SYNTHESIS OF DI(4-ETHOXYCARBONYL-5-METHYL-3-THIENYL)AMINE AND (4-ETHOXYCARBONYL-5-METHYL-3-THIENYL)HYDRAZINE

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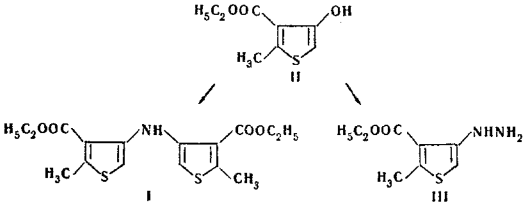
We have obtained di(4-ethoxycarbonyl-5-methyl-3-thienyl)amine (I) in 74% yield by heating 4-ethoxycarbonyl-3-hydroxy-5-methylthiophene (II) with a fivefold excess of ammonium acetate for 1 hr. When the reaction was carried out under other conditions, I was isolated only in insignificant yield [1]. The accessibility of I opens up prospects for the synthesis of condensed heterocycles—analogs of phenothiazine derivatives.

The reaction of II with hydrazine acetate under conditions analogous to the synthesis of I gave us an 83% yield of (4-ethoxycarbonyl-5-methyl-3-thienyl)hydrazine (III).



Di(4-ethoxycarbonyl-5-methyl-3-thienyl)amine (I). Green crystals, mp 105–106° C (from methanol). IR spectra, cm^{-1}: 3270 (NH), 1690 (ester C=O), 790 (thiophene ring). UV spectrum (methanol): λ_{max} 248, 279, and 345 nm, log ε 4.36, 4.02, and 3.61. Found, %: C 54.41; H 5.38; N 4.06; S 18.31. Calculated for $C_{16}H_{19}NO_4S_2$, %: C 54.36; H 5.42; N 3.95; S 18.14.

(4-Ethoxycarbonyl-5-methyl-3-thienyl)hydrazine (III). White crystals, mp 69–70° C (from ether). IR spectrum, cm^{-1}: 3200, 3130 (NH, NH_2), 1710 (ester C=O), 810 (thiophene ring). UV spectrum (methanol): λ_{max} 226 nm, log ε 4.01. Found, %: C 47.99; H 5.88; N 14.20; S 16.28. Calculated for $C_8H_{12}N_2O_2S$, %: C 47.98; H 6.04; N 13.99; S 16.01.

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THE CONFORMATIONAL MOBILITY OF THE MOLECULE OF N, N'-BIS(TRIMETHYLSILYL)PIPERAZINE ACCORDING TO PMR DATA

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In order to study the influence of a silicon atom on the conformational mobility of the piperazine ring, we have investigated the temperature dependence of the PMR spectrum of N, N'-bis(trimethylsilyl)piperazine (I).

The results obtained show that in methylene chloride solution the molecule of I undergoes rapid conformational transitions right down to the solidification temperature of the solution (−80° C). At the same time, in the molecule of N, N'-dimethylpiperazine (II) the chair$\rightleftarrows$chair transitions become fairly slow even at −8.5° C [1].

It may be assumed that the role of the $Si(CH_3)_3$ group in I reduces to increasing the conformational mobility of the whole skeleton of the heterocycle through an increase in the valence angles of the nitrogen atoms and an increase in the order of the nitrogen—silicon bond ($p_\pi - d_\pi$ interaction), facilitating the transition between the intermediate state.

The PMR spectra were studied for 20% solutions of I in methylene chloride on a YaMR-553 TsLA spectrometer. The chemical shifts, which were measured for a sample containing hexamethyldisiloxane as internal standard, did not change when the temperature was lowered (CH_3Si–10.00 τ and CH_2N–7.33 τ).

Compound I was obtained by the reaction of piperazine with hexamethyldisilane in the presence of ammonium sulfate, bp 82–83° C (7 mm); d_4^{20} 0.8635; n_D^{20} 1.4500; MR_D 71.60; found 71.71 (according to the literature [2], bp 217–218° C; $n_D^{21.5}$ 1.4499).

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