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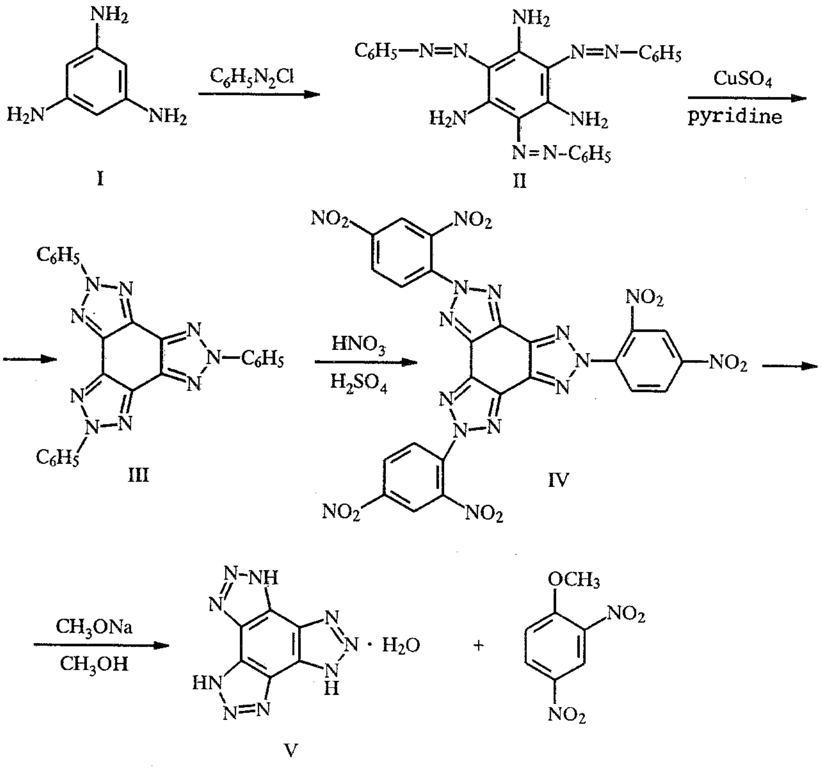
SYNTHESIS OF BENZOTRISTRIAZOLE. 4-NITROBENZO[1,2-*d*:3,4-*d*′]BISTRIAZOLE AND 4,4′-DICARBOXY-5,5′-1H-1,2,3-TRIAZOLE

V. A. Samsonov, L. B. Volodarskii, V. L. Korolev, and G. Kh. Khisamutdinov

The treatment of 2,5,8-tri(2,4-dinitrophenyl)benzotristriazole, 2,7-di(2,4-dinitrophenyl)-4-nitrobenzo[1,2-d:3,4-d']bistriazole, and 4,4'-dicarboxy-5,5'-bis[2-(2,4-dinitrophenyl)-2H-1,2,3-triazole with sodium methylate leads to loss of the 2,4-dinitrophenyl group as 2,4-dinitroanisole and formation of benzotristriazole, 4-nitrobenzo[1,2-d:3,4-d']bistriazole, and 4,4'-dicarboxy-5,5'-bis-1H-1,2,3-triazole, respectively, in good yields.

The reported methods for the synthesis of benzotristriazole are complicated and this compound has not been readily available [1, 2]. We have developed a simple method for the preparation of benzotristriazole, which gives this compound in good yield.

The azo coupling of triaminobenzene (I) with the phenylazonium salt obtained from aniline and sodium nitrite in hydrochloric acid gives 1,3,5-triamino-2,4,6-triphenylazobenzene (II), whose oxidation leads to 2,5,8-triphenylbenzotristriazole (III) [1]. The nitration of (III) by fuming nitric acid (molecular mass 1.5) in concentrated sulfuric acid at 40-60°C gives 2,5,8-tri(2,4-dinitrophenyl)benzotristriazole. More than six nitro groups may be introduced into this compound under more vigorous conditions [3]. The nitrophenyl groups in 2H-benzotriazole derivatives are readily lost by the action of nucleophilic reagents [4, 5, 6]. The treatment of IV with sodium methylate in methanol indeed led to the loss of the dinitrophenyl groups as 2,4-dinitroanisole and formation of benzotristriazole (V) in good yield.



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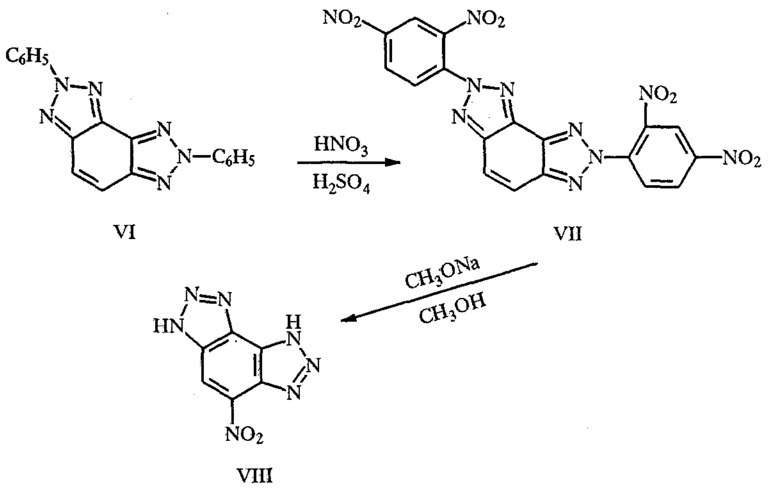
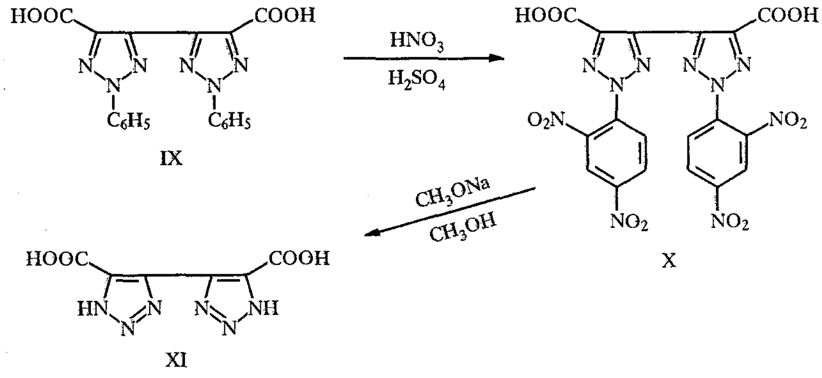
An analogous procedure was used to synthesize 4-nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole. The nitration of 2,7-diphenylbenzo[1,2-*d*:3,4-*d'*]bistriazole (VI), obtained according to the procedure described by Schmidt and Hagenbocker [7], by nitric acid in sulfuric acid smoothly led to 2,7-di(2,4-dinitrophenyl)-4-nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole (VII). The reaction of VII with sodium methylate in methanol at 25-40°C gave bistriazole VIII in good yield.



4,4'-Dicarboxy-5,5'-bis(2-phenyl-2H-triazole) (IX) is readily formed upon the oxidation of VI [8]. The nitration of IX by nitric acid in sulfuric acid leads to 4,4'-dicarboxy-5,5'-bis[2-(2,4-dinitrophenyl)-2H-triazole] (X). Treatment of X with sodium methylate gave 4,4'-dicarboxy-5,5'-bis-1H-1,2,3-triazole (XI).



Thus, the good leaving properties of the dinitrophenyl group upon the action of nucleophilic agents may be used to obtain 1H-1,2,3-triazole derivatives from 2-phenyl-2H-1,2,3-triazoles.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer for KBr pellets (0.25% concentration). The UV spectra were taken on a Specord UV-VIS spectrometer and the PMR spectra were taken on a Varian A-56-60 spectrometer. The ^{13}C NMR spectra were taken on a Bruker WP-200 spectrometer. The mass spectra were taken on a Finnigan MAT MS-8200 mass spectrometer at 70 eV. The M^+ peak and peaks with intensity greater than 10% in the mass spectra are given. The melting points were determined on a Koeffler block. The elemental analysis was carried out at the Microanalytical Laboratory of the Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences.

The elemental analysis data for C, H, and N corresponded to the calculated values.

2,5,8-Tri(2,4-dinitrophenyl)benzotristriazole (IV, $C_{24}H_9N_{15}O_{12}$). A sample of 30 g (0.07 mole) 3,5,8-triphenylbenzotristriazole (III) was added to 500 ml concentrated sulfuric acid. The mixture was stirred at 50-60°C until the precipitate completely dissolved. Then, 50 ml (2.38 mole) nitric acid (molecular mass 1.5) was added dropwise with stirring to the homogeneous solution maintaining the temperature at 40-50°C. The solution was maintained for 1 h at 40°C, cooled, and poured into 2 kg ice. The precipitate was filtered off, washed with water, and dried to give about 40 g (83%) IV, mp >360°C.

Benzotristriazole (V, $C_6H_3N_2 \cdot H_2O$). A sample of 34 g (0.63 mole) sodium methylate was added in portions with stirring to a suspension of 40 g (0.057 mole) IV in 1500 ml methanol. The solvent was distilled off in vacuum and the residue was suspended in chloroform. The precipitate was filtered off, washed with chloroform, dried, and dissolved in 300 ml water. Activated charcoal was added and the suspension was stirred for 20 min. The charcoal was filtered off and the filtrate was acidified to pH 3 by the addition of 10% hydrochloric acid. The precipitate was filtered off, washed with water, and dried to give about 8 g (69%) benzotristriazole V, mp 300°C (dec.) [mp 300°C (dec.) [1]). UV spectrum: λ_{max} (log ε) 222 (4.4), 320 (2.8). Mass spectrum *m/z* (%): 201 (100) M^+, 173 (40), 90 (40), 77 (20), 63 (20), 52 (20), 44 (20). ^{13}C NMR spectrum (D_2 + NaOH) with DMSO-d_6 as the standard: 136.17 ppm.

2,7-Di(2,4-dinitrophenyl)-4-nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole (VII, $C_{18}H_3N_{11}O_{10}$). A sample of 10 ml (0.24 mole) nitric acid (molecular mass 1.5) was added dropwise with stirring to a solution of 10 g (0.0318 mole) VI in 100 ml sulfuric acid. The temperature was raised to 70°C. The mixture was stirred for 1 h and poured into 800 ml ice water. The precipitate was filtered off, washed with water, and dried to give 17.0 g (99%) VII, mp 234-236°C. IR spectrum: 1350, 1560 cm^{-1} (NO_2). Mass spectrum, *m/z* (%): 537 (100) M^+, 507 (20), 492 (10), 184 (10), 77 (20), 44 (50).

4-Nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole (VIII, $C_6H_3N_7O_2 \cdot H_2O$). A sample of 7.0 g (0.13 mole) sodium methylate was added to a suspension of 15 g (0.028 mole) VII in 500 ml methanol and the mixture was stirred for 2 h at 50°C. The solvent was distilled and 500 ml chloroform was added to the residue. The precipitate was filtered off, washed with chloroform on the filter, dried, and dissolved in 200 ml water. The solution was brought to pH 3 by the addition of 10% hydrochloric acid. The precipitate was filtered off, washed with water, and dried to give 4.8 g (77%) benzobistriazole VIII. Crystals of VIII darken at 250°C and decompose at 302°C (from 10% nitric acid). IR spectrum: 1350, 1560 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 222 (4.3), 330 (3.9). PMR spectrum in D_2SO_4: 8.25 (1H, s, =CH). ^{13}C NMR spectrum in D_2SO_4: 121.16 (CH), 126.76, 127.48, 133.34, 138.56, 140.23. Mass spectrum, *m/z* (%): 205 (100) M^+, 177 (40), 149 (40), 76 (60), 64 (30), 52 (70), 44 (95).

4,4'-Dicarboxy-5,5'-bis[2-(2,4-dinitrophenyl)]-2H-1,2,3-triazole (X, $C_{18}H_8N_{10}O_{12}$). A sample of 15 ml (0.36 mole) nitric acid (molecular mass 1.5) was added dropwise with stirring to a solution of 21 g (0.056 mole) IX in 200 ml concentrated sulfuric acid, maintaining the temperature at 40-50°C. The reaction mixture was stirred at this temperature for 1 h, cooled, and poured onto 800 ml crushed ice. The precipitate was filtered off, washed with water and dried to give 26.5 g (85%) nitro derivative X, mp 304-305°C (dec.). IR spectrum: 1710 cm^{-1} (C=O), 1360, (191550 cm^{-1} (NO_2). UV spectrum, λ_{max} (log (ε): 205 (4.7), 305 (4.5).

4,4'-Dicarboxy-5,5'-bis-2H-1,2,3-triazole (XI, $C_6H_4N_6O_4$). A sample of 10 g (0.185 mole) sodium methylate was added to a suspension of 24.5 g (0.044 mole) bistriazole X in 400 ml methanol and stirred for 2 h at room temperature. The precipitate was filtered off, washed with chloroform, dried, and dissolved in 200 ml water. The solution was acidified by adding 10% hydrochloric acid to pH 3. The precipitate was filtered off and dried to give 9.5 g (97%) diacid XI, mp 156-157°C (dec.). IR spectrum: 1580 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 208 (3.9), 268 (3.8). Mass spectrum, *m/z* (%): 224 (100) M^+.

REFERENCES

1. V. Chmatal, Z. I. Allan, and F. Muzik, Coll. Czech. Chem. Commun., **24**, 484 (1959).
2. I. Z. Kondyukov, V. L. Korolev, G. Kh. Khisamutdinov, I. Sh. Abdrakhmanov, S. P. Smirnov, and A. A. Fainzil'berg, Abstracts of the Fifth All-Union Conference on the Chemistry of Nitrogen Heterocyclic Compounds [in Russian], Part 1, Chernogolovka (1991), p. 150.
3. T. Kompolthy, G. Bencz, and J. Deres, Hungarian Patent No. 164,312; Ref. Zh. Khim., 11R322 (1977).
4. L. I. Vereshchagin, V. M. Nikitin, I. I. Meshcheryakov, G. A. Gareev, L. P. Kirillova, and V. M. Shul'gina, Zh. Org. Khim., **25**, No. 8, 1744 (1989).
5. R. A. Renfrow, M. J. Strauss, S. Cohen, and E. Buncel, Austral. J. Chem., **36**, 1843 (1983).
6. J. M. Dust and E. Buncel, Can. J. Chem., **69**, 978 (1991).
7. M. P. Schmidt and A. Hagenbocker, Ber., **54**, 2191 (1921).
8. A. Beretta, Ann. Chim. Applicata, **16**, 129 (1926).