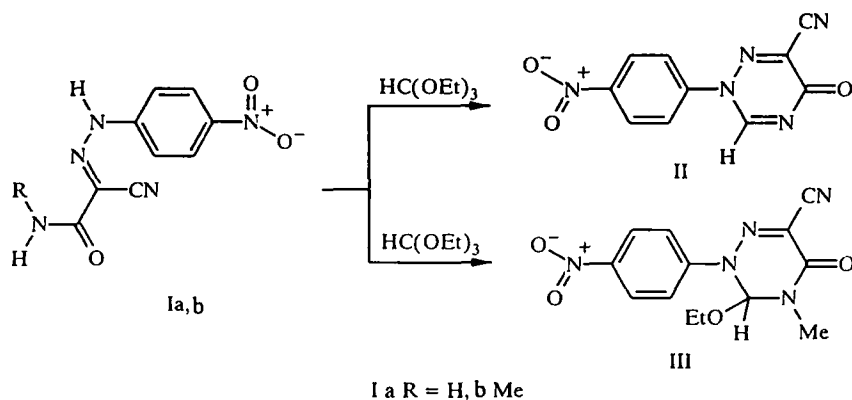


A NEW METHOD FOR THE SYNTHESIS OF 1,2,4-TRIAZIN-5-ONES

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Methods for synthesis of triazine structures are based on the (4+2) atom combination of fragments of the required structures [1]. We have proposed a new suitable method for the preparation of substituted triazines in which the cyclic structure is formed from 5 atoms of arylhydrazoneacetamides and a carbon atom from an ortho ester. In this way the structure of the 1,2,4-triazine products is determined completely by the structure of the 2-hydrazoneacetamide starting material.

For example, reaction of 2-(4-nitrophenylhydrazone)-2-cyanoacetamide Ia (R = H) with ethyl orthoformate in acetic anhydride led to the formation 6-cyano-2-aryl-1,2,4-triazin-5-one II, whereas reaction of the N-methylacetamide Ib on boiling with an excess of ethyl orthoformate led to examples of the poorly studied class of 5,6-tetrahydro-triazinones III.



5(2H)-Oxo-2-(4-nitrophenyl)-1,2,4-triazin-6-carbonitrile (II). Hydrazone I a (0.5 g, 2 mmol) and triethyl orthoformate (0.2 ml, 3 mmol) were dissolved in acetic anhydride (10 ml) and boiled for 10 h. The reaction mass was cooled, the precipitate was filtered off and washed with dry isopropanol. Yield 55%. Found, %: C 49.51, H 2.15, N 28.51. Calc. for $C_{10}H_5N_5O_3$, %: C 49.38, H 2.06, N, 28.81. M.p. 248-250°C. 1H NMR spectrum (DMSO- D_6): 8.01 and 8.45 (4 H, AB_{system}, $J = 9.0$ Hz, CH_{arom}), 9.52 ppm (1 H, s, CH).

4-Methyl-5(4H)-oxo-2-(4-nitrophenyl)-3-ethoxy-2,3-dihydro-1,2,4-triazin-6-carbonitrile (III). Hydrazone Ib (0.5 g, 2 mmol) was suspended in triethyl orthoformate (5 ml) and boiled for 30 h. The reaction mass was cooled and the precipitate was filtered off. Yield 50%. Found, %: C 51.61, H 4.15, N 22.81. Calc. for $C_{13}H_{13}N_5O_4$, %: C 51.49, H 4.29, N 23.10. M.p. 149-150°C. 1H NMR spectrum (DMSO- D_6): 1.07 (3 H, t, $J = 7.0$ Hz, CH_3), 3.14 (3 H, s, N- CH_3), 3.50 (2 H, q, $J = 7.0$ Hz, CH_2) 7.20 (1 H, s, CH), 7.78 and 8.36 ppm (2 H, AB_{system}, $J = 9.5$ Hz, CH_{arom}).

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