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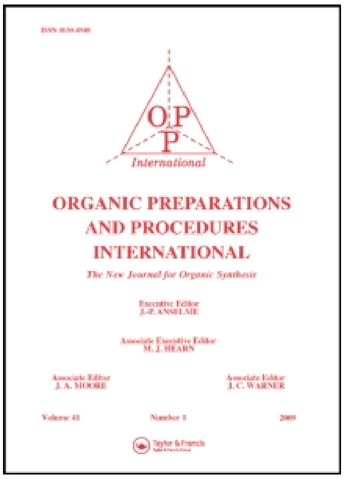

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SOME NITRO-1,2,3-TRIAZOLES

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SOME NITRO-1,2,3-TRIAZOLES

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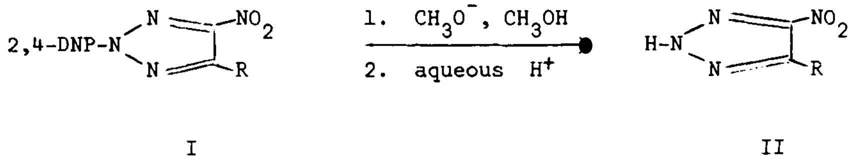

a, R=H; b, R=CH_3; 2,4-DNP=2,4-dinitrophenyl

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Several years ago, one of us[1] reported the synthesis of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (Ia) and its proof of structure by methoxide fission yielding 2,4-dinitroanisole. No attempts were made at that time to isolate the accompanying fission product, 4-nitro-1,2,3-triazole (IIa). Recent syntheses of IIa and some of its 1-substituted derivatives by 1,3-additions of azides to nitro-olefins[2,3] prompt us to report that IIa and also 4-methyl-5-nitro-1,2,3-triazole (IIb) are readily accessible in excellent yields via methoxide fission of the corresponding 2-(2,4-dinitrophenyl) compounds I (which, in turn, are readily available by trinitration of the corresponding 2-phenyl-1,2,3-triazoles).

These compounds are of interest as analogs of azomycin (2-nitroimidazole), and as precursors of triazolopyrimidine and triazolopyridine species. Work is in progress on these aspects.

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EXPERIMENTAL[4]

Typical trinitration procedure

To 30 g (0.19 mole) of 4-methyl-2-phenyl-1,2,3-triazole[5] in 200 ml of sulfuric acid (d, 1.84) was added 80 ml of nitric acid (d, 1.42) and 60 ml of sulfuric acid (d, 1.84) (external cooling necessary). The reaction mixture was heated on a steam bath for 2 hrs., allowed to cool at 80°C, and poured onto cracked ice. The precipitate was collected, washed with saturated aqueous $NaHCO_3$, and crystallized from ethanol, yielding 50.0 g (90%) of 2-(2,4-dinitrophenyl)-4-methyl-5-nitro-1,2,3-triazole (Ib), m.p. 132-133° (n.m.r. spectrum in $CDCl_3$: 3H (s) 2.70 (methyl); 1H (d, $J = 9.0$ Hz) 8.25 (6-hydrogen); 1H (q, $J = 9.0$ & 2.0 Hz) 8.70 (5-hydrogen); 1H (d, $J = 2.0$ Hz) 8.77 (3-hydrogen). Corresponding treatment of 2-phenyl-1,2,3-triazole provided 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (Ia), m.p. 104° (lit.[1] 104°) in 94% yield.

4-Nitro-1,2,3-triazole (IIa)

To 2 l. of 0.4M methanolic sodium methoxide was added 100 g (0.36 moles) of Ia; the mixture was heated under reflux for 3 hrs., concentrated to 400 ml., cooled and filtered to remove 2,4-dinitroanisole; the filtrate was added to 800 ml. of water and refiltered. The filtrate was acidified and extracted continuously overnight with ethyl acetate. Evaporation of the ethyl acetate followed by crystallization of the residue from ethanol yielded 37.4 g (92%) of 4-nitro-1,2,3-triazole (IIa), m.p. 160-161°.

Anal. Calcd. for $C_2H_2N_4O_2$: C, 21.06; H, 1.77; N, 49.10.

Found: C, 21.06; H, 1.72; N, 48.79.

(n.m.r. spectrum in CF_3CO_2D: ring proton at δ 8.72.)

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4-Methyl-5-nitro-1,2,3-triazole,(IIb)

This compound was obtained under similar conditions to compound IIa: 117 g (0.40 mole) of 2-(2,4-dinitrophenyl)-4-methyl-5-nitro-1,2,3-triazole yielded 46.0 g (90%) of 4-methyl-5-nitro-1,2,3-triazole (IIb), m.p. 177-178° (from ethanol).

Anal. Calcd. for $C_3H_4N_4O_2$: C, 28.13; H, 3.15; N, 43.74.

Found: C, 27.88; H, 3.06; N, 43.76.

(n.m.r. spectrum in CF_3CO_2D: methyl group at δ 2.83)

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