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INTERACTION OF 4-AMINOBENZOFURAZAN WITH ARYLDIAZONIUM SALTS

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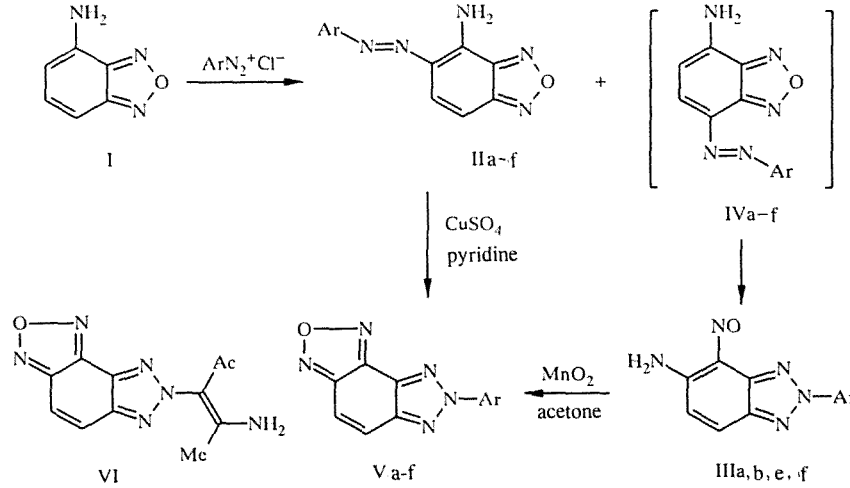
The reaction of 4-aminobenzofurazan with aryldiazonium salts leads to the formation of 4-amino-5-aryl-azobenzofurazans and 5-amino-2-aryl-4-nitroso-2H-benzotriazoles, products of the rearrangement of the initially formed 4-amino-7-(arylazo)benzofurazans. Oxidation of the benzofurazan as well as of the triazole derivatives gives 7-aryl-1,2,3-triazolo[4,5-e]benzofurazans. The chemical properties of some of the compounds obtained have been investigated.

The azo coupling of phenyldiazonium salts with aromatic amines is being widely used in the production of aminoazo derivatives for dyestuffs and intermediates [1]. In the present study we have investigated the azo coupling of aryldiazonium salts with 4-aminobenzofurazan (I) [2]. The reaction of the salt, obtained from aniline and sodium nitrite in hydrochloric acid, led to two compounds. Based on spectral and analytical data the structure 4-amino-5-(phenylazo)benzofuran (IIa) was assigned to the red product and the structure 5-amino-4-nitroso-2-phenyl-2H-benzotriazole to the green product (IIIa). The formation of compound (IIIa) is attributed to the ease of rearrangement of the initially formed 4-amino-7-(phenylazo)benzofurazan (IVa), which is converted to the nitrosamine IIIa during separation and even faster by heating in solvents. A similar rearrangement of 4-oxy-7-(phenylazo)benzofurazan to 5-hydroxy-4-nitroso-2-phenyl-2H-benzotriazole has been described earlier in [3]. Based on a series of aryldiazonium salts the benzofurazans (IIIb-f) and the nitrosoaminobenzotriazoles (IIIb, d, e) were synthesized. When using the salts obtained from p-nitroaniline and o-nitroaniline, the nitrosoamines (IIIc, d) could not be obtained in pure form. The oxidation of benzofurazan (IIa) with copper sulfate in pyridine [4] and of the nitrosoamine IIIa with manganese dioxide in acetone gave the same product: 7-phenyl-1,2,3-triazolo[4,5-e]benzofurazan (Va), which has been described earlier in [5]. Compounds IIb-f and IIIb, e, f were converted to the corresponding triazolobenzofurazans Vb-f in the same way.



II—V a) Ar = C_6H_5, b) Ar = C_6H_4OH-*o*, c) Ar = $C_6H_4NO_2$-*p*, d) Ar = $C_6H_4NO_2$-*o*, e) Ar = C_6H_4Ac-*p*, f) Ar = 3,5-dimethylisoxazolyl-4

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TABLE 1. Characteristics of Synthesized Compounds

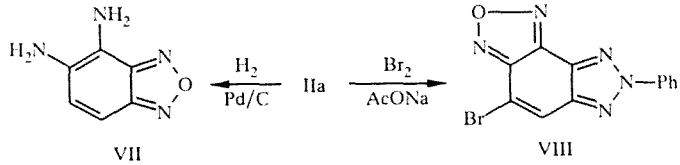
Compound	Empirical formula	mp, °C*	UV spectrum, λ_{max}, nm (log ε)	Yield, %
IIa	$C_{12}H_6N_5O$	163...165	230 (4,22), 315 (4,25), 390 (3,93), 460 (3,93)	51
IIb	$C_{12}H_6N_5O_2$	196 (decomp.)	222 (4,28), 316 (4,27), 380 (4,04), 492 (4,13)	13
IIc	$C_{12}H_8N_6O_3$	230 (decomp.)	228 (4,30), 320 (4,29), 400 (4,05), 495 (4,20)	70
IId	$C_{12}H_8N_6O_3$	296 (decomp.)	228 (4,39), 320 (4,25), 390 (3,95), 490 (4,04)	47
IIe	$C_{14}H_{11}N_5O_2$	210...212	225 (4,25), 318 (4,32), 390 (4,00), 490 (4,11)	48
IIf	$C_{11}H_{10}N_6O_2$	208...210	228(4,13), 310(4,28), 395(3,90), 455(3,90)	68
IIIa	$C_{12}H_9N_5O$	249 (decomp.)	236 (4,20), 325 (4,37), 430 (3,90)	47
IIIb	$C_{12}H_9N_5O_2$	242 (decomp.)	232 (4,25), 342 (4,34), 438 (3,96)	11
IIIe	$C_{14}H_{11}N_5O_2$	251 (decomp.)	224 (3,95), 282 (3,75), 342 (4,20), 430 (3,64)	40
IIIf	$C_{11}H_{10}N_6O_2$	312 (decomp.)	230 (4,25), 316 (4,25), 435 (3,92)	15
Va	$C_{12}H_7N_5O$	181...182	266 (4,46), 305 (4,34)	60
Vb	$C_{12}H_7N_5O_2$	165...168	247 (4,25), 262 (4,25), 322 (4,06)	45
Vc	$C_{12}H_6N_6O_3$	226...228	248 (4,20), 270 (4,24), 330 (4,42)	80
Vd	$C_{12}H_6N_6O_3$	218...220	248 (4,35), 305 (3,93)	75
Ve	$C_{14}H_9N_5O_2$	203...205	232 (3,00), 270 (4,50), 314 (4,20)	68
Vf	$C_{11}H_8N_6O_2$	166...168	260 (4,41), 300 (4,04)	46
VI	$C_{11}H_{10}N_6O_2$	165...167	232 (4,19), 288 (4,25), 290 (3,96), 410 (3,64)	25
VIII	$C_{12}H_6BrN_5O$	192...193	222 (4,22), 270 (4,37), 315 (4,19)	67
IX	$C_{13}H_9N_5O_2$	247...249	275 (4,80)	85
X	$C_{12}H_7N_5O_2$	266 (decomp.)	282 (4,60)	85
XIII	$C_{12}H_9N_5O_2$	207 (decomp.)	230 (4,12), 288 (4,42)	85
XIV	$C_{12}H_7N_5O_2$	196...198	285 (4,38), 340 (4,04)	42**
XV	$C_{12}H_4N_8O_7$	206...209	270 (4,25), 338 (4,35)	98
XVI	$C_6H_2N_6O_3$	155...157	225 (4,20), 328 (3,71), 372 (3,71)	78

*Compounds IIIa-f, VI, and XVI were recrystallized from ethyl acetate–hexane 3:1; IIIa, b, e, f from dimethylformamide; Va-f from chloroform; VIII, IX, X, XIII-XV from ethanol.

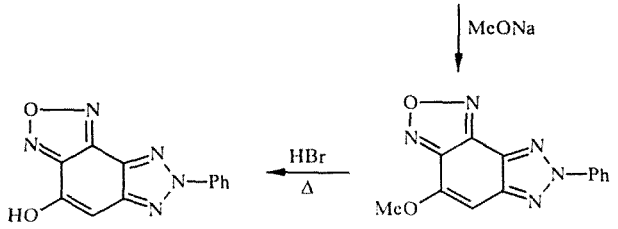
**By method D. The yield by method E was 60%.

Compounds Va-f are colorless crystalline substances, readily soluble in chloroform and ethanol, but not soluble in water. Oxidation of azobenzofuran IIe gave, besides the corresponding triazolobenzofurazan Ve, a second product to which the structure 7-(2-amino-4-oxopenten-2-yl-3)-1,2,3-triazolo[4,5-e]benzofurazan (VI) was assigned, based on analytical and spectral data. Information on the chemical properties of triazolobenzofurazans are missing in the literature, although the benzotriazoles and their derivatives have been attracting the interest of the researchers [6].

The study of some chemical properties of the prepared compounds showed that the reduction of azobenzofurazan IIa leads to the well-known 4,5-diaminobenzofurazan (VII) [7], while oxidation with bromine in acetic acid in the presence of sodium acetate gives 4-bromo-7-phenyl-1,2,3-triazolo-[4,5-e]benzofurazan (VIII). It was concluded that the bromine atom is located in position 4 of the condensed system by comparing the ^{13}C NMR spectra of compounds IIa and VIII. This atom is easily replaced by the action of sodium methylate on the methoxy group to form the corresponding 4-methoxy derivative (IX), which is converted by heating with hydrobromic acid to 4-hydroxy-7-phenyl-1,2,3-triazolo-[4,5-e]-benzofurazan (X).



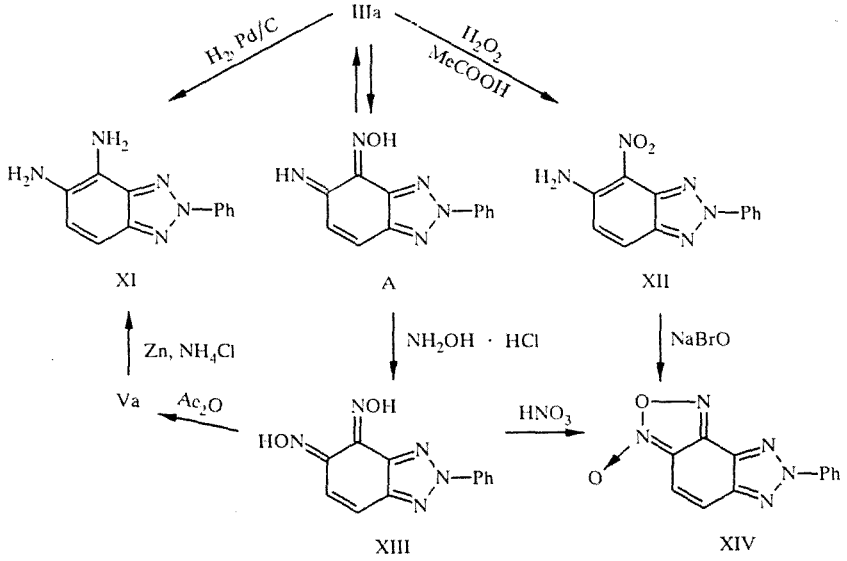
VII VIII



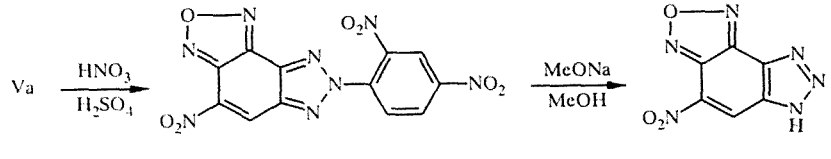
X IX

The reduction of the nitrosoamine IIIa by hydrogen over palladium on active carbon leads to the diamine (XI). The same product is readily formed in the reduction of triazolobenzofurazan Va with zinc in ethanol in the presence of ammonium chloride. The nitrosoamine IIIa is oxidized to the nitroamine (XII) with hydrogen peroxide in acetic acid. The dioxime (XIII) is formed by refluxing of compound IIIa with hydroxylamine hydrochloride in ethanol; the formation of the dioxime can be explained if we assume that the initial compound IIIa is present in the iminooxime form A.

Treatment of compound XIII with acetic anhydride gives the triazolobenzofurazan Va. Oxidation of the nitroamine XII with sodium hypobromite in ethanol and oxidation of the dioxime XIII with nitric acid in chloroform leads to the same product: triazolobenzofuroxan (XIV).



The nitration of 7-phenyltriazolobenzofurazan Va with nitric acid in sulfuric acid leads to the 7-(2,4-dinitrophenyl)-4-nitro derivative (XV). The presence of a nitro group in the latter in position 4 of the condensed system has been confirmed by comparison of the ^{13}C NMR spectra of the triazolobenzofurazans Va, VIII, and XV. The treatment of compound XV with sodium methylate in methanol readily splits off the dinitrophenyl grouping in the form of 2,4-dinitroanisole to give 4-nitro-1,2,3-triazolo[4,5-e] benzofurazan (XVI). Analogous conversions have been described in [8].



Thus, routes have been proposed in the present article for the preparation of heterocyclic compounds with several nitrogen atoms, in which the furazan or the furoxan ring is lined to the benzotriazole system.

TABLE 2. PMR Spectra of Synthesized Compounds*

Compound	Chemical shifts δ, ppm, KCCB (J), Hz
IIa	7,12 (1H, d, H_{an})**, 8,00 (1H, d, H_{an}), 7,38...7,55 (3H,m, H_{Ar}), 7,77...7,86 (2H,m, H_{Ar}), 7,32 (2H, br.s , NH_2)
IIb	6,80...8,27 (6H,m, $2H_{an}$ and $4H_{Ar}$), 8,50 (2H, br.s , NH_2), 10,20 (1H, br.s , OH)
IIc	7,12 (1H, d, H_{an}), 8,00 (1H, d, H_{an}), 8,00...8,48 (4H,m, H_{Ar}), 8,90 (2H, br.s , NH_2)
IId	7,04 (1H, d, H_{an}), 7,57 (1H, d, H_{an}), 7,33...8,10 (4H,m, H_{Ar}), 9,06 (2H, br.s , NH_2)
IIe	2,59 (3H, s, CH_3), 7,03 (1H, d, H_{an}), 7,89 (1H, d, H_{an}), 8,00 (4H, br.s , H_{Ar}), 8,70 (2H, br.s , NH_2)
IIf	2,40 (3H, s, CH_3), 2,63 (3H, s, CH_3), 7,00 (1H, d, H_{an}), 7,80 (2H, br.s , NH_2)
IIIa	7,15 (1H, d, H_{an}), 8,20 (1H, d, H_{an}), 7,35...7,70 (3H,m, H_{Ar}), 7,75...8,10 (2H,m, H_{Ar}), 11,89 (2H, br.s , NH_2)
IIIb	6,87...7,35 and 7,73...8,23 (6H,m, $2H_{an}$ and $4H_{Ar}$), 8,80 (2H, br.s , NH_2), 10,60 (1H, br.s, OH)
Va	7,47...8,30 (7H,m, $2H_{an}$ and $5H_{Ar}$)
Vb	6,63...8,00 (6H,m, $2H_{an}$ and $4H_{Ar}$), 10,00 (1H, br.s , OH)
Vc	7,90 (2H, s, H_{an}), 8,33 (4H, s, H_{Ar})
Vd	7,40...8,10 (6H,m, $2H_{an}$ and $4H_{Ar}$)
Ve	2,67 (3H, s, CH_3), 7,74 (1H, d, H_{an}), 7,84 (1H, d, H_{an}), 8,15 (2H, d, H_{Ar}, J_{AB} = 8), 8,41 (2H, d, H_{Ar}, J_{AB} = 8)
Vf	2,47 (3H, s, CH_3), 2,68 (3H, s, CH_3), 7,92 (1H, s, H_{an}), 8,00 (1H, c, H_{an})
VI	2,43 (3H, s, CH_3), 2,53 (3H, s, CH_3), 7,07 (1H, d, H_{an}), 7,93 (1H, d, H_{an}), 7,32 (2H, br.s , NH_2)
VIII	7,42...7,62 (3H,m, H_{Ar}), 8,03 (1H, s, H_{an}), 8,13...8,33 (2H,m, H_{Ar})
IX	4,17 (3H, s, OCH_3), 7,30...7,60 (3H,m, H_{Ar}), 8,05 (1H, d, H_{an}), 8,20...8,30 (2H,m, H_{Ar})
X	6,75 (1H, d, H_{an}), 7,50...7,70 (3H,m, H_{Ar}), 8,14...8,20 (2H,m, H_{Ar}), 3,44 (1H, br. s, OH)
XIII	6,80...7,60 (5H,m, $2H_{an}$ and $3H_{Ar}$), 7,80...8,10 (2H,m, H_{Ar}), 12,6 (2H, br.s , 2 OH)
XIV	7,45 (1H, d, H_{an}), 7,80 (1H, d, H_{an}), 7,50...7,75 (3H,m, H_{Ar}), 8,10...8,25 (2H,m, H_{Ar})
XV	8,54...9,00 (2H,m, H_{Ar}), 9,00 (1H, s, H_{Ar}), 9,25 (1H, s, H_{an})
XVI	9,23 (1H, s, H_{an}), 9,28 (1H, br.s , NH)

*The PMR spectra of compounds IIa, Vd, Ve, and IX were recorded in $CDCl_3$, the spectra of the remaining compounds in $(CD_3)_2SO$.

**H_{an} is the proton of the annelated benzene ring; for $2H_{an}$ J_{AB} is in all cases equal to ~10 Hz (if the signals of these protons are not overlapped by H_{ar} signals).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr (concentration 0.25%). The UV spectra were obtained on a UV-vis Specord spectrometer in ethanol. The PMR spectra were taken on a Varian 56-60A spectrometer and the ^{13}C NMR spectra on a Bruker WP-200 spectrometer. The mass spectra were recorded on a Finnigan MAT-8200 mass spectrometer with an ionizing potential of 70 eV. The products obtained were separated and purified by column chromatography on alumina. The eluents are given below. The melting points were determined on a heated Kofler microstage. The characteristics of the synthesized compounds are given in Table 1-3. The elemental analysis data of the compounds correspond to the calculated values; 4-aminoisoxazole-3,5-dimethyl was obtained by the procedure described in [10].

4-Amino-5-(arylazo)benzofurazans (IIa-f) and 5-Amino-2-aryl-4-nitroso-2H-benzotriazoles (IIIa, b, e, f). A solution of 8.1 g (60 mmole) of amine I in 100 ml methanol is treated at 0°C by the dropwise addition of a solution of a phenyldiazonium salt, prepared from 5.4 g (60 mmole) aniline and 4.3 g (61 mmole) sodium nitrite in 30 ml of 15% HCl. The reaction mixture is stirred at room temperature for 2 h and poured into 1 liter of water; 5% Na_2CO_3 solution is added to pH 8 and the precipitate formed is filtered off, washed with water, and dried. Obtained 14.7 g of a mixture of compounds IIa and IIIa, which is refluxed in 300 ml chloroform. The precipitate is filtered off and washed with 100 ml chloroform, yield 6.77 g of product IIIa. The filtrate is evaporated and 7.27 g of the product IIa isolated by chromatography (eluent chloroform).

TABLE 3. Chemical Shifts in the ^{13}C NMR Spectra of Some Synthesized Compounds, ppm*

Compound	C_{ArH}, CH_3	C_{an}**H	Carbon atoms not bonded to hydrogen
IIa	122,0, 129,1, 133,8	102,7, 130,3	152,6, 149,5, 146,2, 131,0, 130,0
IIf	11,8, 12,0	127,9, 130,6	167,0, 153,5, 149,5, 146,0, 132,7, 131,3, 128,0
IIIa	119,0, 129,5, 128,8	123,9, 128,2	135,8, 138,8, 139,0, 144,0, 159,7
Va	119,7, 129,5, 129,9	116,4, 124,7	132,4, 138,8, 142,0, 145,7, 149,8
Vb	117,7, 119,4, 131,6, 126,5	115,8, 124,8	151,3, 127,4, 142,0, 145,1, 149,8, 172,0
Vc	126,0, 122,1	119,8, 123,0	132,4, 139,0, 139,8, 141,0, 147,8, 148,5
Vf	10,4, 11,7	116,4, 124,4	118,6, 131,4, 141,4, 145,4, 149,6, 154,5, 164,0
VI	11,5, 27,7	103,1, 128,3	116,4, 126,1, 142,3, 145,7, 146,6, 148,5, 192,5
VIII	119,9, 129,5, 129,6	126,2	108,4, 132,2, 139,3, 141,3, 146,3, 150,0
X	119,7, 129,4, 129,8	90,2	133,0, 138,8, 139,8, 142,3, 151,0, 152,2
XIV	130,0, 129,6, 119,7	121,5, 113,7	146,5, 145,5, 138,8, 133,5, 113,0
XV	121,6, 125,4, 128,1	128,9	148,1, 144,8, 144,6, 142,9, 142,2, 138,6, 136,0, 134,1
XVI	—	125,6	144,0, 141,8, 140,4, 135,9, 131,7

*The spectra of compounds IIa, IIf, VI, and VIII were recorded in $CDCl_3$; of VIc in H_2SO_4; of the remaining compounds in $(CD_3)_2SO$.

**C_{an} is the carbon atom of the annelated benzene ring.

Based on the amine I and aryldiazonium salts prepared from o-aminophenol, p-nitroaniline, o-nitroaniline, n-aminoacetophenone, and 4-amino-3,5-dimethylisoxazole, the compounds IIb-f and IIIb, e, f were synthesized in the same way.

7-Aryl-1,2,3-triazolo[4,5-e]benzofurazans (Va-e). A. A solution of 3.0 g (12.5 mmole) of compound IIIa in 500 ml acetone is stirred with 40 g manganese dioxide at room temperature for 48 h. The precipitate is filtered off and the filtrate evaporated. Obtained from the residue 1.70 g of compound Va by chromatography (eluent chloroform–hexane 1:4).

B. A solution of 3.0 g (12.5 mmole) of compound IIa in 30 ml pyridine is refluxed 3 h with 3.5 g (14 mmole) $CuSO_4 \cdot 5H_2O$ and 5 ml water. After cooling the reaction mixture is poured into 200 ml 5% sulfuric acid; the precipitate formed is filtered off, washed with water, and dried. Yield 2.4 g of compound Va.

In the same way the oxidation of compounds IIIb, e, f by method A and of compounds IIb-e by method B gives the corresponding triazolobenzofurans Vb-e.

7-(3,5-Dimethylisoxazol-4-yl)-1,2,3-triazolo[4,5-e]benzofurazan (Vf) and 7-(2-Amino-4-oxopenten-2-yl)-1,2,3-triazolo[4,5-e]benzofurazan (VI). A solution of 1.5 g (5.8 mmole) of amine IIf in 20 ml pyridine is refluxed for 2 h with 5 g (28 mmole) $CuSO_4 \cdot 5H_2O$ and 5 ml water. After cooling the mixture is poured into 200 ml water and adjusted the pH of the solution to 3 with 10% H_2SO_4. The precipitate formed is filtered off, washed with water, and dried; chromatography (eluent chloroform–hexane, 1:2) of the residue gives 0.69 of product Vf and 0.38 g of product VI. Mass spectrum, *m/z* (I, %) for Vf: M^+ 256(50), 239(25), 159(25), 43(100); for VI: M^+ 258(100), 215(10), 148(20), 118(10), 43(50).

4,5-Diaminobenzofurazan (VII). Compound IIa (6.2 g, 26 mmole) in 300 ml methanol is hydrogenated in the presence of 2.0 g 5% Pd on active carbon and 0.1 ml hydrochloric acid at atmospheric pressure and room temperature in a hydrogenation apparatus until absorption of hydrogen has stopped. The catalyst is filtered off and the filtrate evaporated. Yield 3.52 g (90%) of diamine VII; mp 152-154°C (from benzene). Literature mp 152°C [7].

4-Bromo-7-phenyl-1,2,3-triazolo[4,5-e]benzofurazan (VIII). A solution of 2.39 g (10 mmole) of compound IIa in 100 ml acetic acid, containing 3.28 g (48 mmole) sodium acetate, is treated dropwise with 3.2 g (20 mmole) bromine with stirring and cooling (to 10°C). Stirring is continued for 2 h at room temperature; the reaction mixture is then evaporated to

~10 ml and 200 ml water added. The precipitate formed is filtered off, washed with water, and dried. Chromatography on alumina (eluent chloroform) gives 2.10 g of product VIII.

4-Methoxy-7-phenyl-1,2,3-triazolo[4,5-e]benzofurazan (IX). A solution of 1.23 g (3.9 mmole) of bromide VIII in 150 ml methanol, containing 2 g (39 mmole) of sodium methylate, is refluxed for 6 h. After cooling the precipitate is filtered off, washed with water, and dried. Yield 0.88 g of compound IX.

4-Hydroxy-7-phenyl-1,2,3-triazolo[4,5-e]benzofurazan (X). A mixture of 1 g (37.4 mmole) of the methoxy derivative and 40 ml hydrobromic acid is refluxed for 3 h. The mixture is cooled, the precipitate is filtered off, washed with water, and dried. Yield 0.83 g of compound X.

4,5-Diamino-2-phenyl-2H-benzotriazole (XI). A. A sample of 1.0 g (4.5 mmole) of compound IIIa in the form of a suspension in 100 ml methanol is hydrogenated in the presence of 0.5 g of 5% Pd on active carbon and 0.1 ml hydrochloric acid as described in the preparation of product VII. The residue after evaporation of the filtrate is triturated with hexane. Yield 0.7 g of diamine XI; mp 126°C. Literature mp 126°C [10].

B. A solution of 10 g (42 mmole) of compound Va in 400 ml ethanol, containing 20 g (370 mmole) ammonium chloride is heated to the boil and treated in portions with 15 g zinc powder under intensive stirring. The precipitate is filtered off and the filtrate evaporated. The residue is treated with 50 ml water, the precipitative is filtered off, washed with water, and dried. Yield 8.28 g (80%) of the diamine XI.

4,7-Dihydroxyimino-4,7-dihydro-2-phenyl-2H-benzotriazole (XIII). A mixture of 4.0 g (16.8 mmole) of nitrosoamine IIIa, 4.0 g (5.5 mmole) hydroxylamine hydrochloride, and 200 ml methanol is refluxed for 4 h. The methanol is tripped off and the residue treated with 400 ml water; the precipitate is filtered off and dried. Yield 3.62 g of dioxime XIII.

A mixture of 1.0 g (3.9 mmole) of dioxime XIII and 15 ml of acetic anhydride is refluxed for 10 min. The acetic anhydride is stripped off and 100 ml water added to the residue. After 3 h the precipitate is filtered off, washed with water, and dried. Yield 0.62 g of compound IIa.

4-Amino-5-nitro-2-phenyl-2H-benzotriazole (XII). A mixture of 5 g (19.4 mmole) of nitrosoamine IIIa, 50 ml 30% hydrogen peroxide, and 50 ml acetic acid is kept at room temperature for 48 h. The mixture is treated with 100 ml water, the precipitate is filtered off, washed with water, and dried. Yield 4.12 g of nitrosamine XII; mp 310°C. Literature mp 310°C [10].

7-Phenyl-1,2,3-triazolo[4,5-e]benzofuroxan (XIV). A. A suspension of 16.5 g (65 mmole) of dioxime XIII in 800 ml chloroform is treated dropwise with 15 g (840 mmole) nitric acid (density 1.5) under intensive stirring; stirring is continued for 2 h. The solution obtained is washed with water, dried over magnesium sulfate, and evaporated. Chromatography of the residue (eluent chloroform) yields 8.2 g of compound XIV. Mass spectrum, *m/z* (I, %): M^+ (100), 193(50), 91(50), 77(20), and 64(20).

B. A solution of 1.0 g (3.7 mmole) nitroamine XII in 100 ml methanol is treated dropwise with stirring with a solution of sodium hydrobromite, prepared from 6.2 g (39 mmole) bromine and 40 ml 10% NaOH. The reaction mixture is stirred for 2 h. The methanol is evaporated, chromatography (eluent chloroform) of the residue yield 0.6 g of compound XIV.

7-(2,4-Dinitrophenyl)-4-nitro-1,2,3-triazolo[4,5-e]benzofurazan (XV). A solution of 2.4 g (10 mmole) triazolobenzofurazan IIa in 15 ml sulfuric acid is treated with 2 ml (47.5 mmole) nitric acid (density 1.5). The mixture is kept with stirring on a boiling water bath for 20 min, cooled, and poured onto 200 g ice. the precipitate is filtered off, washed with water, and dried. Yield 3.74 g of compound XV.

4-Nitro-1,2,3-triazolo[4,5-e]benzofurazan (XVI). A solution of 3.0 g (8 mmole) of compound XV in 150 ml methanol is treated with 3.0 g (56 mmole) sodium methylate and the mixture stirred at 40-50°C for 2 h. The solvent is removed in vacuum, the residue is suspended in 200 ml chloroform; the precipitate formed is washed with 500 ml chloroform and dried. The precipitate is dissolved in 200 ml water, the acidity adjusted with hydrochloric acid to Ph 3 and the product extracted with ethyl acetate (4 × 50 ml). The extract is washed with a saturated sodium chloride solution, dried over magnesium sulfate, and evaporated. The residue is suspended in hexane and the precipitate filtered off. Yield 1.2 g of compound XVI. Mass spectrum, *m/z* (I, %): M^+ 206(100), 160(20), 146(40), 130(20), 116(20), and 75(30).

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