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FORMATION OF o-NITROSOALKYLAMINOBENZENES IN THE REACTION OF BENZOFURAZAN S WITH ALCOHOLS IN ACIDIC CONDITIONS

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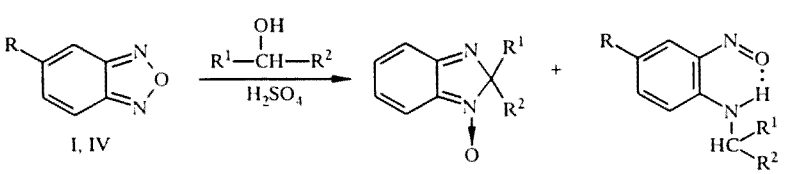
In the reaction of benzofurazan with isopropanol cyclohexanol o-nitrosoalkylaminobenzenes are formed besides 2,2-dialkyl-2H-benzimidazole-oxides. In the instance of 4-aminobenzofurazan only 2-nitroso-3-alkylamino-anilines are obtained. 5-Nitrobenzofurazan reacts with isopropanol in sulfuric acid to form 4-nitro-2-nitrosoisopropylaminobenzene; however, in the instance of 4-nitrobenzofurazan derivatives the formation of o-nitrosoalkylaminobenzenes has not been observed.

We have shown earlier that in the reaction of benzofuroxans with alcohols or alkyl halides 2H-benzimidazole-1,3-dioxides are formed in the presence of acids with high yields [1]. It could be expected that 2H-benzimidazole-1-oxides will be formed in the reaction of benzofurazans with alcohols at analogous conditions. In order to check this assumption we have reacted benzofurazan (I) with cyclohexane in sulfuric acid and indeed, the corresponding 2H-benzimidazole-1-oxide (IIa) was isolated from the reaction mixture with a yield of about 40% [2]. Besides the compound IIa the dark-green compound IIIa was isolated from the reaction mixture with a yield of about 20%. The mass spectrum of compound IIIa shows a peak of the molecular ion with m/z 204. Elemental analysis gives the empirical formula $C_{12}H_{15}N_2O$. The PMR spectrum in $CDCl_3$ contains the signals of the protons of the cyclohexane ring in the region 1.10-2.00 (10H, m, $5CH_2$) and a multiplet with the center at 3.50 ppm (1H, m, CH), the signals of aromatic protons: 6.78 (2H, m, 2CH arom.), 7.29 (1H, t, CH arom.) and 8.51 ppm (1H, d, CH arom.). At 11.2 ppm the broad signal of a single proton is observed which can be attributed to the proton of the amino group, taking part in the formation of a hydrogen bond. It was shown by the dual resonance method that the proton of the amino group participates in the spin–spin interaction with the methyne proton of the cyclohexane ring. The ^{13}C NMR spectrum contains signals of the carbon atoms of the cyclohexane ring: at 24.0, 25.2, and 32.2 of the CH_2 groups and at 49.7 ppm of the CH group. Signals are also present of sp^2-hybridized carbon atoms of the CH groups at 114.0, 115.5, and 137.0 ppm and a strongly broadened signal at 139.7 ppm. Signals are also present of sp^2-hybridized carbon atoms which do not contain hydrogen atoms as constituents, at 135.1 (broadened signal) and at 156.0 ppm.



I, IV

III a, b V

I, IIIa, b R = H; IV, V R = NO_2; IIa, IIIa $R^1 + R^2 = -(CH_2)_5-$; IIb, IIIb, V $R^1 = R^2 = CH_3$

Based on these data the structure of 2-nitrosocyclohexylaminobenzene was attributed to compound IIIa. In the same way the benzofurazan (I) reacts with isopropanol to give 2,2-dimethyl-2H-benzimidazole-1-oxide (IIb) and 2-nitrosoisopropylaminobenzene (IIIb).

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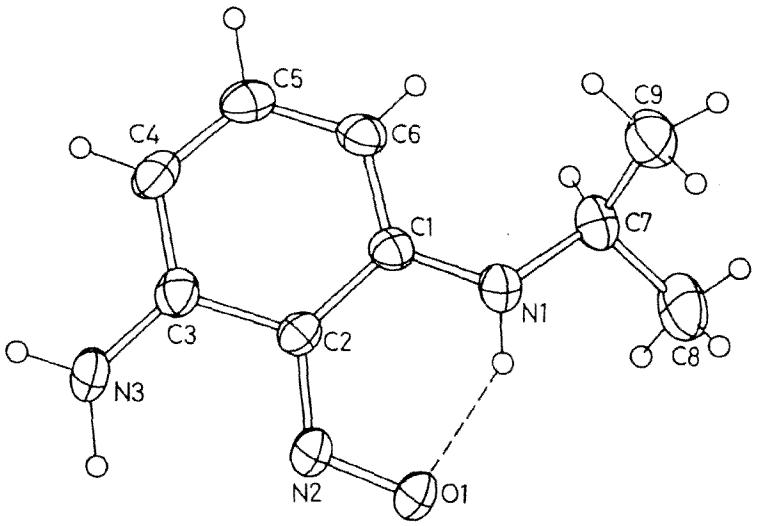


Fig. 1. Structure of the molecule of nitrosoalkylaminobenzene VIIb. The selected bond lengths (Å) and valence angles (degree): $C_{(1)}-C_{(2)}$ 1.444(4), 1.445(4), $C_{(2)}-C_{(3)}$ 1.450(4), 1.443(4), $C_{(1)}-N_{(1)}$ 1.337(4), 1.342(4), $C_{(2)}-N_{(2)}$ 1.350(4), 1.352(4), $N_{(2)} = O_{(1)}$ 1.281(3), 1.285(3), $C_{(3)}-N_{(3)}$ 1.348(3), 1.342(4), $O_{(1)}...H_{(N(1))}$ 1.87(3), 1.77(3), $N_{(1)}-C_{(1)}-C_{(2)}$ 118.9(3), 119.6(3), $C_{(1)}-C_{(2)}-N_{(2)}$ 126.5(3), 126.3(3), $C_{(1)}-C_{(7)}$ 126.6(3), 125.7(3), $C_{(2)}-N_{(2)} = O_{(2)}$ 118.3(3), 118.2(3)

The reaction of 5-nitrobenzofurazan (IV) with isopropanol led to the isolation of 4-nitro-2-nitrosoisopropylaminobenzene (V) as the main product. The conclusion that the nitro group in this compound is in position 4, not 5, of the ring was based on the comparison of the PMR spectrum of compound V with the PMR spectra of 2,4-dinitroaniline and m-nitroaniline [3]. The chemical shift of the hydrogen atom in position 3 of the ring in compound V is 9.44, for 2,4-dinitroaniline 8.81, and for m-nitroaniline 7.51 ppm.

The reaction of 4-aminobenzofurazan (VI) [4] with isopropanol and with cyclohexanol in sulfuric acid gave the dark-blue products VIIa, b respectively, with yields of about 50%. The PMR and ^{13}C NMR spectra contained the double set of signals, indicating the presence of two isomeric products, that differed from each other in that the nitroso group participates in the formation of an intramolecular hydrogen bond with the amino or the alkylamino group. The ratio of the isomers, based on the PMR data on the interval intensity of the signals in $CDCl_3$, measured for compound VIIb was 1:2 and in $(CD_3)_2SO$ 1:3.

In order to confirm the structure of compound VIIb, it was investigated by x-ray diffraction. The structure of the nitrosoamine VIIb molecule is shown in Fig. 1. The geometry of the two crystallographically independent VIIb molecules conforms within the limits of error. The VIIb molecules are plane, except the $C_{(8)}$ and $C_{(9)}$ atoms of the isopropyl group. The bond lengths $C_{ar}-N_{sp^2}$ are close to those expected [5]. The lengthening of the N=O bond in the nitroso group to 1.281(3) and 1.285(3) Å must be pointed out, in comparison with the values obtained in the gaseous phase (1.20-1.23 Å) [6].

The summary effect of the intra- and intermolecular hydrogen bonds probably manifests itself here, as well as the contribution of the oxime tautomeric structure. The latter effect must be small, since according to the calculations by the quantum-chemical methods MNDO and RMZ (MNDO program [7]) the oxime is less stable by 7 and 14 kcal/mole respectively. The lengthening of the $C_{(1)}-C_{(2)}$ and $C_{(2)}-C_{(3)}$ bonds is probably caused by steric factors: calculation by the RMZ method gives 1.43 and 1.42 Å respectively. In the crystal the nitrosoalkylaminobenzene molecules are bound by a network of hydrogen bonds into bifilar chains, oriented along the c axis.

From the XRD data it follows that compound VIIb is 2-nitroso-3-isopropylaminoaniline and compound VIIa by analogy is 2-nitroso-3-cyclohexylaminoaniline.

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Thermal Factors ($Å^2 \times 10^3$) of the Atoms of Independent Nitrosoalkylaminobenzene Molecules VIIb

Atom	x/a	y/b	z/c	U_{eq}
		Molecule 1		
$C_{(1)}$	-813(2)	3915(3)	3367(2)	45(1)
$C_{(2)}$	67(2)	3304(3)	3133(2)	44(1)
$C_{(3)}$	314(2)	3508(3)	2153(2)	48(1)
$C_{(4)}$	-312(3)	4291(3)	1460(3)	56(1)
$C_{(5)}$	-1118(3)	4884(3)	1728(3)	56(1)
$C_{(6)}$	-1376(3)	4730(3)	2649(3)	53(1)
$C_{(7)}$	-1755(3)	4353(3)	4723(3)	61(1)
$C_{(8)}$	-1442(4)	4071(5)	5896(3)	82(1)
$C_{(9)}$	-2975(3)	4109(5)	4189(4)	76(1)
$N_{(1)}$	-1029(2)	3707(3)	4273(2)	55(1)
$N_{(2)}$	773(2)	2581(2)	3778(2)	56(1)
$N_{(3)}$	1152(3)	2945(3)	1957(2)	64(1)
$O_{(1)}$	602(2)	2311(2)	4648(2)	71(1)
		Molecule 2		
$C_{(1)}$	5368(2)	1177(3)	4097(2)	47(1)
$C_{(2)}$	4340(2)	1692(2)	4106(2)	42(1)
$C_{(3)}$	4201(2)	2063(3)	5091(2)	47(1)
$C_{(4)}$	5075(3)	1960(3)	6002(2)	59(1)
$C_{(5)}$	6044(3)	1461(3)	5971(3)	62(1)
$C_{(6)}$	6215(3)	1069(3)	5068(3)	57(1)
$C_{(7)}$	6464(3)	253(3)	3055(3)	60(1)
$C_{(8)}$	6119(4)	-299(4)	1979(4)	75(1)
$C_{(9)}$	7431(4)	1043(5)	3174(4)	75(1)
$N_{(1)}$	5496(2)	837(2)	3180(2)	52(1)
$N_{(2)}$	3436(2)	1843(2)	3263(2)	48(1)
$N_{(3)}$	3234(3)	2511(3)	5098(3)	68(1)
$O_{(1)}$	3494(2)	1560(2)	2349(2)	57(1)

TABLE 2. Characteristics of the Synthesized Compounds IIa, b, IIIa,b, V, VIIa, b, VIIIa, b, IX, X, and XII

Compound	M^+	mp, °C	UV spectrum, λ_{max} (log ε)	Yield, %
II a	—	86 [2]	—	40
II b	—	65 [2]	—	34
III a	204	102...104	232(4,34), 302(3,98), 468(3,73)	20
III b	164	38...40	232(4,62), 302(4,00), 468(3,78)	23
V	209	78...80	285(4,34), 348(4,25), 445(3,83)	38
VII a	219	51...53	226(4,30), 243(4,34), 370(3,98), 568(3,60)	55
VII b	179	86...87	226(4,26), 243(4,35), 370(3,96), 568(3,64)	51
VIII a	261	116...118	232(4,57), 262(3,71), 350(4,02), 518(3,88	78
VIII b	221	81...82	232(4,54), 350(4,10), 515(3,70)	76
IX	—	207...209*2 (decomp.)	217(4,38), 250(3,88), 300(3,64)	72
X	191	Oil	232(4,69), 410(3,92)	75
XII	222	114...116	230(4,15), 338(3,93), 465(4,42)	45

*Compound IX recrystallized from concentration HCl, compound XII from ethanol, the rest from hexane.

*2Dihydrochloride.

TABLE 3. Spectral Characteristics of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}, in CCl_4	Chemical shifts of protons, δ, ppm (J, Hz)							
		Solvent	NH broad.	CH m	3-H d	4-H t	5-H d	6-H d	Other signals
III a	–	$CDCl_3$	11,20	3,50	6,78 (7)	7,29	6,78 t	8,51 (7)	1,10...2,00 (10H, m, $5CH_2$)
		$(CD_3)_2SO$	11,10	3,66	7,08 (7)	7,47	6,87 t	8,38 (7)	1,20...1,91 (10H, m, $5CH_2$)
III b	–	$CDCl_3$	11,00	3,77	6,74 (7)	7,20	6,75 t	8,50 (7)	1,20 (6H, d, 2CH3, J = 6,5 Hz)
V	1345, 1580 (NO_2)	$CDCl_3$	10,55	3,89	6,91 (10)	8,12 d.d (10,2)	–	9,44 s	1,28 (6H, d, $2CH_3$, J = 6,5 Hz)
VIIa*	3400, 3480, 3510 (NH_2)	$CDCl_3$	11,90	3,33	5,80 (8)	6,98	5,74 (8)	–	1,10...2,00 (10H, m, 5CH2), 5,68 (2H, broad. s, NH_2)
VII b	3400, 3480, 3510 (NH_2)	$CDCl_3$	11,72	3,68	5,83 (8)	7,10	5,86 (8)	–	1,17 (6H, d, $2CH_3$, J = 6,5 Hz)
VIIb*2	–	$CDCl_3$	7,70	3,71	5,50 (8)	7,08	5,50 (8)	–	1,24 (6H, d, $2CH_3$, J = 6,5Hz), 5,55 (2H, broad. s, NH_2)
VII b	–	$(CD_3)_2SO$	11,56	3,70	5,73 (8)	7,12	5,96 (8)	–	1,15 (6H, d, $2CH_3$, J = 6,5 Hz)
VII b*2	–	$(CD_3)_2SO$	7,38	3,80	5,82 (8)	7,12	5,74 (8)	–	1,25 (6H, d, $2CH_3$, J = 6,5 Hz)
VIII a	3380 (NH), 1690 (C=O)	$CDCl_3$	12,30	3,66	6,67 (8)	7,43	7,67 (8)	–	1,21...2,08 (10H, m, $5CH_2$), 2,20 (3H, s, CH_3), 10,50 (1H, s, NH amid.)
VIII b	3380 (NH), 1700 (C=O)	$CDCl_3$	12,30	3,78	6,38 (8)	7,30	7,74 (8)	–	1,22 (6H, d, $2CH_3$, J = 6,5 Hz), 2,18 (3H, s, CH_3), 9,98 (1H, s, NH amid.)
IX	–	CF_3COOH	–	3,38	6,90 m	7,28 m	7,28 m	–	0,90...1,60 (10H, m, $5CH_2$)
X	3410 (NH)	$CDCl_3$	4,96	–	6,85 (8)	7,12	6,18 (8)	–	1,40 (9H, s, $3CH_3$)
XII	1330, 1570 (NO_2), 3310, 3360 (NH)	$CDCl_3$	6,53	4,01	–	8,35 d (9)	6,15 (9)	–	1,36 (6H, d, $2CH_3$, J = 6,5 Hz)

*Intensity of signals of the second isomer in the PMR spectrum was less than 10%.

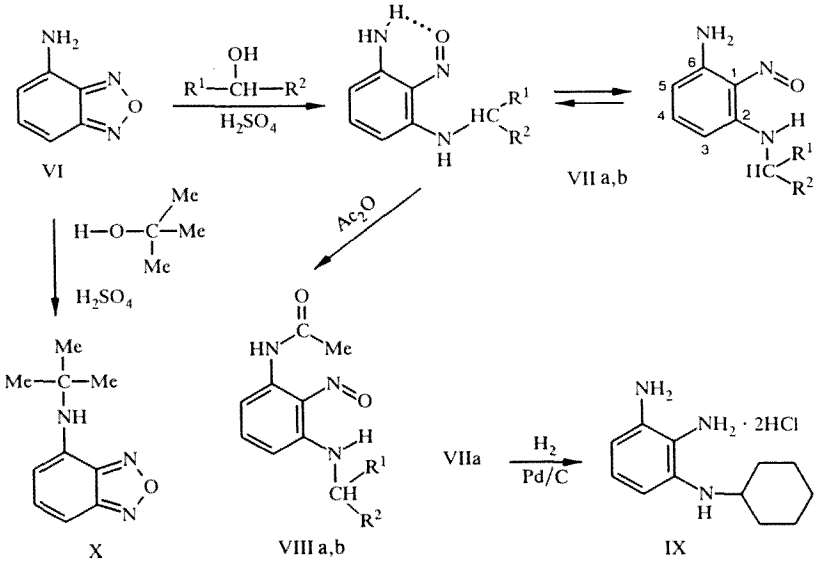
*2Spectra of isomer present in the mixture in smaller quantities.

TABLE 4. Chemical Shifts in the ^{13}C NMR Spectra of the Synthesized Compounds (in $CDCl_3$)

Compound	C=C arom.	CH arom.	Other signals
III a	135,1, 156,0	114,1, 115,5, 137,5 139,7	24,0, 25,2, 32,2 (CH_2), 49,7 (CH)
III b	134,9, 156,0	113,9, 115,6, 137,6, 139,6	22,1 ($2CH_3$), 42,8 (CH)
V	136,4, 138,5, 152,8	115,0, 130,9, 135,9	22,0 ($2CH_3$), 44,0 (CH)
VII a*	137,6, 146,9, 153,9	98,5, 98,7, 142,7	23,6, 25,0, 31,8 (CH_2), 49,5 (CH)
	137,1, 147,9, 151,8	96,2, 100,6, 146,9	24,2, 25,1, 32,3 (CH_2), 50,7 (CH)
VIIb*	137,6, 147,1, 154,1	98,8, 99,0, 142,8	22,0 ($2CH_3$), 42,8 (CH)
	136,9, 148,0, 152,1	96,5, 100,8, 142,5	22,3 ($2CH_3$), 43,7 (CH)
VIII a	135,9, 142,4, 146,7	104,8, 108,5, 141,9	23,6, 24,8, 31,7 (CH_2), 24,5 (CH_3), 49,1 (CH), 168,9 (C=O)
VIII b	136,6, 142,1, 145,6	104,3, 107,6, 142,4	22,3 ($2CH_3$), 25,0 (CH_3), 43,2 (CH), 168,2 (C=O)
X	134,3, 145,7, 149,7	100,6, 102,5, 133,8	28,6 ($3CH_3$), 51,4 (=C=)
XII	124,4, 143,1, 143,6, 143,9	98,7, 136,6	21,5 ($2CH_3$), 45,8 (CH)

*The signals of the carbon atoms with lower intensities are given in the lower line.

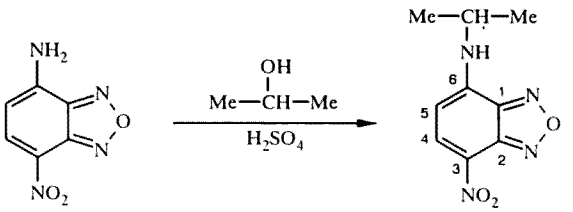
Treatment of compounds VIIa, b with acetic anhydride gives the corresponding acyl derivatives VIIIa, b, whereby the PMR and ^{13}C NMR spectra of these compounds contain only one set of signals; this indicates the presence of only one isomer, where the alkylamino and the nitroso groups participate in the formation of an intramolecular hydrogen bond. The reduction of compound VIIa with hydrogen in the presence of a catalyst (5% Pd on carbon) leads to 1,2-diamino-3-cyclohexylaminobenzene IX, which was separated and characterized as the hydrochloride



VII, VIII a $R^1 + R^2 = -(CH_2)_5-$; b $R^1 = R^2 = Me$

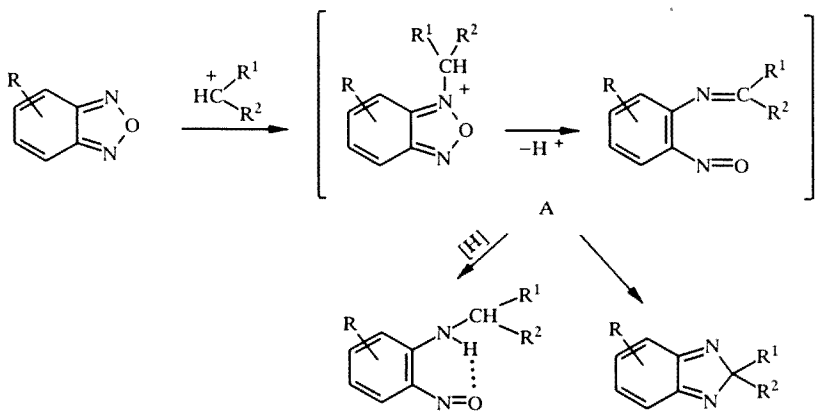
It must be pointed out that in the IR spectra of compounds IIIa, b, VIIa, b, and VIIIa, b, recorded in CCl_4, the absorption bands of the valence vibrations of the NH group in the region 3300-3500 cm^{-1} are missing due to the formation of an intramolecular hydrogen bond; they probably coincide with the absorption bands of the valence vibrations of the CH bonds near 3000 cm^{-1} [8].

We attempted to determine the limits of applicability of this reaction to the synthesis of other o-nitroso-alkylaminobenzenes. It was found that with methanol and ethanol no reaction occurs with benzofurazans in sulfuric acid; with tert-butanol the benzofurazans I and IV do not react and with the 4-aminobenzofurazan VI and 4-tert-butylaminobenzofurazan X is obtained. At the same conditions 4-nitrobenzofurazan does not react with alcohols and remains unchanged even at prolonged heating. Only 4-nitro-7-isopropylaminobenzofurazan (XII) is formed in the reaction of 4-nitro-7-aminobenzofurazan (XI) with isopropanol in sulfuric acid. The nitro group in position 4 of the ring probably inhibits opening of the furazan ring with the formation of o-nitrosoalkylaminobenzenes.



XI XII

The scheme of the formation of o-nitrosoalkylaminobenzenes from benzofurazan derivatives includes, as in the instance of the benzofuroxans [1], an initial attack of the carbcation at the nitrogen atom of the heterocycle, formed from the alcohol in the acid, opening of the furazan ring with the formation of the nitrosoimine A, followed by cyclization of A into 2H-benzimidazole-1-oxide or by the reduction of A into nitrosoalkylaminobenzene. We have shown that at the reaction conditions 2H-benzimidazole-1-oxides are then converted to o-nitrosoalkylaminobenzenes.



Thus, it has been found that in the reaction of benzofurazans with secondary alcohols in sulfuric acid ring opening occurs with the formation of o-nitrosoalkylaminobenzenes besides the formation of 2H-benzimidazole-1-oxides. It must be pointed out that hitherto the preparation of these compounds was difficult [9] and that the proposed route for the synthesis of o-nitrosoalkylaminobenzenes is of interest for the preparation of these not easily accessible compounds.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr (concentration 0.25%) and CCl_4, the UV spectra were obtained on a Specord UV-vis spectrometer in ethanol. The PMR and ^{13}C NMR spectra were taken on a Bruker WP-200SY spectrometer. The mass spectra were recorded on a MS-8200 spectrometer of the firm Finnigan MAT by direct introduction of the sample into the ion source at an ionizing potential of 70 eV. The temperature of the ionization chamber was 120-200°C.

A single crystal of nitrosoalkylaminobenzene VIIb was investigated by x-ray diffraction on a SYNTEX-$P2_1$ diffractometer by using CuK_α radiation with a graphite monochromator. The crystals of VIIb belong to the monoclinic system: a = 12.690(7), b = 11.939(6), c = 13.294(6) Å, β = 107.59(4)°, V = 1920(2) Å^3, spatial group $P2_{1/c}$ $C_9H_{13}N_3O$, Z = 8, d_{calc} = 1.24 g/cm^3, crystal size 0.1 × 0.5 × 2.00 mm^3. Intensities of 2412 independent images with $2\theta < 114°$ were measured by $\theta/2\theta$ scanning. Corrections were introduced for absorption by the analytical method on the crystal face (transmission 0.61-0.89). The structure was interpreted by the direct method using the SHELX-86 program and the precision improved by the least-squares method in a full-matrix anisotropic–isotropic approximation (for H atoms) by the SHELX-93

program to WR_2 = 0.1514 for all images (R = 0.0533 for 1728 F > $4\sigma_F$), S = 1.00. The position of the hydrogen atoms was established by differential synthesis. The coordinates of the atoms obtained are given in Table 1. The melting points were determined on a Kofler heated microstage. The yields, melting points, and spectral data of the synthesized compounds are presented in Tables 2-4.

The elemental analysis data of the synthesized compounds conform with the calculated values.

2-Spirocyclohexane-2H-benzimidazole-1-oxide (IIa, $C_{12}H_{14}N_2O$ and 2-Nitrosocyclohexylaminobenzene (IIIa, $C_{12}H_{16}N_2O$). A solution of 2, 4 g (20 mmole) of benzofurazan (I) in 15 ml of concentration sulfuric acid is treated with 2.2 ml (22 mmole) cyclohexanol with intensive stirring. The mixture is stirred for 0.5 h by maintaining the temperature in the mass at 50°C; it is cooled, and poured into 100 ml water; the solution obtained is brought with 25% aqueous ammonia to pH 9 and extracted (3 × 50 ml) with ethyl acetate. The extract is washed with 100 ml of a saturated solution of sodium chloride and dried over magnesium sulfate, evaporated, and the residue chromatographed on silica gel with diethyl ether as the eluent. Yield 0.82 g of compound IIIa and 1.64 g of compound IIa, mp 84-86° (86°C according to [2]).

Compounds **IIb ($C_9H_{10}N_2O$), IIIb ($C_9H_{12}N_2O$), V ($C_9H_{11}N_3O_3$), VIIa ($C_{12}H_{17}N_3O$)**, and **VIIb ($C_9H_{13}N_3O$)** are obtained in the same way.

2-Nitroso-3-isopropylaminoacetanilide (VIIIb, $C_{11}H_{15}N_3O_2$). A sample (0.9 g, 5 mmole) of nitrosamine VIIb is treated with 10 ml acetic anhydride. The mixture is stirred at room temperature for 2 h. The mixture is poured into 100 ml water and after 2 h extracted with ethyl acetate (3 × 50 ml). The ethyl acetate extract is washed with 100 ml saturated aqueous sodium chloride solution and dried over magnesium sulfate. The solvent is stripped off and the residue chromatographed on silica gel with diethyl ether as the eluent. Yield 0.84 g of compound VIIIb.

Compound **VIIIa ($C_{14}H_{19}N_3O_2$)** is obtained in the same way.

1,2-Diamino-3-cyclohexylaminobenzene (IX, $C_{12}H_{14}N_3$). A solution of 1.1 (5 mmole) of nitrosoamine VIIa in 100 ml methanol is treated with 0.1 ml hydrochloric acid in the presence of a catalyst (5% Pd on carbon). The mixture is hydrogenated in a hydrogenation apparatus at atmospheric pressure and room temperature until the absorption of hydrogen has stopped. The catalyst is filtered off, the filtrate is evaporated and 5 ml concentration hydrochloric acid is added to the residue. The precipitate is filtered off and dried. Yield 1.0 g of the hydrochloride of compound IX.

4-Isopropylamino-7-nitrobenzofurazan (XII, $C_9H_{10}N_4O_3$). A solution of 0.9 g (5 mmole) of compound XI in 10 ml concentration sulfuric acid is treated with 2 ml (28 mmole) isopropanol and the mixture heated on a boiling water bath for 1 h. The mixture is cooled and poured into 100 ml water, brought to pH 9 with an aqueus solution of 25% ammonia, and extracted with ethyl acetate (3 × 50 ml). The extract is washed with 100 ml of a saturated sodium chloride solution and dried over magnesium sulfate. The solvent is stripped off and the residue chromatographed on silica gel with chloroform as the eluent. Yield 0.5 g of compound XII.

4-tert-Butylaminobenzofurazan (X, $C_{10}H_{13}N_3O$). A solution of 0.7 g (5 mmole) of 4-aminobenzofurazan (VI) in 10 ml concentration sulfuric acid is treated with 1.0 ml (135 mmole) of tert-butanol. The mixture is stirred for 1 h at room temperature and poured into 100 ml of water. The alkalinity is adjusted to pH 9 with a 25% aqueous ammonia solution and extracted with chloroform (3 × 50 ml). The extract is washed with water and dried over magnesium sulfate. The solvent is stripped off and the residue chromatographed on silica gel with chloroform as the eluent. Yield 0.86 g of compound X.

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