ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 1, pp. 135–137. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © de Vekki, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 1, pp. 144–147.

Synthesis of 6(5)-Methyl-5,7(4,6)-dinitro-1*H*-benzo[1.2.3]triazole under Thermal Conditions and under Microwave Irradiation

D. A. de Vekki

St. Petersburg State Institute of Technology,
Moskovskii pr. 26, St. Petersburg, 190013 Russia

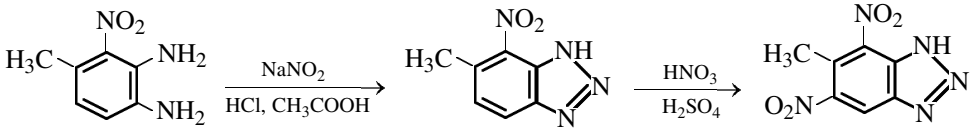
Received October 12, 2006

Abstract — 6(5)-Methyl-5,7(4,6)-dinitro-1*H*-benzo[1.2.3]triazole was synthesized by nitration of 6(5)-methyl-7(4)-nitro-1*H*-benzo[1.2.3]triazole under thermal conditions and under microwave irradiation. Advantages of the microwave irradiation mode are shown.
DOI: 10.1134/S1070363207010203

Substituted benzotriazoles are widely applied as corrosion inhibitors, antifogging agents, and components with UV-sensitive layers for recording devices, laser generators, and other technical fields [1–4]. According to preliminary data, nitro substitution in the 7 position of the benzotriazole ring endows this molecule with photochromism. Introduction of the second nitro group into the nitrobenzotriazole molecule can enhance this property because of the enhanced electron withdrawal from the ring and thereby accelerated redox processes in the molecule.

In this connection, we considered it of interest to develop an optimal synthetic procedure for 6(5)-methyl-5,7(4,6)-dinitro-1*H*-benzo[1.2.3]triazole, potentially perspective photosensitive compound.

The synthesis was performed by two procedures: by nitration of 7(4)-nitro-6(5)-methyl-1*H*-benzo[1.2.3]-triazole **II** thermally (procedure *A*) or under microwave irradiation (procedure *B*) that was for the first time applied to nitration processes. Compound **II** was prepared from 4-methyl-3-nitrobenzene-1,2-diamine (**I**).



I **II** **III**

Procedure A. A detailed procedure for preparing dinitromethylbenzotriazole **III** has not been described, but a synthetic approach, by nitration of 6-methyl-7-nitrobenzotriazole, has been proposed [5]. Examination of this method confirmed its correctness (the ^{1}H NMR spectrum in DMSO-d_6 contained singlet signals at δ 2.83 and 9.05). Thus, our task consisted in the development of optimal reaction conditions. We found that decrease of the concentration of nitric acid from 100 to 63% reduces the yield of the target product: The yield of compound **III** was 15% with 70% nitric acid (4.5 h, 70°C) and 27% with 80% nitric acid under the same conditions.

Varying the molar component ratio in the nitrating mixture (optimally, $HNO_3 : H_2SO_4$ 1 : 2.8) both by increasing and decreasing the HNO_3 content reduces the conversion of the starting reagents, thus resulting in a much longer reaction time. The decrease of the activity of the nitrating mixture can be explained by the fact that the maximum concentration (12.5%) of the attacking reagent, nitronium cation, is achieved just at the above ratio of nitric and sulfuric acids [6].

By varying the reaction temperature we found that its increase (above 85°C) or decrease (below 60°C) leads, respectively, to oxidative destruction of the product (the ^{1}H NMR spectrum in DMSO-d_6 shows new signals at δ, ppm: 2.79 s , 3.30 s, 3.87 s, 7.36 m, 7.92 m, 9.06 m, 9.00 s, 9.20 s, 9.47 s) or to reduced conversion of compound **II**.

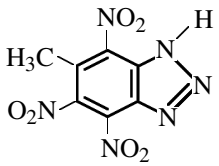
The reaction was found to be favored by stepwise addition of nitric acid: first at a room temperature with subsequent heating of the reaction mixture and then in the course of the process. This procedure allowed us to increase the yield of compound **III** to 66% (from 40% when the acid was never added in one portion).

Procedure B. In the second part of our work, substrate **II** was nitrated under microwave irradiation. This method has never been used for nitration, but it was found highly effective in the synthesis of organic [7, 8] and, more often, heterocyclic compounds [9–12] by cycloaddition, esterification, Knoevenagel condensation, isomerization, cyclization, and polymerization reactions, as well as in various rearrangements [13]. In our experiments we used a mixture with the same reagents ratio as in procedure *A*, but nitric acid was charged in one portion before irradiation.

It was found that single irradiation time depends on the radiation power and nitric acid concentration. Upon single exposures longer than 80 s, overheating of the reaction mixture to 93°C occurs, accompanied by vigorous evolution of nitrogen oxides and strong oxidative destruction of organic components. Therefore, in standard experiments we applied pulse irradiation for 10–20 s with 1–5 min intervals between pulses; the interval depends on both the radiation power and the temperature of the reaction mixture (70–80°C).

Microwave irradiation of 300–400 W with 10-s pulses and 3-min delays did not cause a significant improvement of the yield of benzotriazole **III**. As the radiation power was increased to 750 W (delay 5 min, 99.6% nitric acid), the conversion of the starting substrate achieved, according to ^{1}H NMR data, 71% (10 pulses for 10 s) and 91% (15 pulses); therewith, the yield of compound **III** was 71%.

At 900 W, in the ^{1}H NMR spectrum of the reaction mixture in DMSO-d_6 we observed a new methyl signal at δ 2.78 ppm, assigned to trinitro derivative **IV**. In the case, the maximum yield of product **IV** from **II** did not exceed 10%, whereas nitration of compound **III** directly under microwave irradiation is accompanied by oxidative destruction with explosion.



IV

Thus, the use of the microwave technique in the nitration reaction allowed, for example, the reaction time to be shortened 415 times at the same yield of benzotriazole **III** (66%). The only disadvantage of this procedure is the necessity to work with 100% nitric and sulfuric acids and to select reaction conditions for each specific compound.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WC-400 and AC-200 instruments at 400.14, 200.13 (^{1}H) and 50.33 (^{13}C) MHz, respectively, in $(CD_3)_2CO$, $(CD_3)_2SO$, and $CDCl_3$ solutions. The chemical shifts were measured in ppm against TMS. The IR spectra were obtained on UR-20 and Shimadzu FTIR-8400S spectrometers in KBr pellets. The electronic absorption spectra were recorded on a Specord UV-Vis M-40 spectrophotometer in quartz cells (layer thickness 10 mm) in aqueous ethanol (50 vol %). The elemental analysis was performed on a Perkin Elmer C,H,N analyzer. The melting points were measured on a Kofler hot stage with a microscope, heating rate 2.5 deg min^{-1}. The nitration experiments were carried out in a Moulinex OG-900 (900 W, 2.45 MHz) microwave oven adapted for performing chemical reactions under manual control.

2-Propanol, chloroform, sodium nitrite, acetic acid, hydrochloric and nitric acids of chemical pure grade and sulfuric acid of pure grade were used. 3-Nitro-4-methylbenzene-1,2-diamine (**I**) was prepared as described in [4].

5(6)-Methyl-4(7)-nitro-1*H*-benzo[1.2.3]triazole (II). The reaction vessel was charged consecutively with 1.54 g of diamine **I**, 20 ml of water, 1.5 ml of concentrated hydrochloric acid, and 0.5 ml of glacial acetic acid. The resulting mixture was heated to 50°C and then cooled to 3°C, after which 0.9 ml of a 38.5% solution of sodium nitrite was added in one portion with stirring. A flaky precipitate formed immediately. When all diamine had reacted (visual control, about 2.5 h), the reaction mixture was stirred for an additional 0.5 h and slowly heated to room temperature. The precipitate was filtered off in a vacuum, washed with cold water to neutral washings, and dried in a thermostat at 40°C. Yield of crude compound 1.61 g (98.3%). Recrystallization from 60% 2-propanol gave 1.23 g (75.1%) of a light beige needle solid, mp 253–255°C (255°C [5, 14]). Found, %: C 47.11, H 3.35, N 31.40. $C_7H_6N_4O_2$. Calculated, %: C 47.19, H 3.17, N 31.46, O 17.98. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 2.93 s (3H, CH_3), 7.60 d (1H, H_{arom}, *J* 8.4 Hz), 8.36 d (1H, H_{arom}, *J* 8.4 Hz), 15.34 s (1H, NH); $(CD_3)_2SO$: 2.82 s (3H, CH_3), 7.48 d (1H, H_{arom}, *J* 8.7 Hz), 8.31 d (1H, H_{arom}, *J* 7.5 Hz), 16.2 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (DMSO-d_6):

20.4 s (1C, CH_3), 124.1 s (1C, C^3), 128.9 s (1C, C^5), 132.8 s (1C, C^6), 135.3 s (2C, C^2, C^4), 144.1 s (1C, C^1). IR spectrum, cm^{-1}: ν_{as}(N–O) 1535, ν_s(N–O) 1335, ν(N–N, nitro) 835, ν(N–N, imide) 1000–1300, δ(N–H) 1630, δ(C–H, methyl) 1405. UV spectrum, λ_{max}, nm (log ε): 240.8 (3.42), 310.9 (3.97).

6(5)-Methyl-5,7(4,6)-dinitro-1*H*-benzo[1.2.3]triazole (III). *Procedure A.* Benzotriazole **II**, 41.3 mg (0.23 mmol), was dissolved in 0.6 ml of sulfuric acid at room temperature under stirring in a 5-ml flack and then 0.2 ml of 99.6% nitric acid was added in one portion. The reaction mixture was heated at 60–70°C for 5 h, two 0.1-ml portions of nitric acid were then added to at that temperature at an interval of 3 h, and heating was continued for 4 h. After that the reaction mixture was poured into 10 ml of ice water, and the precipitate formed after its conglomeration (12 h) was filtered off, washed with water to neutral washings, and dried in a thermostat at 70°C. Yield of crude product 34.2 mg (66%), yellow solid, mp 194–207°C (decomp). Recrystallization from chloroform followed by double crystallization from 50% aqueous 2-propanol gave 23.4 mg (30.6%) of light yellow needle crystals, mp 219–220°C. Found, %: C 37.55, H 2.16, N 30.65. $C_7H_5N_5O_4$. Calculated, %: C 37.67, H 2.22, N 31.38, O 28.73. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6): 2.83 s (3H, CH_3), 9.04 s (1H, H_{arom}), 14.0 s (1H, NH); $CDCl_3$: 2.91 s (3H, CH_3), 8.8 s (1H, H_{arom}), 13.9 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm (DMSO-d_6): 15.3 s (1C, CH_3), 119.5 s (1C, C^6), 126.8 s (1C, C^3), 130.3 s (1C, C^1), 134.6 s (1C, C^4), 144.3 s (1C, C^2), 148.1 s (1C, C^5). IR spectrum, cm^{-1}: ν_{as}(N–O) 1565, ν_s(N–O) 1350, ν(N–N, nitro) 900, ν(N–N, imide) 1030–1235, δ(N–H) 1650, δ(C–H, methyl) (not resolved). UV spectrum, λ_{max}, nm (log ε): 243.2 nm (4.10), 205.3 nm (4.42), 290 (3.92) (shoulder).

Procedure B. Benzotriazole **II**, 181 mg, was dissolved in 2.6 ml of 100% sulfuric acid at room temperature in a 10-ml flask, and then 0.7 ml of 99.6% nitric acid was added. The flask was placed into a microwave oven and exposed to microwave radiation at 750 W (7 × 10 s). Then the reaction vessel was cooled in air at room temperature for 0.5 h and exposed again (6 × 10 s). After cooling, the reaction mixture was poured into 50 ml of ice water. A precipitate formed and was filtered off, washed to neutral washings, and dried in a thermostat at 70°C. Yield 150 mg (66.3%), light yellow substance, mp 194–207°C. Recrystallization gave white needle crystals, mp 222°C. The NMR, IR, and UV spectra of the obtained compound were fully identical to those of the dinitro derivative prepared by procedure *A*.

REFERENCES

1. US Patent 5677110, *Chem. Abstr.,* 1997, vol. 127, no. 26, 364180n.
2. Koktish, D.S., Mamedov, A.A., Korzun, G.M., Belenkov, V.V., and Rakhmanov S.K., *Izv. Akad. Nauk Belarusi, Ser. Khim.,* 1996, no. 3, p. 108.
3. Jpn. Patent 09235311, *Chem. Abstr.,* 1997, vol. 127, no. 19, 263655r.
4. El'tsov, A.V., Selitrennikov, A.V., and Rtishchev, N.I., *Zh. Obshch. Khim.,* 1997, vol. 67, no. 2, p. 304.
5. FRG Patent 2031254, *Chem. Abstr.,* 1971, vol. 74, no. 9, 118358d.
6. Orlova, E.Yu., *Khimiya i tekhnologiya brizantnykh vzryvchatykh veshchestv* (Chemistry and Technology of Brisant Explosives), Moscow: Izd. Oboronnoi Literatury, 1960.
7. Alupei, V. and Ritter, H., *Nachr. Chem.,* 2005, vol. 53, no. 5, p. 518.
8. Kappe, C.O., *Angew. Chem., Int. Ed. Engl.,* 2004, vol. 43, no. 46, p. 6250.
9. Strauss, C.R. and Trainor, R.W., *Aust. J. Chem.,* 1995, vol. 48, no. 10, p. 1665.
10. Hamelin, J., and Bazureu, J.-P., in *Microwave in Organic Synthesis,* 2002, p. 253.
11. Xu, Y. and Guo, Q.-X., *Heterocycles,* 2004, vol. 63, no. 4, p. 903.
12. Molteni, V. and Ellis, D.A., *Curr. Org. Synthesis,* 2005, vol. 2, no. 3, p. 333.
13. Keller, W.E., *Schweiz. Lab.-Z.,* 2005, vol. 62, no. 3, p. 39.
14. Katrizky, A.R., Ji, F.-B., Fan, W.-Q., Gallos, J.K., Grecnhill, J.V., King, K.W., and Stell, P.J., *J. Org. Chem.,* 1992, vol. 57, no. 1, p. 190.