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SYNTHESIS OF 1-(4-ALKANOYLPHENYL)-2-PYRAZOLINES BASED ON DITHIOLIUM SALTS

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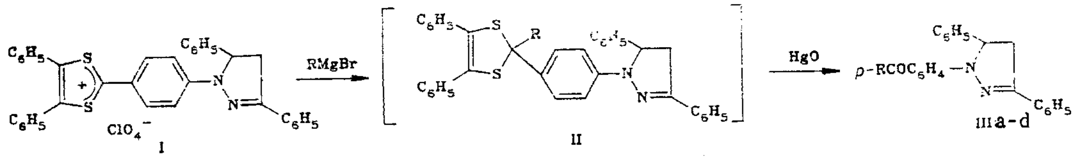
UDC 547.738'778.07

Dithiolium salts of 2-pyrazoline derivatives (I), which have been reported previously by us [1], may be regarded as convenient precursors for the preparation of 1-(4-alkanoylphenyl)-3,5-diphenyl-2-pyrazolines (IIIb-d), based on the known conversion reaction of 1,3-dithiols to ketones [2]. We have found that reaction of compound I with Grignard reagents, followed by hydrolysis of the intermediate dithiols II according to [2], leads to the formation of 1-(4-alkanoylphenyl)-2-pyrazolines, and have demonstrated that the pyrazoline ring is not disturbed under these conditions. Although the yields obtained are not very high (35-40%), the method described here is quite general in character and allows one to vary the nature of the substituent R significantly. The direction of the reaction was verified by an independent synthesis of pyrazolines IIIa and IIIb, based on the formylation and acetylation of 1,3,5-triphenyl-2-pyrazoline [3, 4]. As a result of side reactions, the aldehyde IIIa, which was separated chromatographically, was also formed in all cases in addition to ketones IIIb-d.



III a R=H, b R=CH_3, c R=C_4H_9, d R=$C_{10}H_{21}$

A suspension of 0.8 g (1.2 mmole) of salt I in 50 ml absolute ether was treated with 2 mmole of freshly prepared Grignard reagent and stirred at 30-35°C until the violet deposit of salt I had completely disappeared and a stable yellow color was observed. After workup of the reaction mixture with saturated NH_4Cl solution, the ether layer was washed with water and dried over $CaCl_2$, and the solvent was evaporated. The residue was hydrolyzed by dissolving in 3-5 ml tetrahydrofuran and adding it in one portion to a suspension of 0.9 g (4.2 mmole) of HgO in 2 ml of 35% HBF_4 in 10 ml tetrahydrofuran. After completion of the reaction (which was monitored by TLC with chloroform eluent for complete disappearance of compound II), the suspension was extracted with benzene, dried, and the solvent was evaporated. The residue was subjected to chromatography on a SiO_2 column (chloroform eluent) and crystallized from heptane.

Compound IIIa, mp 118-120°C (according to [3], mp 122-123°C), R_f 0.28, yield 60%; IIIb, mp 150-152°C (according to [4], mp 152°C, R_f 0.38, yield 40%; IIIc, mp 137-139°C, R_f 0.41, yield 50%; IIId, mp 108-109°C, R_f 0.42, yield 35%. Compounds IIIb-d exhibit identical electronic absorption spectra in toluene [λ_{max} 375 nm (ε $3 \cdot 10^4$)] and ethanol [λ_{max} ($\varepsilon \cdot 10^{-3}$):

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379 (30), 308 (6.0), 244 nm (11.0)], as well as emission spectra [$\lambda_{max}^{fluoresc.}$ 415-416 nm (toluene)]. IR spectrum: 1596-1598 (C═N), and 1664-1670 cm^{-1} (C═O).

The composition of the samples was confirmed by elemental analysis.

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REACTION OF DIENDIAMINODIKETONES WITH NUCLEOPHILIC REAGENTS. SYNTHESIS OF 2-PYRIDONE AND 2-PYRIDINETHIONE DERIVATIVES

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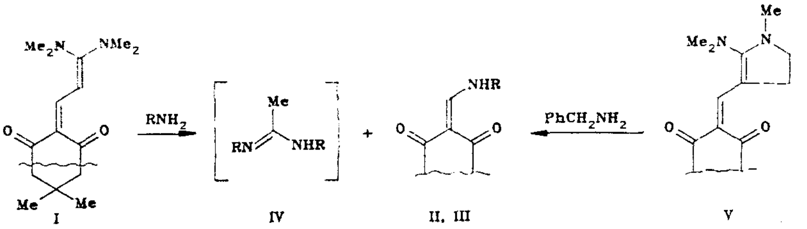
Enamines react readily with primary amines to give peramination products [1]. In experiments dealing with this type of reaction for benzylamine and aniline with diendiaminoketone I [2], we have found, unexpectedly, that the process is accompanied by cleavage of the β,γ-carbon—carbon bond, resulting in the formation of the known compounds, N-substituted aminomethylene-dimedones II and III [3, 4]. For the reaction with benzylamine, it was established that the mother liquor contained, in addition, a compound of molecular weight 238 (mass spectrum), which would appear to be a secondary product arising from cleavage of the C—C bond, namely, N,N-dibenzylacetamide (IV). Reaction of the five-membered analog of compound I (V) with benzylamine proceeded similarly and gave enamine II.



II R=Ph; III,IV R=CH$_2$Ph;

In continuation of these results, we have examined the reactions of diendiaminodiketone (I) with compounds containing an active methylene group, such as cyanacetamide (VI) and cyanthioacetamide (VII). Reaction of compounds I and VI gave 6-dimethylamino-3-cyano-2-pyridone (VIII) [yield 43%, mp 282-283°C (from ethanol), $M^{+\cdot}$ 163], which was identical to an authentic sample prepared by an independent method [5]. Dimedone (IX) was detected in the mother liquor by mass spectroscopy ($M^{+\cdot}$ 140), along with 3-dimethylamino-5,5-dimethylcyclohexen-2-one (X), ($M^{+\cdot}$ 167). In an analogous manner, reaction of compounds I and VII gave 6-dimethylamino-3-cyano-2-pyridinethione (XI) [yield 76%, mp 206-209°C (from ethanol). Mass spectrum, m/e: 179 (M^+), 164, 150, 135].

Reaction of diendiaminodiketone I with compounds VI and VII has been shown to occur with cleavage of the γ,δ-bond and can be postulated in the following manner:

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