIa): mp 241-242°C from a mixture of CH_3CN and DMF, yield 60%. IR spectrum (KBr): 700 (C—S), 1520 (C=C), 1620 (C=O), 3290 cm^{-1} (NH). PMR spectrum (DMSO-D_6), δ: 9.12 (1H, d, NH), 6.55-7.53 ppm (10H, m. arom protons, CH=). Mass spectrum, m/z: 253 (M^+), 148, 105, 77.

(IIIb): mp 237-283°C (from CH_3CN), yield 62%. IR spectrum (KBr): 710 (C—S), 1545 (C=C), 1625 (C=O), 3240 cm^{-1} (NH). PMR spectrum, δ: 9.28 (1H, d, NH), 6.61-7.88 ppm (8H, m, arom. protons, C_4H_3S, CH=). Mass spectrum, m/z: 259 (M^+), 148, 111, 108, 83.

(IIIc): mp 165-166°C (from CH_3CN—ether), yield 42%. IR spectrum (KBr): 715 (C—S), 1580 (C=C), 1620 (C=O), 3260 cm^{-1} (NH). PMR spectrum, δ: 9.45 (1H, s, NH), 6.71-7.60 ppm (12H, m, arom. protons, C_4H_3S).

The elemental analyses of these compounds corresponded to the calculated values.

LITERATURE CITED

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