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LETTERS TO THE EDITOR

REGIOSELECTIVE SYNTHESIS OF 2-N-SUBSTITUTED 6-NITRO- AND 4,6-DINITROINDAZOLES

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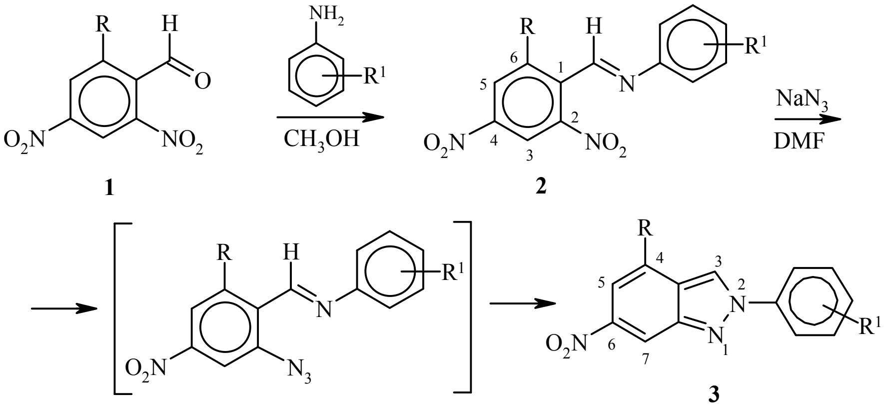
2-N-Substituted indazoles can be obtained from N-(2-nitrobenzylidene)amines *via* reduction by carbon monoxide in the presence of iron carbonyls [1], and also by treatment with triethyl phosphite [2]. In continuing studies on synthesis of nitroindazoles [3], we have developed an alternative method for regioselective synthesis of 2-N-substituted 6-nitro- and 4,6-dinitroindazoles in 60% to 70% yield by reaction of azomethines **2** with sodium azide in DMF.



1-3 a R = R^1 = H; **b** R = NO$_2$, R^1 = H; **c** R = NO$_2$, R^1 = 4-CH$_3$; **d** R = NO$_2$, R^1 = 4-NO$_2$

General Procedure for Obtaining Azomethines 2. A solution of 2,4-dinitro- or 2,4,6-trinitrobenzaldehyde **1** (4.0 mmol) was boiled with the corresponding amine (4.2 mmol) in methanol (3-4 ml) for a period of 10 min to 3 h. Then it was cooled and the residue was filtered off and washed with cold methanol (3 ml).

N-(2,4-Dinitrobenzylidene)phenylamine (2a). Yield 88%; mp 129-130°C (methanol). ^{1}H NMR spectrum (DMSO-d$_6$, 500 MHz), δ, ppm, *J*, Hz; 7.31 (3H, d, *J* = 4.03, Ph); 7.48 (2H, t, Ph); 8.45 (1H, d, *J* = 6.00, 6-H); 8.62 (1H, d, *J* = 6.00, 5-H); 8.80 (1H, s, 3-H); 8.96 (1H, s, CH=N). Found, %: C 56.94; H 3.43; N 15.75. $C_{13}H_9N_3O_4$. Calculated, %: C 57.56; H 3.32; N 15.50.

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N-(2,4,6-Trinitrobenzylidene)phenylamine (2b). Yield 83%; mp 169-170°C (methanol) (according to data in [4], mp 170-171°C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.20 (2H, d, Ph); 7.32 (1H, t, Ph); 7.45 (2H, t, Ph); 8.92 (1H, s, CH=N); 9.10 (2H, s, 3-H, 5-H).

N-(2,4,6-Trinitrobenzylidene)-4-methylphenylamine (2c). Yield 90%; mp 193-194°C (methanol) (according to data in [4], mp 177-178°C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 2.39 (3H, s, CH3); 7.13 (2H, d, *J* = 7.27, Ph); 7.29 (2H, d, *J* = 6.37, Ph); 8.93 (1H, s, CH=N); 9.11 (2H, s, 3-,5-H).

N-(2,4,6-trinitrobenzylidene)-4-nitrophenylamine (2d). Yield 78%; mp 171-172°C (methanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.38 (2H, d, *J* = 8.24, Ph); 8.35 (2H, d, *J* = 8.12, Ph); 9.06 (1H, s, CH=N); 9.17 (2H, s, 3-,5-H). Found, %: C 42.67; H 2.01; N 19.42. $C_{13}H_7N_5O_8$. Calculated, %: C 43.21; H 1.94; N 19.39.

2-N-Phenyl-6-nitroindazole (3a). Azomethine **2a** (0.813 g, 3 mmol) was suspended in DMF (0.5 ml). Sodium azide (0.234 g, 3.6 mmol) was added, and the mixture was heated at 115-120°C until evolution of nitrogen ceased (40-60 min). The solution was cooled and the completely solidified mass was filtered off and washed with water. After recrystallization from acetone, 0.453 g (63%) of white powder was obtained; mp 137-138°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.51 (1H, t, Ph); 7.62 (2H, m, Ph); 7.86 (1H, d, *J* = 9.23, Ph); 8.02 (1H, d, *J* = 9.23, Ph); 8.12 (2H, d, *J* = 8.30, Het); 8.70 (1H, s, Het); 9.30 (1H, s, Het). Found, %: C 65.13; H 3.92; N 17.71. $C_{13}H_9N_3O_2$. Calculated, %: C 65.27; H 3.77; N 17.57.

General Procedure for Obtaining 2-N-Aryl-4,6-nitroindazoles (3b-d). Azomethine **2b-d** (3 mmol) was suspended in DMF (1-2 ml). Sodium azide (3.15 mmol) was added at ~20°C and the mixture was stirred until completely solidified (3-5 min). The azide formed was converted to indazole by one of the following methods. A. The solidified mass was heated to 60°C and held at this temperature for 40-50 min. The residue was filtered off on cooling, washed with water and recrystallized from chloroform.

B. The azide was filtered off, dissolved in chloroform, and boiled for 20-30 min. The solution was evaporated down to a fairly small volume and cooled. The residue of indazole was filtered off and dried.

2-N-Phenyl-4,6-dinitroindazole (3b). Yield 68%; mp 203-204°C (chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.55-7.65 (3H, m, Ph); 8.25 (2H, d, *J* = 9.68, Ph); 8.80 (1H, s, Het); 9.15 (1H, s, Het); 9.63 (1H, s, Het). Found, %: C 54.52; H 3.06; N 19.97. $C_{13}H_8N_4O_4$. Calculated, %: C 54.93; H 2.82; N 19.72.

2-N-(4-Methylphenyl)-4,6-dinitroindazole (3c). Yield 64%; mp 237-238°C (chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 2.45 (3H, s, CH_3); 7.45 (2H, d, *J* = 7.09, Ph); 8.13 (2H, d, *J* = 6.07, Ph); 8.76 (1H, s, Het); 9.19 (1H, s, Het); 9.60 (1H, s, Het). Found, %: C 56.15; H 3.42; N 19.02. $C_{14}H_{10}N_4O_4$. Calculated, %: C 56.37; H 3.35; N 18.79.

2-N-(4-Nitrophenyl)-4,6-dinitroindazole (3d). Yield 62%; mp 253-254°C (chloroform). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 8.49 (2H, d, *J* = 8.03, Ph); 8.60 (2H, d, *J* = 9.04, Ph); 8.79 (1H, s, Het); 9.22 (1H, s, Het); 9.89 (1H, s, Het). Found, %: C 47.32; H 2.28; N 21.36. $C_{13}H_7N_5O_6$. Calculated, %: C 47.42; H 2.13; N 21.28.

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