Compound II. ^{13}C NMR spectrum: form A: 178.0 and 177.6 (C=S), 152.8 and 152.3 (C=N), 71.8, 71.7, 71.5, 71.2, 64.0, 63.0, 61.2, 59.6; form B: 182.8 (C=S), 96.0 [$C_{(2)}$], 82.0 [$C_{(5)}$], 77.3, 74.7, 62.5, 61.2; form C: 182.5 (C=S), 94.4 [$C_{(2)}$], 81.6 [$C_{(5)}$], 77.1, 74.8, 64.0, 63.7; form D: 182.6 (C=S), 90.3 ppm [$C_{(2)}$]. The carbon atoms of the methyl groups give a signal at 30.9-31.1 ppm.

Compound III. ^{13}C NMR spectrum: form A: 177.9 and 177.4 (C=S), 153.2 and 152.7 (C=N), 71.5, 71.2, 70.9, 69.5, 63.9, 63.8, 61.2, 59.7; form B: 182.8 (C=S), 96.1 [$C_{(2)}$], 82.0 [$C_{(5)}$], 78.1, 74.8, 61.8, 61.2; form C: 182.4 (C=S), 94.4 [$C_{(2)}$], 81.7 [$C_{(5)}$], 77.0, 74.8, 63.8, 63.3; form D: 182.5 (C=S), 90.5 ppm. The carbon atoms of the CH_2 groups resonate at 47.0-47.2 ppm, while the carbon atoms of the benzene ring resonate at 127.5-139.6 ppm.

The amounts of the linear forms in the equilibrium range from 60% to 65%, as compared with 15-20% each for the furanose forms and no more than 5% for the pyranose form. Satisfactory results of elementary analysis for C, H, and N were obtained for I-III.

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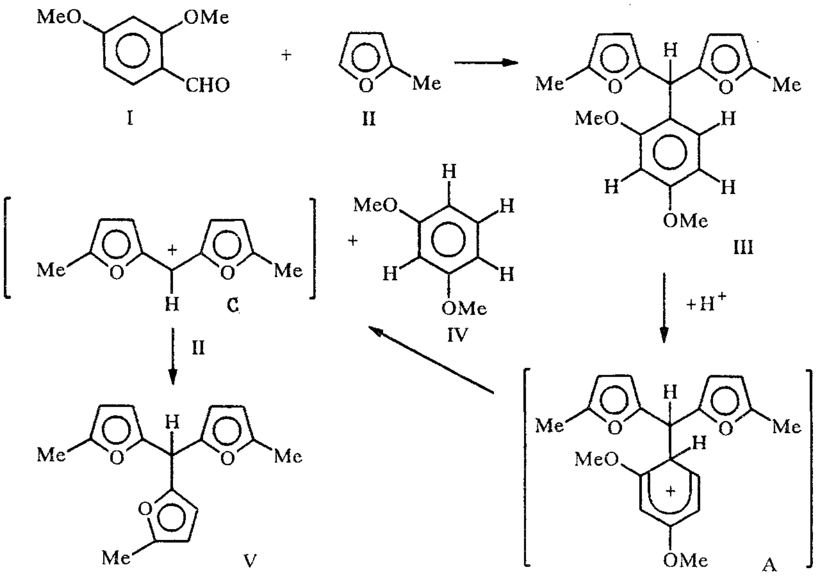
UNUSUAL REACTION OF 2,4-DIMETHOXYBENZALDEHYDE AND 2-METHYLFURAN

A. V. Butin and V. G. Kul'nevich

Cleavage of the C—C bond in polyarylmethanes has been known for a long time. This phenomenon was observed in superacid media by means of NMR spectroscopy [1], in concentrated sulfuric acid by means of UV spectroscopy [2], and preparatively using equimolar amounts of Friedel—Crafts catalysts [3].



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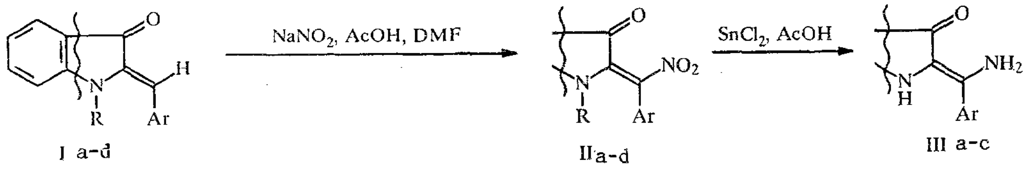
Conjugated nitroalkenes act as multifaceted intermediates in organic synthesis [1]. The existing methods for obtaining them are not general and are, as a rule, fraught with a number of limitations — multistep character, low yields of the desired substances, inaccessibility and toxicity of the reagents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