3000, 3080. PMR spectrum: 1.32 s (9H, CH_3), 1.5-3.2 m (7H, CH_2, HC^3), 1.61, 1.65, and 1.84 br.s (9H, CH_3), 4.84 and 4.97 br.s (2H, $H_2C{=}C$), 4.87 br.t (1H, HC=C, J = 6.5). Found, %: C 72.90; H 10.33; S 11.13. M^+ 280. $C_{17}H_{28}OS$. Calculated, %: C 72.80; H 10.06; S 11.43; mol. mass 280.5.

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MONO- AND DI-(2-NITROGUANIDINO)BENZENES AND SOME OF THEIR AMINO AND NITRO DERIVATIVES

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A method was developed for the synthesis of mono- and di-(2-nitroguanidino)benzenes and some of their amino and nitro derivatives, based on the reaction of aniline and phenylenediamines with S-methylisothionitrourea, followed by oxidation of the aminophenyl-2-nitroguanidines or by nitration of aryl-2-nitroguanidines. It was shown that o-phenylenediamine reacts with S-methylisothionitrourea to form 2-nitraminobenzimidazole.

As known, aryl-2-nitroguanidines exhibit biological activity [1]. The main method for their synthesis comprises the reaction of arylamines with 1-methyl-1-nitroso-2-nitroguanidine (MNNG) [1-3]. Unfortunately, this method cannot be regarded as suitable for the preparation of aryl-2-nitroguanidines, since, on the one hand, aromatic amines, having strong electron-acceptor substituents, especially in the o- and p-position to the amino group undergo this reaction with difficulty or not at all, while on the other hand, MNNG displays strong carcinogenic properties.

We therefore studied the possibility of preparation of aryl-2-nitroguanidines based on the action of aniline and o-, m-, and p-phenylenediamines with S-methylisothionitrourea (MITNU). The phenylenediamines were selected because the formation of aminophenyl-2-nitroguanidines from them opens a new path for preparing various aryl 2-nitroguanidines, including those having strong electron-acceptor properties, in particular, the nitro groups.

It was found that MITNU undergoes the reaction with the arylamines studied relatively readily, at temperatures of 60-80°C, whereby the yield and structure of the compounds thus formed are dependent on both the conditions of carrying out the reaction and the structure of the amine used. Heating of MITNU with aniline, and also with p- and m-phenylenediamines

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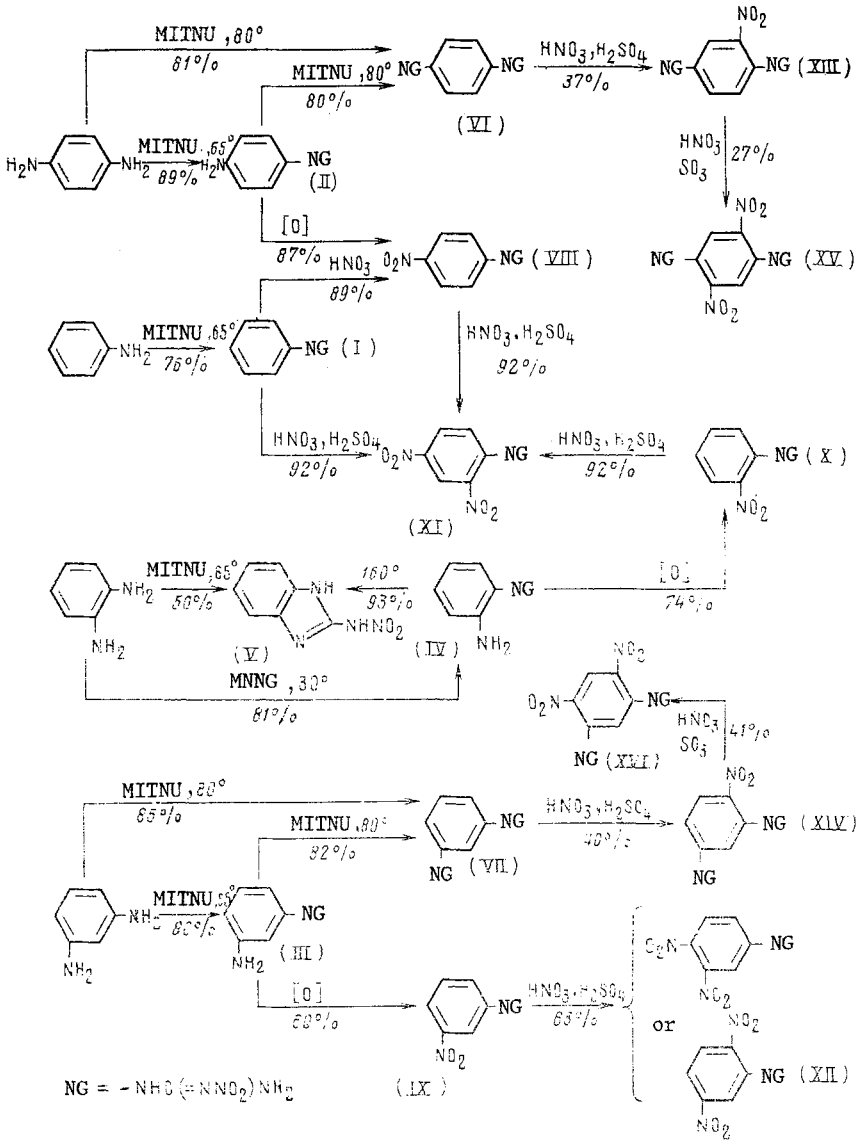
at 65°C in water, leads to the formation of the desired phenyl-2-nitroguanidine (I) and its p-(II) and m-amino derivatives (III), respectively (see scheme). After standing for 1 h their yields were 76, 89, and 80%, respectively, i.e., the reactions proceed fairly selectively.

Scheme of Synthesis and Chemical Transformations of Mono- and Di-(2-nitroguanidino)benzenes



A different result is observed in the reaction under similar conditions of MITNU with o-phenylenediamine. At first glance it would appear that also here the corresponding (2-aminophenyl)-2-nitroguanidine (IV) should be obtained, since the properties of the thus-obtained compound coincide with the properties of a compound to which the structure of (IV) has been ascribed previously [4], the more so since this compound was separated from the products of the reaction of o-phenylenediamine with MNNG. However, it was found that the compound obtained by us under the above conditions differed from (IV) with respect to its elemental composition by NH_3, which in combination with the IR and PMR spectral data, made it possible to ascribe to it the structure of 2-nitraminobenzimidazole (V).* Its formation can be easily explained as due to the transformation of the initially formed (IV) under the

*Compound (V) can possibly exist in various tautomeric forms, the structure of which was not investigated.

reaction conditions. If this explanation is correct, then it could be hoped that compound (IV) could be obtained by lowering the reaction temperature. In fact, on carrying out the reaction at 20-30°C (for this purpose MNNG had to be used instead of MITNU), we were able to synthesize (IV) in a high yield.

It was shown that compound (IV) substantially differs from (V) in its physicochemical and spectral properties. At a temperature of 150-160°C compound (IV) converts into (V) in a yield of 93%.

The formation of (II)-(IV) in high yields indicated that the replacement of the amino group in the initial phenylenediamines by the nitroguanidine fragment substantially decreases the activity of the remaining amino groups in similar reactions. In fact, it was found that for the preparation of 1,3- and 1,4-bis(2-nitroguanidino)benzenes (VI) and (VII) in the yields (80-85%), it is necessary to raise the reaction temperature to 80°C and to increase the duration of the process to 10-30 h, whereby the reaction can be carried out with equal success starting both from phenylenediamines and from aminophenyl-2-nitroguanidines.

Since it is difficult to carry out a direct synthesis of aryl-2-nitroguanidines from arylamines containing strong electron-acceptor substituents in the aromatic ring, we studied the possibility of synthesizing certain derivatives of this type, in particular the nitro derivatives, by two paths: oxidation of aminophenyl-2-nitroguanidines and nitration of aryl-2-nitroguanidines. It was found that the oxidation of aminophenyl-2-nitroguanidines by peracetic acid in $CHCl_3$ is a convenient method for the synthesis of nitrophenyl-2-nitroguanidines. The yield of the oxidation product is noticeably influenced by the mutual disposition of the substituents in the ring: for o- and p-derivatives the yield is 75-85%, decreasing to 60% for (m-aminophenyl)-2-nitroguanidine. This method of synthesis of nitrophenyl-2-nitroguanidines is advantageous first of all because with its use derivatives with a predetermined mutual disposition of the substituents can be obtained. Moreover, it provides a useful alternative to the method of their preparation consisting in the nitration of aryl-2-nitroguanidines. The structure of the products formed in the latter case is determined by the nature of the nitrating agent and also by the character, the number and mutual disposition of substituents in the aromatic ring.

Phenyl-2-nitroguanidine is selectively nitrated by concentrated HNO_3 at 0°C, forming in a yield of 90% (4-nitrophenyl)-2-nitroguanidine (VIII), which is identical to the oxidation product of the amino derivative (II).

By using a stronger nitrating system for the nitration of (I) – a mixture of equal volumes of conc. HNO_3 and conc. H_2SO_4 – two nitro groups can be introduced into the ring; in this case, as in the preceding one, only one of the possible isomers is obtained, namely (2,4-dinitrophenyl)-2-nitroguanidine (XI) (yield 92%). In addition to spectral and elemental analysis methods, the structure of the latter was additionally confirmed by a counter-synthesis – nitration of (VIII) and (X) by a mixture of sulfuric and nitric acids. In both cases, the yields of (XI) are 92%.

Treatment of the 3-nitrophenyl-substituted derivative (IX) with a conc. HNO_3–conc. H_2SO_4 mixture results in the formation of compound (XII) in which the second nitro group (according to the PMR spectral data) enters into the p- or o-position of the ring with respect to the nitroguanidine fragment (NG).

In contrast to aryl-2-nitroguanidines, nitration of compounds containing two NG fragments proceeds under more rigorous conditions and less unequivocally. In this case, the use of a mixture of sulfuric and nitric acids makes it possible to introduce only one nitro group into the ring: thereby, from the 1,4-dinitro derivative (VI) [2-nitro-1,4-di(2-nitroguanidino)benzene (XIII) is formed, while from 1,3-dinitroguanidine derivative (VII) [4-nitro-1,3-di(2-nitroguanidino)]benzene (XIV) is obtained. The second nitro group can be introduced into the ring by means of a strong nitrating system – conc. HNO_3–50% oleum – at 20°C. The nitration by this mixture proceeds more smoothly and in higher yields when mononitro derivatives (XIII) and (XIV) are used as the starting compounds; symmetric dinitro derivatives are thereby formed: [2,5-dinitro-1,4-di(2-nitroguanidino)]benzene (XV) and [4,6-dinitro-1,3-di(2-nitroguanidino)]benzene (XVI), respectively.

The yields of the nitration products of compounds with two NG fragments (XIII)-(XVI) do not exceed 41%, which may be due to the stability of the starting compounds and/or the final products in the strongly acidic nitrating medium. It should also be noted that the

nitration of 1,3-dinitroguanidine derivatives (VII) and (XIV) gives yields of the nitro compounds which are somewhat higher than during the nitration of (VI) and (XIII), which is possibly due to the synchronous orientation of the nitro group by two NG fragments in the o- and p-positions of the aromatic ring in the case of (VII) and (XIV).

In general, it can be seen that for the introduction of the nitro group into aryl-2-nitroguanidines, a mixture of sulfuric and nitric acids should be used if two NG radicals or an NG radical and a nitro group are already present in the ring, and HNO_3–oleum should be used if there are two NG radicals and a nitro group or two nitro groups and an NG radical present in the aromatic ring. In all the known cases, the nitroguanidine substituents act as strict p- and o-orientants, whereby the nitro groups enter into the o-position only when the p-position is occupied.

The synthesized mono- and di-(2-nitroguanidino)benzenes are greyish-beige (monosubstituted) or yellow compounds (disubstituted), which are practically insoluble in Et_2O, C_6H_6, and are poorly soluble in MeCN, Me_2CO, EtOH, DMSO, EtOH, DMF. Their melting points (or decomposition points) vary within 150-230°C. Compound (IV) has the lowest thermal stability, but in the present case it is correct to refer to the intramolecular chemical transformation of the compounds rather than its decomposition.

The structure of the syntheiszed compounds was confirmed by the IR, PMR spectral and elemental analysis data, and, as has already been noted, by a countersynthesis.

EXPERIMENTAL

The PMR spectra were obtained on a Bruker WM-250 spectrometer with a working frequency of 250.13 MHz with respect to protons; the chemical shifts were measured relative to DMSO; H^1 (δ 2.5 ppm). The IR spectra were obtained on UR-20 and Specord IR-75 spectrometers in KBr tablets. For TLC, Silpearl UV 254 silica gel was used with a $MeOH:C_6H_6:Et_2O$ (1:2:7) mixture as eluent. The melting points were determined on a Boetius type heating stage.

Phenyl-2-nitroguanidine (I). A 9.8-g portion (105 mmoles) of $PhNH_2$ was added to a suspension of 8.1 g (60 mmoles) of MITNU in 100 ml of H_2O. The reaction mixture was stirred for 2 h at 60-65°C and was then allowed to cool by itself to 20-25°C; 100 ml of Et_2O was added and the mixture was stirred for ~30 min. The white precipitate was filtered off, washed with H_2O, EtOH, and several times with Et_2O, and dried in air. Yield, 8.0-8.3 g of (I) (73-76%), mp 151-153°C (cf. [3]: mp 152-153°C).

(4-Aminophenyl)-2-nitroguanidine (II). A 4.32-g portion (40 mmoles) of p-phenylenediamine was added to a suspension of 2.7 g (20 mmoles) of MITNU in 60 ml of H_2O. The mixture was stirred for 2 h at 65°C, and was then allowed to stand for 5-12 h at ~20°C. The precipitate was filtered off, washed with H_2O, EtOH, Et_2O, and dried in air. After crystallization from 50% aq. EtOH, 3.3 g (89%) of (II) was obtained, mp 228-230°C (decomp.) [cf. [4]: mp 219-220°C (decomp.)]. PMR spectrum (DMSO-d_6, δ, ppm): 5.20 s (NH_2 arom.), 6.58 d, 6.91 d (C_6H_4), 7.9 br.s (NH_2), 9.43 br.s (NH). IR spectrum (ν, cm^{-1}): 3435 w, 3355 m, 3320 w, 3225 m, 3170 w, 1645 m, 1620 m, 1600 m, 1575 s, 1520 w, 1450 w, 1420 s, 1345 m, 1330 w, 1280 m, 1275 m, 1180 s, 1115 w, 1055 w, 1020 w, 970 w, 810 w, 845 w.

(3-Aminophenyl)-2-nitroguanidine (III) was obtained in a similar way as (II) from MITNU and m-phenylenediamine. Yield, 78-80%, mp 158.5-160°C. PMR spectrum (DMSO-d_6, δ, ppm): 5.25 s (NH_2 arom.), 6.42 m, 7.02 t (C_6H_4), 8.13 br.s (NH_2), 9.5 br.s (NH). IR spectrum (ν, cm^{-1}): 3420 w, 3335 m, 3220 m, 3175 m, 1645 m, 1635 w, 1600 s, 1575 s, 1555 m, 1540 w, 1495 w, 1467 w, 1425 s, 1355 m, 1320 s, 1310 s, 1295 m, 1143 m, 1163 m, 1125 w, 1067 w, 1000 w, 985 w, 895 w, 880 w, 830 w. Found, %: C 43.02; H 4.71; N 36.01. $C_7H_9N_5O_2$. Calculated, %: C 43.07 H 4.65; N 35.89.

(2-Aminophenyl)-2-nitroguanidine (IV) was obtained in analogy with (I) by the method described in [3]. A 1.4-g portion (9.5 mmoles) of MNNG was added to a suspension of 2.75 g (25.3 mmoles) of o-phenylenediamine in 10 ml of 50% aq. EtOH, and the mixture was stirred for 1 h at 20-30°C. The precipitate was filtered off, washed with H_2O, EtOH, Et_2O, and dried in air. Yield 1.5 g (81%) of (IV), mp 155-160°C (from 50% aq. EtOH) (cf. [4]: mp 250°C). PMR spectrum (DMSO-d_6, δ, ppm): 5.1 br.s (NH_2 arom.), 6.8 m (C_6H_4), 7.85 br.s (NH_2), 9.2 br.s (NH). IR spectrum (ν, cm^{-1}): 3430 s, 3400 m, 3555 s, 3325 w, 3235 m, 3165 s, 1663 m, 1635 m, 1610 w, 1580 s, 1555 m, 1505 w, 1465 w, 1430 s, 1340 s, 1320 s, 1285 m, 1270 s, 1185 m, 1150 w, 1083 w, 1035 w, 943 w, 855 w. Found, %: C 43.01; H 4.69; N 35.39. $C_7H_9N_5O_2$. Calculated, %: C 43.07; H 4.65; N 35.89.

2-Nitraminoimidazolidine (V) was obtained: a) similarly to (II) from MITNU and o-phenylenediamine (yield 50%, needles from 50% aqueous EtOH, beginning of decomposition temperature 250°C); b) by heating 31.6 mg of (IV) for 15-20 min at 150-160°C [yield 26.8 mg (93%) of (V), beginning of decomposition temperature 250°C]. PMR spectrum (DMSO-d_6, δ, ppm): 7.27 m, 7.46 m (C_6H_4, an AA'BB' type spectrum); 13.0 br.s (NH). IR spectrum (ν, cm^{-1}): 3390 w, 3330 w, 1280-1320 w, 1635 m, 1600 m, 1590 m, 1500 m, 1470 m, 1440 w, 1360 m, 1305 m, 1285 s, 1225 w, 1185 m, 1155 w, 1110 w, 1080 m, 1010 w, 990 w, 885 w, 880 w, 810 w, 795 w, 775 w, 745 m. Found, %: C 47.56; H 3.09; N 31.20. $C_7H_6N_4O_2$. Calculated, %: C 47.19; H 3.39; N 31.45.

1,4-Di-(2-nitroguanidino)benzene (VI). a) A mixture of 42 g (21.5 mmoles) of (II) and 5.8 g (43 mmoles) of MITNU in 100 ml of H_2O was stirred for 20-30 h at 80°C (up to the disappearance of the spot of mono-product according to TLC). After cooling to 20-25°C, the yellow fine-crystalline precipitate was filtered off, washed with H_2O, 50% aqueous EtOH, and several times with warm Me_2CO. Yield 4.85 (80%) of (VI), decomp. temp. ~200°C. PMR spectrum (DMSO-d_6, δ, ppm): 7.25 s (C_6H_4), 8.1 br.s (NH_2), 9.6 br.s (NH). IR spectrum (ν, cm^{-1}): 3433 m, 3225 m, 3255 s, 3165 w, 3110 w, 1645 m, 1630 m, 1585 s, 1575 s, 1555 m, 1535 w, 1520 w, 1505 w, 1440 m, 1405 s, 1345 s, 1297 s, 1270 s, 1240 s, 1130 w, 1100 w, 1033 w, 980 w, 955 w, 863 w, 828 w. Found, %: C 33.88; H 3.42; N 38.90. $C_8H_{10}N_8O_4$. Calculated, %: C 33.99; H 3.57; N 39.81. (For the elemental analysis, the product was reprecipitated from DMSO by H_2O.)

b) A mixture of 1.08 g (10 mmoles) of p-phenylenediamine and 5.4 g (40 mmoles) of MITNU in 50 ml of H_2O was stirred for 20-30 h at 80°C. After cooling to 20°C, the precipitate was filtered off, washed with H_2O and warm Me_2CO, and dried in air. Yield, 2.3 g (81.5%) of (VI), decomp. temp. ~200°C.

1,3-Di-(2-nitroguanidino)benzene (VII) was obtained in a similar way as (VI): a) from MITNU (50% molar excess) and (III), the mixture was stirred for 8-10 h at 80°C, washed with H_2O, EtOH, yield 82.5%, mp 215-217°C (decomp. from EtOH); b) from MITNU (50% molar excess) and m-phenylenediamine, the mixture was stirred for 8-10 h at 80°C, yield 85%, mp 215-217°C (decomp). PMR spectrum (DMSO-d_6, δ, ppm): 7.22 t, 7.4 t (C_6H_4); 8.25 br.s (NH_2); 9.7 br.s (NH). IR spectrum (ν, cm^{-1}): 3420 m, 3315-3100 m, 1665 w, 1645 m, 1635 m, 1605 m, 1585 m, 1575 m, 1555 w, 1535 w, 1520 w, 1505 w, 1435 m, 1410 m, 1370 m, 1270 s, 1255 s, 1180 m, 1125 w, 1085 w, 1050 w, 1005 w, 940 w, 915 w, 880 w, 845 w, 785 w, 725 w. Found, %: C 34.20; H 3.64; N 39.26. $C_8H_{10}N_8O_4$. Calculated, %: C 34.05; H 3.57; N 39.71.

General Method of Oxidation of Aminophenyl-2-nitroguanidines (II)-(IV). A 0.55-ml portion (20 mmoles) of a 90% H_2O_2 and a catalytic amount of conc. H_2SO_4 were added with stirring to ice-bath cooled $CHCl_3$ (2.4 ml), and then a solution of 2.26 ml (24 mmoles) of Ac_2O in 2.6 ml of $CHCl_3$ was added in the course of 20-30 min. The oxidizing mixture was heated slowly to boiling and 0.78 g (4 mmoles) of aminophenyl-2-nitroguanidine (II)-(IV) was added in small portions to the boiling solution in the course of 20 min. The reaction mixture was boiled for 30 min, poured onto 12 g of ice, the yellow precipitate was filtered, washed with H_2O, EtOH, Et_2O, and dried in air. Compounds (VIII)-(X) were obtained. a) 0.78 g (87%) of 4-nitrophenyl)-2-nitroguanidine (VIII), mp 214.5°C (decomp. from Me_2CO). PMR spectrum (DMSO-d_6, δ, ppm): 7.55 d, 8.18 d (C_6H_4), 8.4 br.s (NH_2), 9.8 br.s (NH). IR spectrum (ν, cm^{-1}): 3440 m, 3340 s, 3270 m, 1650 m, 1610 m, 1520 m, 1505 s, 1485 m, 1470 m, 1385 w, 1340 s, 1275 s, 1240 s, 1190 m, 1118 m, 1040 w, 950 w, 860 w, 835 w. Found, %: C 37.15; H 3.33; N 31.09. $C_7H_7N_5O_4$. Calculated, %: C 37.34; H 3.13; N 31.11.

b) 0.54 g (60%) of (3-nitrophenyl)-2-nitroguanidine (IX), mp 194-196°C (decomp.) (cf. [1]: mp 194-196°C).

c) 0.67 g (74%) of (2-nitrophenyl)-2-nitroguanidine (X), mp 186-186.5°C (decomp. from EtOH). PMR spectrum (DMSO-d_6, δ, ppm): 7.75 m (C_6H_4), 8.5 br.s (NH_2), 9.65 br.s (NH). IR spectrum (ν, cm^{-1}): 3420 m, 3320 m, 3300 m, 3190 w, 3125 w, 1660 m, 1610 w, 1575 w, 1535 m, 1515 s, 1505 s, 1435 m, 1390 w, 1350 m, 1260 s, 1235 s, 1155 w, 1120 w, 1090 w, 1035 w, 960 w, 940 w, 865 w, 850 w, 785 m, 745 m, 720 m. Found, %: C 37.21; H 3.16; N 31.03. $C_7H_7H_5O_4$. Calculated, %: C 37.34; H 3.13; N 31.11.

(4-Nitrophenyl)-2-nitroguanidine (VIII). Compound (I) (0.5 g, 2.74 mmoles) was added in portions in the course of 5 min to 5 ml of conc. HNO_3 (d = 1.5 g/cm^3) cooled on an ice bath. The mixture was stirred for 30 min at 0-5°C, and poured into 20 g of ice. The precipitate was filtered off, washed with ice water (to the neutrality of the wash water) and dried in air. Yield 0.55 g (89%) of (VIII), mp 214.5°C (decomp. from Me_2CO).

(2,4-Dinitrophenyl)-2-nitroguanidine (XI). Compound (VIII) or (X) (0.5 g, 2.22 mmoles) was added at 0-5°C to the nitrating mixture consisting of 2.5 ml of conc. HNO_3 and 2.5 ml of conc. H_2SO_4. The mixture was stirred for 30 min at 0-5°C, and was allowed to warm up spontaneously to ~20°C. It was then poured onto 25 g of ice, the precipitate was filtered off, washed several times with ice water, and dried in air. Yield 0.55 g (92%) of (XI), mp 183.5-184.5°C (decomp. from EtOH).

Nitration of 0.5 g (2.75 mmoles) of (I) under the conditions described in the preceding procedure gave 0.68 g (92%) of (XI), mp 183.5-184.5°C (decomp. from EtOH). PMR spectrum (DMSO-d_6, δ, ppm): 8.22 m, 8.73 d (C_6H_3), 8.9 br.s (NH_2), 10.05 br.s (NH). IR spectrum (ν, cm^{-1}): 3440 m, 3295 m, 3250 w, 3180 w, 3120 m, 1645 m, 1615 m, 1585 w, 1535 m, 1520 m, 1510 m, 1500 m, 1490 m, 1465 w, 1440 m, 1415 w, 1340 s, 1255 s, 1155 m, 1130 w, 1115 m, 1075 w, 1050 w, 945 w, 920 w, 865 w, 835 w. Found, %: C 31.22; H 2.41; N 31.01. $C_7H_6N_6O_6$. Calculated, %: C 31.12; H 2.24; N 31.11.

[3,4(or 2,5)-Dinitrophenyl]2-nitroguanidine (XII). Nitration of 0.5 g (2.22 mmoles) of (IX) by a mixture consisting of 2.5 ml of conc. HNO_3 and 2.5 ml conc. H_2SO_4 for 30 min at 0-5°C with subsequent holding of the reaction mixture for 30 min at 20°C led to the formation of a mixture of two compounds, one of which substantially predominated (determined by TLC). The mixture obtained was recrystallized from EtOH to yield 0.38 g (63%) of (XII), mp 217-219°C (decomp.). PMR spectrum (DMSO-d_6, δ, ppm): 7.92 m, 8.22 d (C_6H_3), 8.6 br.s (NH_2), 10.07 br.s (NH). IR spectrum (ν, cm^{-1}): 3420 m, 3300 m, 3235 w, 3180 w, 3100 w, 3025 w, 1635 m, 1605 w, 1585 w, 1552 m, 1540 m, 1505 m, 1475 m, 1420 w, 1365 m, 1350 s, 1270 s, 1255 s, 1165 w, 1150 w, 1120 w, 1075 w, 1050 w, 975 w, 930 w, 900 w, 860 w, 850 w, 830 w, 810 w. Found, %: C 31.11; H 2.39; N 30.82. $C_7H_6N_6O_6$. Calculated, %: C 31.12; H 2.24; N 31.11.

[2-Nitro-1,4-di-(2-nitroguanidino)]benzene (XIII). Nitration of 0.5 g (1.77 mmoles) of (V) with a mixture of sulfuric and nitric acids (5 ml) with holding the reaction mixture for 1 h at 0-5°C gave 0.38 g of a crude product, which was dissolved in 150 ml of boiling EtOH. The solution was boiled with charcoal, filtered through a small layer of silica gel, evaporated to 3/4 volume and was allowed to stand for several days. The bright yellow fine-crystalline precipitate was filtered off, washed with EtOH, and dried in air. Yield 0.21 g (37.5%) of (XIII), beginning of decomposition temperature ~200°C. PMR spectrum (DMSO-d_6, δ, ppm): 7.58 m, 8.03 d (C_6H_3), 8.40 br.s (NH_2), 9.70 br.s (NH). IR spectrum (ν, cm^{-1}): 3415 w, 3350 w, 3320 m, 3285 m, 3170 w, 3100 w, 1650 m, 1645 m, 1590 w, 1540 m, 1520 m, 1510 m, 1450 w, 1420 m, 1355 m, 1300 m, 1270 s, 1260 s, 1225 s, 1170 w, 1125 w, 1090 w, 1043 m, 990 w, 935 w, 895 w, 850 w, 833 w. Found, %: C 29.55; H 2.83; N 38.83. $C_8H_9N_9O_6$. Calculated, %: C 29.36; H 2.77; N 38.53.

[2,5-Dinitro-1,4-di-(2-nitroguanidino)]benzene (XV). Compound (XIII) (0.45 g, 1.37 mmoles) was added in portions in the course of 10 min at 0-5°C, with vigorous stirring, to a nitrating mixture prepared from 2.5 ml of conc. HNO_3 and 1.9 ml of 50% oleum, and the mixture was stirred for another 30 min at 0-5°C and for 2 h at 20°C. It was then poured onto 15 g of ice, and then, with cooling on an ice bath, 5.4 g of Na_2CO_3 was added in several portions. The aqueous solution was extracted several times with AcOEt, and the combined extracts were dried over $MgSO_4$. The solvent was evaporated under vacuum to yield 0.36 g of a light-brown residue, from which 0.14 g (27.5%) of (XV) was isolated in the form of an orange-brown fine-crystalline powder, beginning of decomposition temperature ~200°C (from EtOH). PMR spectrum (DMSO-d_6, δ, ppm): 8.29 s (C_6H_2), 8.55 br.s (NH_2), 9.85 br.s (NH). IR spectrum (ν, cm^{-1}): 3420 w, 3330 m, 3260 w, 3180 w, 3110 w, 1645 m, 1635 m, 1590 w, 1555 m, 1540 w, 1500 m, 1490 m, 1410 w, 1355 w, 1260 s, 1240 s, 1125 w, 1060 w, 955 w, 930 w, 900 w, 850 w, 825 w, 810 w. Found, %: C 25.76; H 2.07; N 37.23. $C_8H_8N_{10}O_8$. Calculated, %: C 25.81; H 2.17; N 37.63.

[4-Nitro-1,3-di-(2-nitroguanidino)]benzene (XIV) was obtained in a similar way as (XIII), yield 36-41%, mp 233-235°C (decomp. from EtOH). PMR spectrum (DMSO-d_6, δ, ppm): 7.47 m, 8.08 d (C_6H_3), 8.45 br.s (NH_2); 9.85 br.d (NH). IR spectrum (ν, cm^{-1}): 3415 w, 3320 m, 3175 w, 3125 w, 1660 w, 1635 m, 1625 m, 1595 w, 1570 w, 1530 w, 1515 m, 1505 m, 1495 m, 1485 m, 1475 w, 1433 m, 1385 w, 1325 s, 1295 m, 1245 s, 1210 m, 1125 w, 1110 w, 1057 w, 1035 w, 1010 w, 950 w, 930 w, 895 w, 860 w, 830 w. Found, %: C 29.82; H 3.01; N 38.78. $C_8H_9N_9O_6$. Calculated, %: C 29.37; H 2.77; N 38.53.

[4,6-Dinitro-1,3-di-(2-nitroguanidino)]benzene (XVI) was obtained in a similar way as (XV), yield 41%, mp 199-201°C (decomp. from EtOH). PMR spectrum (DMSO-d_6, δ, ppm): 7.94 s, 8.66 s (C_6H_2), 8.85 br.s (NH_2), 10.0 br.s (NH). IR spectrum (ν, cm^{-1}): 3390 w, 3310 w, 3285 m, 3175 w, 3110 w, 1645 m, 1630 m, 1585 m, 1535 w, 1515 m, 1505 m, 1495 m, 1450 s, 1375 w, 1340 s, 1265 s, 1240 s, 1205 m, 1115 w, 1080 w, 1040 w, 1025 w, 935 w, 885 w, 840 w, 815 w. Found, %: C 25.73; H 2.06; N 37.73. $C_8N_8N_{10}O_8$. Calculated, %: C 25.81; H 2.17; N 37.63.

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