TRI(ETHOXYCARBONYL)CYCLOPENTA[b][1,4]BENZOTHIAZINE – A NEW ISO-π-ELECTRONIC ANALOG OF AZULENE

N. V. Sumlivenko and G. F. Dvorko

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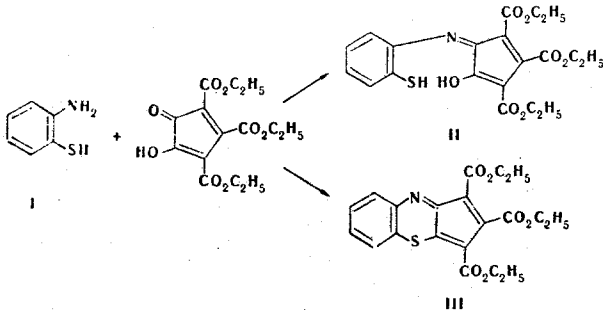
The condensation of tri(ethoxycarbonyl)-1,2-hydroxycyclopentadienone with o-aminothiophenol (I) gives compounds (II) and (III), depending on the conditions. The imine (II) is formed in ~50% yield in methanol (60°C, 10 min) with a twofold excess of (I). After crystallization from a mixture of benzene and hexane (1:1) it formed a yellow crystalline substance (mp 142°C, λ_{max} 420 nm, log ε 3.9 in C_2H_5OH). Found: C 57.6; H 5.1; N 3.4; S 7.9%. $C_{20}H_{21}NO_7S$. Calculated: C 57.3; H 5.1; N 3.3; S 7.6%.



I II III

A new iso-π-electronic analog of azulene – 1,2,3-tri(ethoxycarbonyl)cyclopenta[b][1,4]benzothiazine (III) was obtained in ~35% yield in pyridine (100°C, 10 min) with equimolar concentrations of the reactants (dark-violet crystals with mp 126°C, λ_{max} 558 nm, log ε 3.4 in C_2H_5OH). Found: C 59.4; H 4.6; N 3.6; S 7.8%. $C_{29}H_{19}O_6NS$. Calculated: C 59.8; H 4.8; N 3.5; S 8.0%. Compound (II) is readily converted into (III) by heating it in acetic anhydride.

The IR spectrum of (II) shows a band at 3350 cm^{-1} (OH), which is absent in (III); and the PMR spectrum of (II) ($CHCl_3$), unlike that of (III), shows the signal of the proton of a SH group at 3.55 ppm. The ethyl protons of (II) give six groups of lines at 1.29, 1.32, and 1.38 ppm (CH_3, triplet) and 4.23, 4.29, 4.41 ppm (CH_2, quadruplet). In (III), the ethyl protons in positions 1 and 3 give two groups of lines at 1.37 ppm (CH_3) and 4.50 ppm (CH_2), while the lines of the ethyl protons in position 2 are displaced with respect to them – 1.48 ppm (CH_3) and 4.61 ppm (CH_2). The equivalence of the ethyl protons of the terminal ester groups of (III) is due to the similar values of the charge in these positions (MOH method).

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