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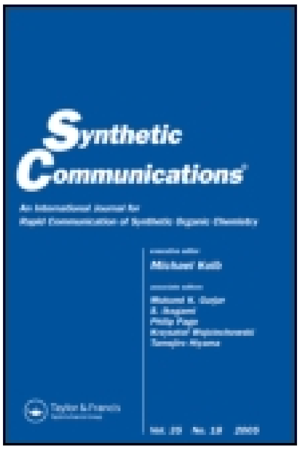

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SYNTHESIS OF 1-ARYL-4,6-DINITRO-1H-INDAZOYL-3-METHYLCARBOXYLATES

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SYNTHESIS OF 1-ARYL-4,6-DINITRO-1*H*-INDAZOYL-3-METHYLCARBOXYLATES

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ABSTRACT

Synthesis of 1-aryl-4,6-dinitro-1*H*-indazoyl-3-methylcarboxylates from 2,4,6-trinitrotoluene derivatives is reported.

In our previous paper we described the synthesis of 2-aryl-4,6-dinitro-2*H*-indazoles.[1] Preparation of 1-aryl(hetaryl)-4,6-dinitro-1*H*-indazoles by intermolecular cyclisation (with the displacement of the *ortho*-nitro group) of 2,4,6-trinitrobenzaldehyde arylhydrazones has been reported before.[2,3]

In order to further modify 4,6-dinitroindazole by introduction of a new substituent, we here report the facile synthesis of methyl esters of 1-aryl-4,6-dinitro-1*H*-indazolyl-3-carboxylic acids **6** from 2,4,6-trinitrotoluene (TNT).

TNT can be easily converted into 2,4,6-trinitrophenylacetic acid (**3**) according to Scheme 1 developed by Z. Bonecki and T. Urbansky.[4]

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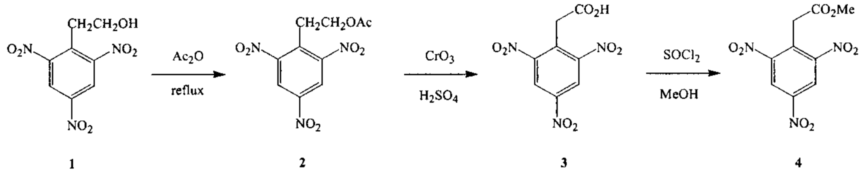
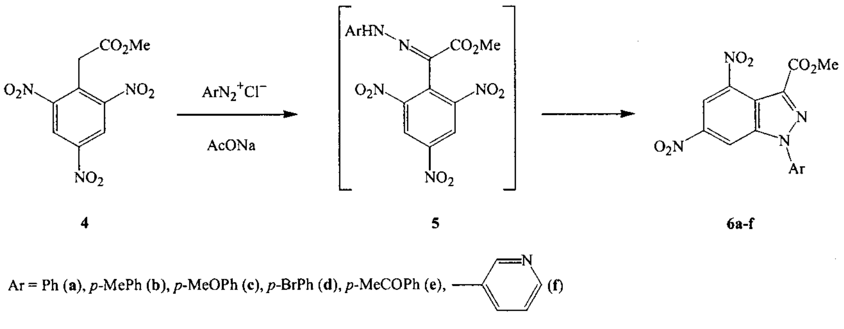


Scheme 1.

The methyl ester was prepared by standard methodology, that is refluxing picryl acetic acid with thionyl chloride in dry methanol.

We found that the ester **4** reacted with diazonium salts to form hydrazones **5**, which undergo cyclisation *in situ* giving indazoles **6**. The cyclisation step includes an intermolecular substitution of the nitro group (Scheme 2) and occurs under very mild conditions, at −10 to −5°C. Most likely, NaOAc, which is added to achieve the condensation of ester **4** with aryldiazonium salts, also promotes the cyclisation reaction.



Scheme 2.

1-Aryl-4,6-dinitroindazolyl-2-methylcarboxylates were obtained in good yields (>80%) and the structures of the new indazoles **6** were established by microanalyses, ^{1}H and ^{13}C NMR spectra.

EXPERIMENTAL

Melting points were measured using a Boetius apparatus and are uncorrected. All reactions were monitored by TLC using Silufol (UV-254) precoated aluminium plates. NMR spectra were recorded on a Bruker AC 200 spectrometer in DMSO-d_6. Chemical shifts are reported in ppm downfield from TMS, coupling constants are reported in hertz. Organic solvents and reagents were purified by accepted literature procedures. A column chromatography was run on silica gel Chemapol 5/40. Picrylethanol (**1**) was obtained by condensation of TNT with formaldehyde according to the known procedure[5] and its NMR spectra are given in Lit.[6]

1-Picrylethyl Acetate (2)

Yield 90%; mp 98–99°C (from Pr^{i}OH); lit.[4] yield 78%; mp 98°C; ^{1}H NMR δ 1.19 (s, 3H, Me), 3.35 (t, 2H, CH_2, $^3J = 5.8$), 4.27 (t, 2H, OCH_2, $^3J = 5.8$), 9.05 (s, 2H, H_{arom}). ^{13}C NMR δ 20.44, 26.59, 62.63, 123.12, 132.33, 146.48, 151.18, 170.00.

Picrylacetic Acid (3)

Yield 72%; mp 164–165°C; lit.[4] yield 77%; mp 163–165°C; ^{1}H NMR (MeOD) δ 4.18 (s, 2H, CH_2), 9.0 (s, 2H, H_{arom}). ^{13}C NMR δ 35.02, 132.51, 131.80, 148.25, 152.62, 170.98.

Methyl Picrylacetate (4)

To a stirred solution of 5 g (18.5 mmol) of picrylacetic acid (**3**) in 50 mL of dry MeOH 22 g (185 mmol) of $SOCl_2$ was added dropwise at 0°C. The mixture was refluxed for 2 h and poured into 100 g of ice. The precipitated solid was collected by filtration, washed with water until neutral reaction and passed through 100 g silica gel using benzene as eluent. Yield 85%; mp 54–56°C (Pr^{i}OH); ^{1}H NMR δ 3.70 (s, 3H, OCH_3), 4.25 (s, 2H, CH_2), 9.10 (s, 2H, H_{arom}). ^{13}C NMR δ 33.89, 52.52, 128.34, 129.69, 146.68, 150.63, 168.31. Calcd for $C_9H_7N_3O_8$: C, 37.91; H, 2.47; N, 14.74. Found: C, 37.95; H, 2.57; N, 14.68.

Synthesis of Indazoles 6. General Procedure

Methyl picrylacetate **4** 0.14 g (0.5 mmol) was dissolved in the mixture of 15 mL of EtOH and 15 mL of pyridine. To this solution was added 0.67 g (8 mmol) of NaOAc. The obtained suspension was left at −10 to −5°C and a rigorously stirred solution of 0.48 mmol of aryldiazonium salt in 5 mL of 15% HCl was added dropwise. The mixture was kept at this temperature for 6 h and then poured into 100 mL 10% HCl. The precipitated solid was collected by filtration, dried on air and crystallized from Pr^{i}OH.

Yields, mp, ^{1}H and ^{13}C NMR Spectra of Compounds 6

Methyl 1-Phenyl-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6a)

Yield 85%; mp 179–180°C; ^{1}H NMR δ 3.95 (s, 3H, MeO), 7.72 (m, 2H, ABB′CC′ spectrum, Ph), 7.79 (m, 2H, ABB′CC′ spectrum, Ph), 8.79 (d, 1H, H_{arom}, $^4J = 1.6$), 8.81 (d, 1H, H_{arom}, $^4J = 1.6$). ^{13}C NMR δ 52.76, 113.30, 114.39, 115.88, 124.35, 129.65, 130.13, 136.04, 137.13, 139.97, 141.31, 145.96, 161.26. Calcd for $C_{15}H_{10}N_4O_6$: C, 52.64; H, 2.94; N, 16.37. Found: C, 52.68; H, 3.01; N, 16.42.

Methyl 1-(*p*-Methylphenyl)-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6b)

Yield 82%; mp 202–203°C; ^{1}H NMR δ 2.45 (s, 3H, Me), 3.94 (s, 3H, MeO), 7.51 (m, 2H, AA′BB′ spectrum, *p*-MePh), 7.73 (m, 2H, AA′BB′ spectrum, *p*-MePh), 8.76 (d, 1H, H_{arom}, $^4J = 1.6$), 8.77 (d, 1H, H_{arom}, $^4J = 1.6$). ^{13}C NMR δ 20.73, 52.77, 113.29, 114.33, 115.78, 124.22, 130.52, 134.70, 135.80, 139.57, 140.00, 141.31, 145.89, 161.29. Calcd for $C_{16}H_{12}N_4O_6$: C, 53.94; H, 3.39; N, 15.73. Found: C, 53.90; H, 3.45; N, 15.72.

Methyl 1-(*p*-Methoxyphenyl)-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6c)

Yield 87%; mp 178–179°C; ^{1}H NMR δ 3.89 (s, 3H, MeO), 3.93 (s, 3H, MeO), 7.24 (m, 2H, AA′BB′ spectrum, *p*-MeOPh), 7.78 (m, 2H, AA′BB′ spectrum, *p*-MeOPh), 8.71 (d, 1H, H_{arom}, $^4J = 1.6$), 8.78 (d, 1H, H_{arom}, $^4J = 1.6$). ^{13}C NMR δ 52.74, 55.67, 113.23, 114.26, 115.18, 115.60, 126.23, 129.96, 135.53, 140.31, 141.33, 145.84, 160.05, 161.35. Calcd for $C_{16}H_{12}N_4O_7$: C, 51.62; H, 3.25; N, 15.05. Found: C, 51.66; H, 3.21; N, 15.09.

Methyl 1-(*p*-Bromphenyl)-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6d)

Yield 88%; mp 184–185°C; ^{1}H NMR δ 3.93 (s, 3H, MeO), 7.83 (m, 2H, AA′BB′ spectrum, *p*-BrPh), 7.91 (m, 2H, AA′BB′ spectrum, *p*-BrPh), 8.79 (d, 1H, H_{arom}, $^4J = 2.1$), 8.87 (d, 1H, H_{arom}, $^4J = 2.1$). ^{13}C NMR δ 52.84, 113.45, 114.53, 115.99, 122.62, 126.35, 133.06, 136.33, 136.42, 140.00, 141.28, 146.08, 161.18. Calcd for $C_{15}H_9BrN_4O_6$: C, 42.78; H, 2.15; N, 13.30. Found: C, 42.75; H, 2.20; N, 13.33.

Methyl 1-(*p*-Acetylphenyl)-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6e)

Yield 81%; mp 187–188°C; ^{1}H NMR δ 2.69 (s, 3H, MeCO), 3.94 (s, 3H, MeO), 8.03 (m, 2H, AA′BB′ spectrum, *p*-MeCOPh), 8.24 (m, 2H, AA′BB′ spectrum, *p*-MeCOPh), 8.81 (d, 1H, H_{arom}, $^4J = 1.6$), 8.92 (d, 1H, H_{arom}, $^4J = 1.6$). ^{13}C NMR δ 26.95, 52.95, 113.64, 114.76, 116.29, 124.15, 130.15, 136.78, 136.95, 139.97, 140.58, 141.35, 146.26, 161.24, 197.12. Calcd for $C_{17}H_{12}N_4O_7$: C, 53.13; H, 3.15; N, 14.58. Found: C, 53.15; H, 3.20; N, 14.54.

Methyl 1-(3-Pyridyl)-4,6-dinitro-1*H*-indazoyl-3-carboxylate (6f)

Yield 81%; mp 193–194°C; ^{1}H NMR δ 3.96 (s, 3H, MeO), 7.78 (m, ABCD spectrum, Py), 8.36 (m, ABCD spectrum, Py), 8.83 (d, 1H, H_{arom}, $^4J = 2.1$), 8.84 (m, ABCD spectrum, Py), 8.96 (d, 1H, H_{arom}, $^4J = 2.1$), 9.10 (m, ABCD spectrum, Py). ^{13}C NMR δ 52.87, 113.59, 114.64, 115.99, 124.80, 132.45, 136.81, 140.48, 141.26, 145.33, 146.20, 150.47, 161.19. Calcd for $C_{14}H_9N_5O_6$: C, 48.99; H, 2.64; N, 20.40. Found: C, 48.95; H, 2.69; N, 20.42.

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REFERENCES

1. Kuvshinov, A.M.; Gulevskaya, V.I.; Rozhkov, V.V.; and Shevelev, S.A. Synthesis **2000**, 1471.
2. Reich, M.S. Bull. Soc. Chim. Fr. **1917**, *21*, 111.
3. Reddy, G. Chem. Ind. **1984**, 144.
4. Bonecki, Z.; Urbanski, T. Bull. Pol. Sci., Ser. Sci. Chim. **1961**, *9*, 461; Chem. Abstract **1964**, *60*, 2813e.
5. Gilbert, E.E. J. Energetic Mater. **1984**, *2*, 215; Chem. Abstract **1985**, *103*, 125944n.
6. Rozhkov, V.V.; Kuvshinov, A.M.; Shevelev, S.A. Org. Prep. Proced. Int. **2000**, *32*, 94.

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