HETEROCYCLIC NITRO COMPOUNDS.

23.* FORMATION OF 1,5-BIS(1,2,4-TRIAZOLYLS) IN THE REACTION OF N-NITRO-1,2,4-TRIAZOLES WITH BASES AND REDUCING AGENTS

M. S. Pevzner, T. N. Kulibabina, and L. A. Malinina

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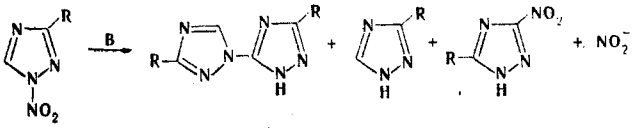
1,5'-Bis(1,2,4-triazolyls) were obtained in 20-70% yields in the reaction of 1-nitro-3-R-1,2,4-triazoles (R = Cl, Br, NO_2) with aqueous solutions of alkali hydroxides and reducing agents (KI, Fe^{2+}, $H_2PO_2^-$) or with triethylamine in acetonitrile. The proposed mechanism for the formation of the dimers is discussed.

During a study of the chemical properties of previously obtained [1] N-nitro-1,2,4-triazoles we observed that a previously unknown reaction that leads to two-ring derivatives of 1,2,4-triazole with a N–C bond between the rings (IV-VI) occurs in the reaction of N-nitrotriazoles I-III, which contain acceptor substituents in the 3 position, with bases (sodium hydroxide, sodium carbonate, and triethylamine) and reducing agents (KI, NaH_2PO_2, and $FeSO_4$). The nitro group is split out in this case and is detected in the reaction medium in the form of the nitrite ion. The structures of IV-VI were proved by determination of the molecular weights, by potentiometric titration (from the presence of one acidic N-H group), and from the PMR spectra.

In addition to IV-VI, denitration products (triazoles VII-IX) and products of rearrangement of the N-nitrotriazoles to C-nitro compounds X and XI (R = Cl, Br) are detected in the reaction mixtures by chromatography and from the PMR spectra:



I-III IV-VI VII-IX X, XI

$B = OH^-, I^-, N(C_2H_5)_3, H_2PO_2^-, Fe^{+2}$

I, IV, VII, X R = Cl; II, V, VIII, XI R = Br; III, VI, IX R = NO_2

The yields of bistriazolyls IV-VI reach 50-70% in the reaction of I-III with aqueous solutions of alkalis and potassium iodide. The yield of IV is considerably lower with triethylamine in acetonitrile after reaction for 1 week. When the reaction is carried out with sodium hypophosphite and ferrous sulfate, IV-VI are recorded only chromatographically and in the PMR spectra.

Two possible mechanisms for the formation of the bistraazolyls may be assumed.

1. Nucleophilic attack on the 5 position in I-III by the triazole anion with splitting out of a nitro group from the 1 position in the form of NO_2^- and a proton from C_5 to give nitrous acid. N-Nitrotriazoles I-III, the decomposition of which to give nitrogen-unsubstituted VII-IX is possible when they are heated or treated with water [1], as well as a result of reaction with reducing agents (similar to N-nitroindazoles [2]), may serve as sources of the triazole anions. Acceptor substituents in the 3 position promote nucleophilic substitution. A similar mechanism has been proposed to explain the formation of 5-aminopyrazoles from N-nitropyrazoles in their reaction with amines [3].

*See [1] for communication 22.

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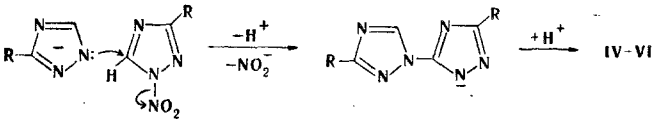
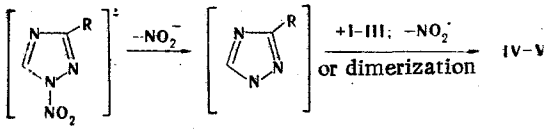


2. One also cannot exclude the possibility of the formation of bistriazolyls through the intermediate anion radical of N-nitro compound XII with its subsequent decomposition to give triazole radical XIII and recombination of two radicals or capture of the radical by a second molecule of N-nitrotriazole with the ejection of the $NO_2^{\cdot}$ radical. The formation of the anion radical is possible in the case of electron transfer from the reducing agent or triazole anion to the N-nitrotriazole molecule.



XII XIII

Judging from the fact that the formation of isomeric two-ring compounds (specifically 1,1'-bistriazolyls) was not established during the reaction, the reaction of radical XIII with starting I-III should be assumed to be more likely.

A choice between the mechanisms presented above can be made in the case of a more detailed study of the reaction.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Perkin–Elmer R-12 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of films of the compounds (applied in acetone) were recorded with a UR=20 spectrometer.

1,5'-Bis(3-chloro-1,2,4-triazolyl) (IV). A) A 3-g (0.029 mole) sample of 3-chloro-1,2,4-triazole was added in portions at 10-15°C to a solution of 4.5 g (0.034 mole) of nitronium tetrafluoroborate in 50 ml of absolute acetonitrile. After 1 h, the mixture was diluted with 50 ml of water* and was made alkaline to pH 9 with sodium hydroxide. The solution was maintained at 20°C for 12 h, after which it was acidified to pH 1 and extracted with ether. The extract was dried with magnesium sulfate, the ether was evaporated, and the residue was crystallized from water to give 1.55 g (52%) of IV with mp 225°C and R_f 0.80 [Silufol UV-254, dioxane–hexane (2:1)]. IR spectrum:† 710, 730, 870, 970, 1000, 1020, 1110, 1220, 1250, 1280, 1305, 1335, 1360, 1395, 1450, 1500, 1570 cm^{-1}. PMR spectrum (DMSO): δ_{CH} 9.45 ppm. Found: C 23.2; H 1.1; Cl 34.8; N 41.0%; M (by potentiometry) 220. $C_4H_2Cl_2N_6$. Calculated: C 23.4; H 1.0; Cl 34.6; N 41.0%; M 205.

B) A 1.3-g sample of 1-nitro-3-chloro-1,2,4-triazole (I), obtained by nitration of 1-trimethylsilyl-3-chloro-1,2,4-triazole [1], was treated with 30 ml of 10% potassium iodide solution at 20°C, during which free iodine was liberated. After standing for a week at room temperature, the mixture was extracted with methylene chloride to remove the iodine, and the aqueous solution was acidified to pH 1 and worked up as described above.

1,5'-Bis(3-bromo-1,2,4-triazolyl) (V). This compound was obtained by the procedure used to prepare chloro derivative IV by method A; bromo derivative V precipitated when the reaction mixture was acidified. The yield of product with mp 280°C (from acetic acid) and R_f 0.66 [Silufol UV-254, dioxane–hexane (1:1)] was 2.15 g (72%). IR spectrum: 700, 730, 870, 990, 1010, 1040, 1110, 1160, 1210, 1250, 1260, 1290, 1350, 1380, 1440, 1490, 1570 cm^{-1}. PMR spectrum (DMSO): δ_{CH} 9.42 ppm. Found: C 16.7; H 0.5; Br 54.1; N 29.0%; M 298 (by potentiometry). $C_4H_2Br_2N_6$. Calculated: C 16.3; H 0.7; Br 54.5; N 28.6%; M 294.

1.5'-Bis(3-nitro-1,2,4-triazolyl) (VI). This compound was also obtained in 50% yield by the procedure used to prepare bistriazolyl IV by method A and had mp 233°C (from ethanol) and R_f 0.40 [Silufol UV-254, dioxane–hexane (3:1)]. IR spectrum: 720, 850, 880, 900, 970, 1020,

*The presence of 1-nitro-3-chlorotriazole was established by chromatography and spectroscopy (from the IR and PMR spectra) in the ether extract before treatment of the reaction mixture with alkali [1].

†The ν_{NH} band was not detected because of the formation of hydrogen bonds.

1045, 1060, 1090, 1125, 1175, 1265, 1320, 1385, 1430, 1465, 1515, 1575, 1610 cm^{-1}. PMR spectrum (DMSO): δ_{CH} 9.74 ppm. Found: C 21.3; H 1.0; N 50.0%; M 25 (by potentiometry). $C_4H_2N_8O_4$. Calculated: C 21.3; H 0.9; N 49.5%; M 226.

Reaction of N-Nitro-3-chlorotriazole with Triethylamine. A 2.4-ml sample of triethylamine was added to 1.2 g of N-nitrotriazole I in 5 ml of dry acetonitrile, and the solution was maintained at 20°C for 1 week. It was then diluted with water, acidified to pH 1, and extracted with ether. Removal of the ether gave 0.3 g of a solid product that was found to be a mixture of three compounds: IV (R_f 0.80; δ_{C-H} 9.45 ppm in DMSO), 3-nitro-5-chloro-1,2,4-triazole (X) (R_f 0.40 with reference spot), and 3-chloro-1,2,4-triazole (VII, δ_{C-H} 8.65 ppm in DMSO,* did not show up on the chromatogram). The IV:VII ratio was ≈10:1.

Reaction of N-Nitro-3-bromo-1,2,4-triazole (III) with Ferrous Sulfate and Sodium Hypophosphite. A 1-g sample of N-nitrotriazole III was heated at 50-60°C for 8 h with a solution of 2 g of ferrous sulfate in 20-25 ml of water, after which the solution was acidified and extracted with ether. The ether was removed by distillation to give 0.3 g of a substance which was found to be a mixture of V (R_f 0.66, δ_{CH} 9.42 ppm in DMSO), 3-nitro-5-bromo-1,2,4-triazole (XI, R_f 0.50 with a reference spot), and 3-bromotriazole VIII* (δ_{CH} 8.65 ppm in DMSO, did not show up on the chromatogram).

Similar results were obtained when triazoles II and III were heated with aqueous sodium hypophosphite solution.

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*When authentic samples of VII or VIII were added to the reaction products, the intensities of the corresponding signals in the PMR spectra increased.

REACTION OF CYANURYL CHLORIDE AND SOME OF ITS MONOSUBSTITUTED DERIVATIVES WITH TOLUENE

V. N. Zaplishnyi, É. S. Avanesyan, and G. M. Pogosyan

UDC 54.547/547.8.87

The Friedel–Crafts reaction of cyanuryl chloride and some of its monosubstituted derivatives with toluene was studied. It is shown that the type and character of the substituent in the 6 position of the starting derivatives of cyanuryl chloride have a strong effect on the course of the reaction. The reaction of cyanuryl chloride and its phenyl and phenoxy derivatives with toluene leads smoothly to the formation of 2,4,6-tris- and 2-substituted 4,6-bis(4'-methylphenyl)-sym-triazines. 4,6-Bis(4'-methylphenyl)2-oxo-2,3-dihydro-sym-triazine is formed in the case of alkoxy-substituted cyanuryl chlorides. In the case of amino derivatives of cyanuryl chloride the reaction with toluene takes place only upon prolonged refluxing and gives the final products in low yields.

A great deal of attention has recently been directed to the synthesis of sym-triazine derivatives. Most study has been devoted to nucleophilic substitution reactions in cyanuryl chloride (Ia) and its mono- and disubstituted derivatives [1]. Not enough study has been devoted to the peculiarities of the behavior of the indicated compounds in Friedel–Crafts reactions. The literature contains only data on the products of the reaction of cyanuryl

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Yerevan 375052.

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