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SHORT COMMUNICATIONS

Synthesis of 4-Aryl-5-nitro-1,2,3-triazoles

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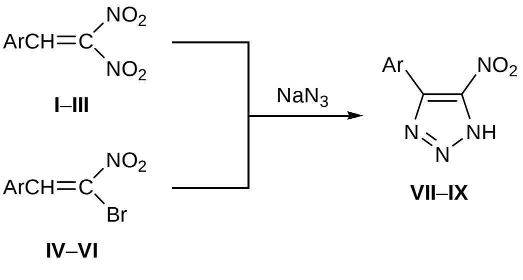
It is known that some 1,2,3-triazole derivatives possess practically important properties. For example, 4-(4-methoxyphenyl)-5-nitro-1,2,3-triazole exhibits antifungal activity, and 4-(4-bromophenyl)- and 4-(4-nitrophenyl)-5-nitro-1,2,3-triazoles are tuberculostatic and fungicide agents [1]. Some 1,2,3-triazoles can be used as photostabilizers and optical bleaching agents [2, 3], and they may be regarded as precursors of azapurines which are potential carcinostatic agents [2].

The synthesis of nitro-1,2,3-triazoles having aryl substituents at the ring carbon atoms was described by Khisamutdinov and co-workers [1, 4]. It is based on the reaction of 2-aryl-1-bromo-1-nitroethenes or 2-aryl-1,2-dibromo-2-nitroethanes with sodium azide in aprotic (DMF, DMSO) or protic (ethanol) solvents.

1,1-Dinitroethene derivatives, specifically β,β-dinitrostyrenes, are highly reactive compounds [5–8] which can be used in the synthesis of nitro-1,2,3-triazoles. We have shown that β,β-dinitrostyrenes **I**–**III** react with 2 equiv of sodium azide under fairly mild conditions, in anhydrous acetonitrile at room temperature. The reaction takes 2.5–4.5 h, and the products are 4-aryl-5-nitro-1,2,3-triazoles **VII–IX** which are formed in 59–77% yield. Compounds **VII–IX** were also synthesized by independent method from the corresponding β-bromo-β-nitrostyrenes and sodium azide in DMF, following a slightly modified procedure [1]. 1,2,3-Triazoles **VIII** and **IX** were previously unknown. It should be noted that 2-aryl-1-bromo-1-nitroethenes failed to react with sodium azide in acetonitrile. Presumably, the reaction of sodium azide with β,β-dinitrostyrenes **I–III**, as well as with geminal bromonitrostyrenes **IV–VI** [1], formally follows 1,3-cycloaddition pattern [3].



I, **IV**, **VII**, Ar = Ph; **II**, **V**, **VIII**, Ar = 4-MeC_6H_4;
III, **VI**, **IX**, Ar = 4-ClC_6H_4.

The structure of aryl-substituted nitro-1,2,3-triazoles was confirmed by elemental analysis and ^1H and IR spectroscopy. The ^1H NMR spectra of 4-aryl-5-nitro-1,2,3-triazoles **VII-IX** contain signals from protons of the aromatic ring at δ 7.31–7.78 ppm. In the IR spectra, absorption bands arising from vibrations of multiple bonds (1610–1615 cm^{-1}), conjugated nitro group (1510–1530 and 1374–1380 cm^{-1}), and 1,2,3-triazole ring (990–1022 cm^{-1}) were present.

Initial 2-aryl-1,1-dinitroethenes **I–III** were synthesized by the procedures described in [9, 10].

5-Nitro-4-phenyl-1,2,3-triazole (VII). *a*. A solution of 0.29 g (1.5 mmol) of 1,1-dinitro-2-phenylethene (**I**) in 12.5 ml of anhydrous acetonitrile was added to a suspension of 0.20 g (3 mmol) of sodium azide in 12.5 ml of anhydrous acetonitrile. The mixture was stirred for 2.5 h at room temperature, the precipitate was filtered off, and the filtrate was poured onto finely crushed ice and acidified with acetic acid. The aqueous phase was extracted with diethyl ether, the organic layer was separated and dried over magnesium sulfate, and the solvent was evaporated. Yield 0.17 g (59%). Colorless crystals, mp 196–198°C (from chloroform); published data [1]: mp 199–201°C (from $CH_3COOH–CCl_4$).

b. A mixture of 0.46 g (2 mmol) of 1-bromo-1-nitro-2-phenylethene (**IV**) and 0.26 g (4 mmol) of sodium azide in 15 ml of DMF was stirred for 2.5 h at room temperature. The mixture was poured onto finely crushed ice and acidified with hydrochloric acid to pH ~1, and the precipitate was filtered off. Yield 0.22 g (52%), mp 195–196°C. The product showed no depression of the melting point on mixing with a sample prepared as described in *a*.

5-Nitro-4-(*p*-tolyl)-1,2,3-triazole (VIII). *a*. Compound **VIII** was synthesized from 1,1-dinitro-2-(*p*-tolyl)ethene (**II**) in a way similar to the synthesis of **VII**. Yield 65%. Colorless crystals, mp 207–209°C (from chloroform). Found, %: C 53.00, 53.07; H 4.09, 4.08; N 27.47, 27.50. $C_9H_8N_4O_2$. Calculated, %: C 52.94; H 3.92; N 27.45.

b. Compound **VIII** was obtained from 1-bromo-1-nitro-2-(*p*-tolyl)ethene (**V**) by the procedure described above for the synthesis of triazole **VII** (method *b*). Yield 51%, mp 205–207°C (from chloroform). No depression of the melting point was observed on mixing with a sample prepared as described in *a*.

4-(4-Chlorophenyl)-5-nitro-1,2,3-triazole (IX). *a*. Compound **IX** was synthesized from 2-(4-chlorophenyl)-1,1-dinitroethene (**III**) as described above for **VII** (method *a*). Reaction time 4.5 h. Yield 77%. Colorless crystals, mp 198–199°C (from chloroform).

b. Compound **IX** was obtained from 1-bromo-2-(4-chlorophenyl)-1-nitroethene (**VI**) by the procedure described above for the synthesis of triazole **VII** (method *b*). Yield 52%. mp 197–198°C. No depression of the melting point was observed on mixing with a sample prepared as described in *a*. Found, %: C 42.75, 42.78; H 2.38, 2.37; N 24.97, 24.91. $C_8H_5ClN_4O_2$. Calculated, %: C 42.76; H 2.22; N 24.94.

The ^1H NMR spectra were recorded on a Bruker AC-200 instrument (200 MHz) in DMSO-d_6. The IR spectra were measured on an InfraLYuM FT-02 spectrometer from samples dispersed in mineral oil.

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REFERENCES

1. Khisamutdinov, G.Kh., Bondarenko, O.A., Kupriyanova, L.A., Klimenko, V.G., and Demina, L.A., *Zh. Org. Khim.*, 1979, vol. 15, p. 1307.
2 *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 4. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1985, vol. 8, p. 430.
3. Gilchrist, T.L., *Heterocyclic Chemistry*, Harlow, Essex, England: Longman Scientific & Technical, 1992, 2nd ed. Translated under the title *Khimiya geterotsiklicheskikh soedinenii*, Moscow: Mir, 1996, p. 351.
4. Khisamutdinov, G.Kh., Bondarenko, O.A., and Kupriyanova, L.A., *Zh. Org. Khim.*, 1975, vol. 11, p. 2445.
5. Berestovitskaya, V.M., Trukhin, E.V., and Korneeva, V.S., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1404.
6. Jamamura, K., Watarai, S., and Kinugasa, T., *Bull. Chem. Soc. Jpn.*, 1971, vol. 44, p. 2440.
7. Kim, T.-R., Kim, J.-H., and Choi, W.-S., *Bull. Korean Chem. Soc.*, 1988, vol. 9, p. 115.
8. Benhaoua, H., Piet, J.-C., Danion-Bougot, R., and Carrie, R., *Bull. Soc. Chim. Fr.*, 1987, vol. 2, p. 325.
9. Novikov, S.S., Belikov, V.M., Dem'yanenko, V.F., and Lapshina, L.V., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1960, p. 1295.
10. Kim, T.R., Lee, Y.H., and Chai, W.S., *Igong Nonjip.*, 1985, vol. 26, p. 195.