Trifurylmethane V and resorcinol dimethyl ether (IV) were isolated along with difurylarylmethane III when the condensation of 2,4-dimethoxybenzaldehyde and 2-methylfuran was carried out under standard conditions [4] using catalytic amounts of perchloric acid. This result can be explained as follows. Under the given rather mild conditions the dimethoxyphenyl residue is readily protonated to give Wheland complex A, which decomposes to ether IV and cation C. The cation reacts with 2-methylfuran to give trifurylmethane V.

(2,4-Dimethoxyphenyl)bis(5-methyl-2-furyl)methane (III, $C_{19}H_{20}O_4$). This compound had mp 87-88°C (from hexane). PMR spectrum (CCl_4): 2.17 (s, 6H, CH_3), 3.61 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 5.51-5.57 (m, 1H, 3'-H), 5.58-5.73 (m, 4H, furan), 6.20-6.38 (m, 1H, 4'-H), 6.30 (s, 1H, CH), 6.70-6.87 ppm (m, 1H, 6'-H); J_{AB} = 9 Hz, J_{BC} = 2.5 Hz.

1,3-Dimethoxybenzene (IV, $C_8H_{10}O_2$). This compound had bp 217-218°C. PMR spectrum (CCl_4): 3.63 (s, 6H, OCH_3), 6.25 (s, 1H, 2-H), 6.25-6.45 (m, 2H, 4- and 6-H), 6.83-7.17 ppm (m, 1H, 5-H).

Tris(5-methyl-2-furyl)methane (V, $C_{16}H_{16}O_3$). This compound had mp 38°C (from hexane). PMR spectrum (CCl_4): 2.11 (s, 6H, CH_3), 5.17 (broad s, 1H, CH), 5.61-5.85 ppm (m, 6H, furan).

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NEW METHOD FOR THE INTRODUCTION OF NITRO AND AMINO GROUPS INTO THE ARYLMETHYLENE SUBSTITUENT OF 1-R-2-ARYLMETHYLENE-3-INDOLINONES

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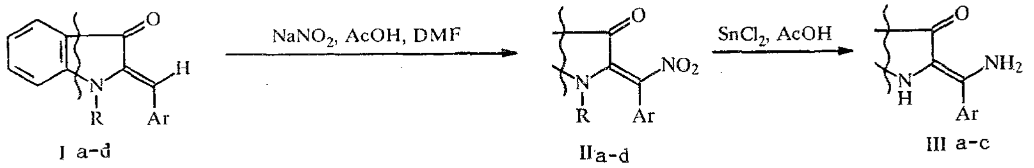
Conjugated nitroalkenes act as multifaceted intermediates in organic synthesis [1]. The existing methods for obtaining them are not general and are, as a rule, fraught with a number of limitations — multistep character, low yields of the desired substances, inaccessibility and toxicity of the reagents used, etc. [1].

We propose a new method for introducing a nitro group at the terminal carbon atom of the vinyl group of 1-R-2-arylmethylene-3-indolinones (indogenides) Ia-d by the action of sodium nitrite in DMF—acetic acid (2:1). The reaction is carried out for 30 min at 50-60°C, and 1-R-2-(α-nitroarylmethylene)-3-indolinones (nitroindogenides) IIa-c are obtained in 80-90% yields; in the case of indogenide Id N-methylisatin (50% yield) is obtained along with nitroindogenide IId (50% yield).



I—III a R = H, Ar = Ph; b R = H, Ar = C_6H_4-4-OMe; c R = H, Ar = C_6H_3-3,4-$(OMe)_2$; d R = Me, Ar = Ph

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The compositions and structures of IIa-d and IIIa-c were established on the basis of the results of elementary analysis and data from the mass, IR, and PMR spectra.

The conversion of indogenides Ia-d to nitroindogenides IIa-d does not occur without acetic acid, and in acetic acid alone the yields of the desired compounds do not exceed 30%. The yields of nitroindogenides IIa-d decrease substantially when DMF is replaced by alcohols, viz., methanol, ethanol, and isopropyl alcohol.

We carried out the regioselective reduction of the nitro group in IIa-c with stannous chloride in acetic acid; this leads to the previously described 2-(α-aminoarylmethylene)-3-indolinones (aminoindogenides) IIIa-c. The method that we propose for obtaining aminoindogenides IIIa-c differs favorably from the known method with respect to the high yields of the desired and its experimental simplicity. Compounds IIIa-c are convenient intermediates for the synthesis of 2-amino-3-aryl-4-quinolones [2], as well as heteroannelated [*a*] and [b] indoles.

2-(α-Nitrophenylmethylene)-3-indolinone (IIa). A 2.5-ml sample of acetic acid was added at 30°C to a suspension of 1.1 g (5 mmole) of indogenide Ia and 1.4 g (20 mmole) of $NaNO_2$ in 5 ml of DMF, and the reaction mixture was stirred for 30 min at 55°C and then poured into 100 ml of water. The resulting precipitate was removed by filtration to give 1.06 g (80%) of nitroindogenide IIa with mp 255-257°C (from dioxane). IR spectrum (thin layer): 1725 (C=O), 3380 cm^{-1} (N—H). PMR spectrum ($CDCl_3$): 7.06-7.56 (9H, m, aromatic protons), 9.96 ppm (1H, s, N—H). M^+ 266.

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REACTION OF ARYLGLYOXALS WITH 3-METHYL-1-PHENYL-5-PYRAZOLONE

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1,3-Disubstituted pyrazolones are active methylene components and react with aromatic aldehydes to form, as a rule, arylidene derivatives of this heterocycle [1] or Michael adducts [2]. In striving to create an enone system we subjected 3-methyl-1-phenyl-5-pyrazolone (I) to reaction with phenylglyoxal and its 4-nitro- and 4-hydroxy-substituted derivatives (IIa-c); the reaction was accomplished in refluxing acetic acid containing two to three drops of H_2SO_4 in 1.5 h. Cooling with subsequent neutralization of the reaction mixture gave red-orange precipitates of IIIa-c, which, according to the results of elementary and spectral analysis, were dehydrogenated Michael adducts. The fact that the yields in the reaction of products IIIa-c increase from 33-35% to 70-75% when the ratio of reactants I and IIa-c is changed from 1:1 to 2:1 is in agreement with this. (See scheme at the top of the next page.)

Compounds IIIa-c are deeply colored (λ_{max} 480-495 nm), and the C=O group of an aroyl fragment is unambiguously identified in their IR spectra. The PMR spectra of IIIa-c contain a signal of an OH proton at weak field. The ^{13}C NMR spectrum of IIIb contains 14 peaks, which, together with the equivalence of the methyl protons in the PMR spectrum, constitutes evidence for a high rate of proton exchange between the OH and C=O groups.

The high reactivity of arylglyoxals is responsible for the formation of Michael adducts, the dehydrogenation of which is, in turn, a thermodynamically justified process, since it leads to an extended π system.

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