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LETTERS TO THE EDITOR

5-(2,4,6-TRINITROPHENYL)FURFURAL

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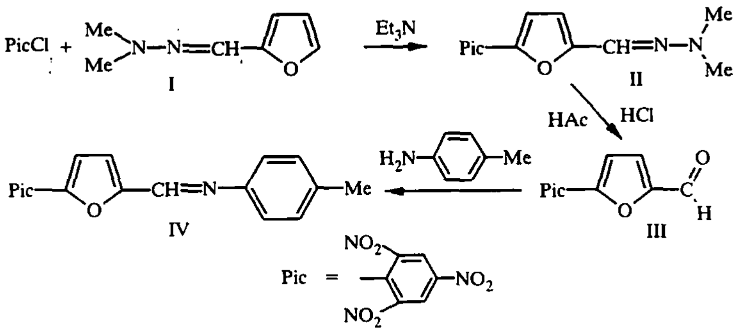
5-Arylfurfurals are synthesized using the Sandmeyer reaction [1]. However, it is not possible to prepare trinitrophenyl derivatives of furfural in this way because of the instability of 2,4,6-trinitrophenyldiazonium chloride. This class of compound is of particular interest thanks to its potentially high biological activity [2].

To synthesize these compounds we chose a method developed for preparation of 5-phosphorylated furfurals [3] involving activation of the furan ring through conversion of the formyl group to an N,N-dimethylhydrazone.

We have now shown that picryl chloride reacts with furfural N,N-dimethylhydrazone (I) to give the N,N-dimethylhydrazone of 5-(2,4,6-trinitrophenyl)furfural (II) in good yield.



Regeneration of the carbonyl group was achieved in satisfactory yield by a modified acid hydrolysis method.

Aldehyde III was converted to azomethine IV [4].

5-(2,4,6-Trinitrophenyl)furfural N,N-dimethylhydrazone (II). A mixture of furfural N,N-dimethylhydrazone (0.01 mole), picryl chloride (0.01 mole), and triethylamine (0.01 mole) in dry benzene (25 ml) was refluxed for 8 h. Upon cooling, a precipitate was separated and the filtrate was evaporated *in vacuo*. The residue was crystallized from hexane. Yield 89%, mp 152°C. PMR spectrum (Varian VXR-300, TMS, $CDCl_3$): 3.053 (6H, s, N−Me); 6.61 (1H, d, J_{34} = 3.8 Hz, 3-H); 6.95 (1H, d, J_{43} = 3.8 Hz, 4-H); 7.01 (1H, s, CH=N); 8.66 ppm (2H, s, Ar). Found, %: C 44.71; H 3.3; N 19.89. $C_{13}H_{11}N_5O_7$. Calculated, %: C 44.70; H 3.15; N 20.06.

5-(2,4,6-Trinitrophenyl)furfural (III). A solution of hydrazone II (0.014 mole) and acetic acid (20 ml) was heated to 60°C and a solution of HCl (15%, 50 ml) was added with constant stirring. The product was stirred for 10 h at 70°C. On cooling, the precipitate was filtered and crystallized from hexane. Yield 56%, mp 159°C. PMR spectrum (Varian VXR-300, TMS, $CDCl_3$): 6.94 (1H, d, J_{34} = 3.6 Hz, 3-H); 7.37 (1H, d, J_{43} = 3.6 Hz, 4-H); 8.96 (2H, s, Ar); 9.73 ppm (1H, s, CH=O). Found, %: C 43.01; H 1.64; N 13.63. $C_{11}H_5N_3O_8$. Calculated, %: C 42.99; H 1.63; N 13.68.

5-(2,4,6-Trinitrophenyl)furyl-2-(p-tolyl)aldimine (IV). A mixture of aldehyde III (0.01 mole) and p-toluidine (0.01 mole) in alcohol (30 ml) was refluxed for 2 h. The alcohol was evaporated *in vacuo* and the residue crystallized from octane. Yield 94%, mp 188°C. PMR spectrum (Varian VXR-300, TMS, $CDCl_3$): 2.37 (3H, s, CH_3); 6.98 (1H, d, J_{34} = 3.9 Hz, 3-H); 7.15 (1H, d, J_{43} = 3.9 Hz, 4-H); 7.17-7.22 (4H, m, Ar); 8.31 (1H, s, CH=N); 8.84 ppm (2H, s, Ar). Found, %: C 54.61; H 3.04; N 14.18. $C_{18}H_{12}N_4O_7$. Calculated, %: C 54.55; H 3.03; N 14.14.

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