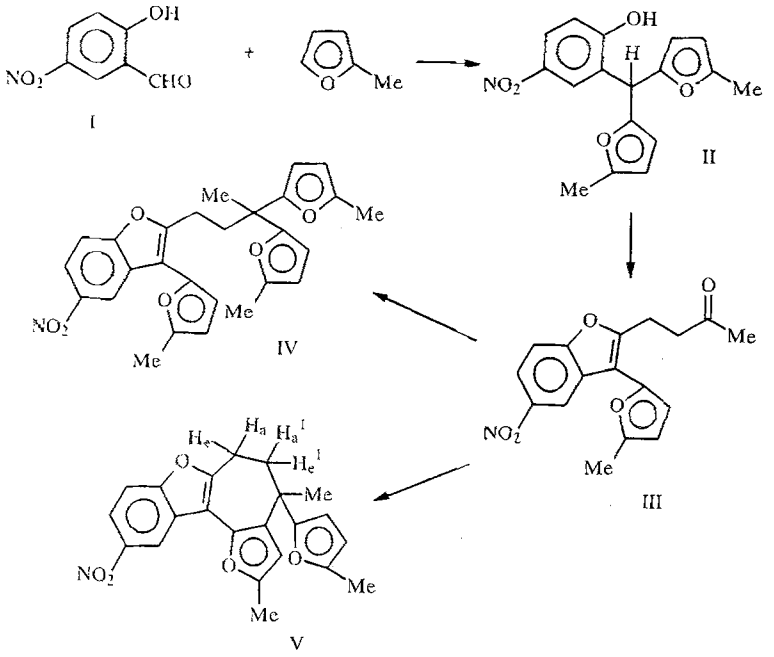
NEW RECYCLIZATION REACTION OF DIFURYLARYLMETHANES

A. V. Butin, V. E. Zavodnik, and V. G. Kul'nevich

Aromatic aldehydes react selectively with 2-methylfuran in the presence of catalytic amounts of perchloric acid to give difurylarylmethanes in high yields [1], and the use of strongly acidic macroporous ion-exchange resins [2], including also the case in which salicylaldehyde is used in the reaction, as catalysts made it possible to raise the yields of difurylarylmethanes to virtually quantitative levels. It is also known that 3-acetylfurans can undergo recyclization reactions under acidic conditions [3].

We have carried out the condensation of 5-nitrosalicylaldehyde and 2-methylfuran in refluxing benzene in the presence of perchloric acid at an aldehyde:2-methylfuran ratio of 1:3. In addition to the expected difurylarylmethane II, another three previously unknown compounds III-V were also isolated from the reaction mixture and identified.



The structures of III and V were confirmed by x-ray diffraction analysis.

One might conclude that the given reaction conditions are favorable for the recyclization of difurylarylmethanes II that contain an activated hydroxy group in the ortho position of the aromatic ring to benzofurans III.

Bis(5-methyl-2-furyl)(5-nitro-2-hydroxyphenyl)methane (II, $C_{17}H_{15}NO_5$). This compound had mp 142-143°C (from CCl_4). PMR spectrum (d_6-acetone): 2.15 (s, 6H, CH_3), 5.77 (s, 1H, CH), 5.87 (s, 4H, furan), 7.02 (d, 1H, 3-H), 7.92 (d, 1H, 6-H), 8.00 (dd, 1H, 4-H), 10.35 ppm (broad s, 1H, OH); $J_{3,4}$ = 9.0 Hz, $J_{4,6}$ = 2.5 Hz. The yield was 18%.

3-(5-Methyl-2-furyl)-5-nitro-2-(3-oxobutyl)benzofuran (III, $C_{17}H_{15}NO_5$). This compound had mp 121-122°C (from ethanol). PMR spectrum ($CDCl_3$): 2.33 (s, 3H, $COCH_3$), 2.42 (d, 3H, 5′-CH_3), 2.97 (t, 2H, β-CH_2), 3.33 (t, 2H, α-CH_2), 6.16 (dq, 1H, 4′-H), 6.55 (d, 1H, 3′-H), 7.47 (d, 1H, 7-H), 8.20 (dd, 1H, 6-H), 8.70 ppm (d, 1H, 4-H); $J_{4',5'\text{-}CH_3}$ = 1.0 Hz, $J_{3',4'}$ = 3.2 Hz, $J_{\alpha,\beta}$ = 6.9 Hz, $J_{6,7}$ = 9.0 Hz, $J_{4,6}$ = 2.5 Hz. The yield was 23%.

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2-(3,3-Bis(5-methyl-2-furyl)butyl]-3-(5-methyl-2-furyl)-5-nitrobenzofuran (IV, $C_{27}H_{25}NO_6$). This compound had mp 118-119°C (from ethanol). PMR spectrum ($CDCl_3$): 1.70 (s, 3H, CH_3), 2.24 (d, 6H, 5″-CH_3), 2.42 (d, 3H, 5′-CH_3), 2.40-2.52 (m, 2H, α-CH_2), 2.91-3.03 (m, 2H, β-CH_2), 5.86 (dq, 2H, 4″-H), 5.98 (d, 2H, 3″-H), 6.12 (dq, 1H, 4′-H), 6.39 (d, 1H, 3′-H), 7.49 (d, 1H, 7-H), 8.21 (dd, 1H, 6-H), 8.73 ppm (d, 1H, 4-H); $J_{4'',5''\text{-}CH_3}$ = 1.0 Hz, $J_{4',5'\text{-}CH_3}$ = 1.0 Hz, $J_{3'',4''}$ = 3.2 Hz, $J_{3',4'}$ = 3.2 Hz, $J_{6,7}$ = 9.0 Hz, $J_{4,6}$ = 2.5 Hz. The yield was 8%.

5,6-Dihydro-2,4-dimethyl-4-(5-methyl-2-furyl)-10-nitro-4H-benzo[b]furo[2,3-h]cyclohepta[b]furan (V, $C_{22}H_{19}NO_5$). This compound had mp 172-173°C [from hexane–chloroform—acetone (4:1:1)]. PMR spectrum ($CDCl_3$): 1.66 (s, 3H, 4-CH_3), 2.08 (ddd, 1H, H'_a), 2.27 (d, 3H, 5′-CH_3), 2.42 (d, 3H, 2-CH_3), 2.48 (ddd, 1H, H'_e), 2.80 (ddd, 1H, H_a), 3.07 (ddd, 1H, H_e), 5.67 (d, 1H, 3′-H), 5.79 (dq, 1H, 4′-H), 5.99 (q, 1H, 3-H), 7.41 (d, 1H, 8-H), 8.17 (dd, 1H, 9-H), 8.97 ppm (d, 1H, 11-H); $J_{a,e}$ = 18.5 Hz, $J_{a,a'}$ =10.5 Hz, $J_{a,e'}$ = 3.1 Hz, $J_{e,a'}$ = 3.0 Hz, $J_{e,e'}$ = 7.0 Hz, $J_{a',e'}$ = 14.0 Hz, $J_{4',5'\text{-}CH_3}$ = 1.0 Hz, $J_{3,2\text{-}CH_3}$ = 1.0 Hz, $J_{8,9}$ = 9.0 Hz, $J_{9,11}$ = 2.5 Hz, $J_{3',4'}$ = 3.2 Hz. The yield was 4%.

The results of elementary analysis of the substances obtained were in agreement with the calculated values.

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