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NEW METHOD OF ISOLATING N-SUBSTITUTED 3-AMINOMETHYLENETHIOL-4-EN-2-ONES

M. A. Kalik, Ya. L. Gol'dfarb, and M. M. Krayushkin

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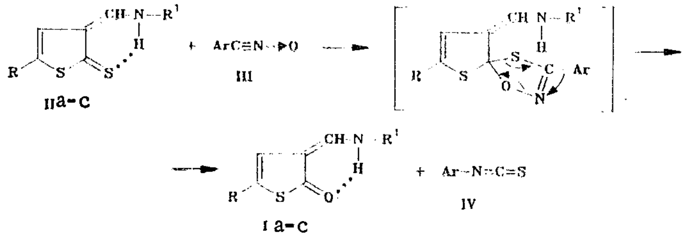
The methods for the synthesis of the little-studied N-substituted 3-aminomethylenethiol-4-en-2-ones (I) — thiophene analogs of aromatic o-hydroxyazomethines — are based on the application of the not readily accessible and labile hydroxy and methoxy derivatives of thiophene [1, 2].

We have found that the compounds (I) can be obtained in good yields (60-80%) by the reaction of the corresponding N-substituted mercaptoaldimines (II) with mesitylnitrile oxide (III) at 20°C for 20-30 min. The resulting oxyaldimines (Ia-c) and mesityl isothiocyanate (IV) are separated by chromatography on silica gel utilizing hexane [for compound (IV)] and $CHCl_3$ [for the substances (I)] as the eluents.



I, II a,b R=Et, c R=OMe; a,c R^1=*cyclo*-C_6H_{11}, b R^1=β-$C_{10}H_7$; Ar=2,4,6-$Me_3C_6H_2$

The structure and composition of the compounds obtained were confirmed by the data of the elemental analysis, IR, UV, PMR, and mass spectra. The oxyaldimines (Ia, b) were identical to the samples previously described by us [2] according to the mps and the spectra. Compound (Ic), $C_{12}H_{17}NO_2S$, had a yield of 70% and mp 119-121°C (from alcohol). The PMR spectrum in $CDCl_3$ was as follows: 3.75 (3H, singlet, OCH_3), 5.38 (1H, singlet, 4-H), 7.00 (1H, doublet, CH=N, $J_{CH,NH}$ = 13.5 Hz), and 9.00 ppm (1H, broad singlet, NH). The mass spectrum (m/z, J, %) was as follows: 239 (100) (M^+), 224 (70), 157 (80), 142 (85), and 114 (20).

The conversion observed can be considered as the selective 1,3-dipolar cycloaddition of the nitrile oxide (III) at the thiocarbonyl group of the mercaptoaldimine (II), and the subsequent opening of the resulting oxathiazole ring with the accompanying migration of the aryl residue to the nitrogen and the elimination of the isothiocyanate (IV) [3].

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