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SYNTHESIS OF 5-HYDROXY-4-NITROSOBENZOTRIAZOLES AND 6-HYDROXY-7-NITROSOINDAZOLES AND THEIR SPLITTING INTO β-TRIAZOLYL- AND β-PYRAZOLYLACRYLIC ACIDS

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5-Hydroxy-4-nitrosobenzotriazoles and 6-hydroxy-7-nitrosoindazoles were synthesized. By the action of benzenesulfonyl chloride in an alkaline medium, only 5-hydroxy-4-nitroso-2-phenyl-benzotriazole and 1-methyl-6-hydroxy-7-nitrosoindazole split into 5-carboxyvinyl-2-phenyl-4-cyano-1,2,3-triazole- and β-(1-methyl-5-cyano-4-pyrazolyl)acrylic acid, respectively, while the fragmentation under electron impact proceeds by another scheme.

We have already shown that o-nitrosohydroxyarenes, which exist preferentially in the tautomeric form of o-quinone monooximes [1, 2], open the quinoid ring to form o-cyanocinnamic acids through the action of benzenesulfonyl chloride in an alkaline medium and on heating [3, 4]. The splitting of monooximes of isatins [5] proceeds in a similar way, and it was shown that the molecular ions of the latter also undergo a similar rearrangement in the mass spectrometer [6]. Therefore, in the present work, we studied the behavior of 1- and 2-methyl-6-hydroxy-7-nitrosoindazoles (I, II), 5-hydroxy-4-nitrosobenzotriazole (XIII) and 5-hydroxy-4-nitroso-2-phenyl-benzotriazole (XVII) both through the action of benzenesulfonyl chloride [7], and under electron impact.

Compounds I and II were synthesized by Scheme 1 from 6-nitroindazole (III), obtained by the method in [8].

In the mass spectrum of compound VIII an intense peak of molecular ion and the peak of the $[M-H]^+$ ion are observed, characteristic of 1-methylindazole [9]. In contrast, the molecular ion of hydroxyisoindazole IX is unstable and its primary decomposition involves a loss of a molecule of hydrocyanic acid (ion* 121), which then vigorously eliminates a molecule of CO (ion 93) or a methyl group (ion 106). This indicates a markedly lower aromatic-

*Here and below, the m/z values are given for the ion peaks.

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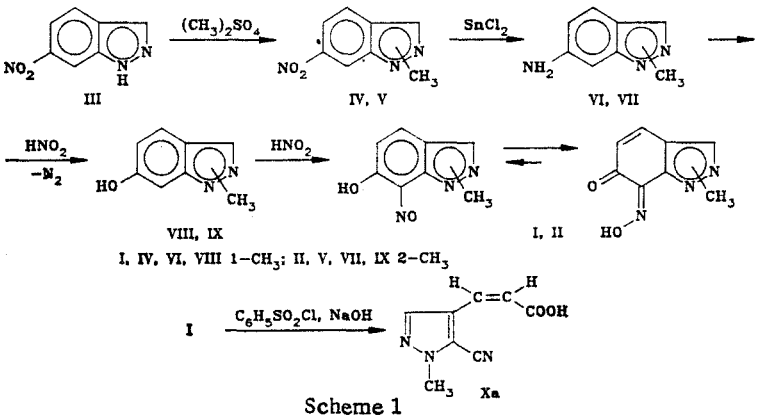
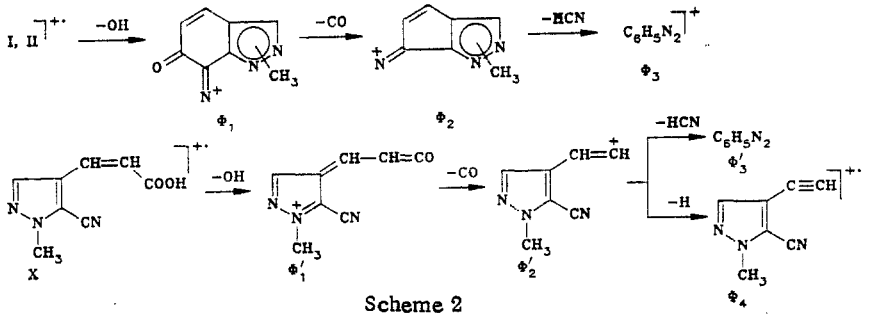


Scheme 1

ity of the hetero-ring, which agrees with structure IX. Similarly, in the UV spectrum of compound I with indazole structure, two long-wave maxima have a longer wave length than the same absorption bands in the spectrum of isoindazole II with a disturbed aromatic system.

When compounds I and II were heated in the presence of a benzene-sulfonyl chloride with a solution of sodium hydroxide, only a cis-acid Xa was obtained. In contrast to the isomeric hydroxynitroso compound, there are only two absorption maxima in the 228 and 276 nm region in the UV spectrum of acid Xa, and the long-wave absorption bands are missing. In its PMR spectrum, there are singlets of three methyl group protons (3.89), a singlet of the pyrazole proton 3-H (8.24) and two doublets of the olefinic protons at 5.93 and 6.68 ppm with SSCC 11 Hz. In the trans-acid Xb, obtained by heating the cis-isomer Xa in boiling pyridine, the PMR spectrum correspondingly consists of: 3.77; 8.17; 6.40; and 7.93 ppm with J = 16 Hz. Comparison of the mass spectrometric behavior of compounds I, II,and Xa, b (Table 3, Scheme 2), revealed three ions Φ_1, Φ_2, and Φ_3, common to their fragmentations.

However, the fragmentation of the molecular ion of acid X leads also to a characteristic ion Φ_4, which is virtually absent in the mass spectra of bicyclic structures I and II, so that we can state with confidence that, up to fragmentation, the molecular ions of these hydroxynitroso compounds do not rearrange into cyanic acid X.



Scheme 2

o-Hydroxynitroso compounds XIII and XVII were synthesized by scheme 3. In the PMR spectrum of compound XIII that we have prepared, there are two clear doublets of protons 6-H (6.23) and 7-H (7.75 ppm) with J = 10 Hz, besides the singlet of the NH proton (3.8). This confirms the entry of the nitroso group into the 4-position (an orbital control). The signals of the same protons in the PMR spectrum of the hydroxynitroso derivative XVII had chemical shifts of 6.47 and 7.85 ppm (J_{67} = 10 Hz). The analysis of the bond orders (the double bond character) in the molecule compound XVII, and also of its oximino-orthoquinoid tautomeric form XVIIa and benzenesulfonate XVIIa (XVIIb) shows that the weakest among them is the $C_{(4)}$-$C_{(3a)}$ bond (Table 5), while in the latter two compounds the $C_{(4)}$-$C_{(5)}$ bond is the most labile. In fact, when the hydroxynitroso derivative XVII is heated in the presence of benzenesulfonyl chloride with an aqueous solution of sodium hydroxide, the cis-acid XVIIIa was obtained in high yield.

Its UV spectrum differs sharply from the spectrum of the isomeric compound XVII, while in the PMR spectrum there are (besides the signals of five phenyl ring protons) two clear doublets of olefinic protons at 6.40 and 6.95 ppm with J = 12 Hz. When acid XVIIIa was

TABLE 1. Characteristics of Compounds XI-XVIII

Compound	mp, °C	R_f*1	UV spectrum, λ_{max}, nm (log ε)	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
XI	141—142	—	—	58,2	5,0	20,1	$C_{10}H_{11}N_3O_2$	58,5	5,4	20,5	98
XII	227—228	0,62 (A)	288 (3,8)	53,1	3,5	30,9	$C_6H_5N_3O$	53,3	3,7	31,1	93
XIII	>300 (dec.)	—	230 (4,1), 286 (3,7), 404 (3,5)	43,7	2,3	33,9	$C_6H_4N_4O_2$	43,9	2,4	34,2	85
XIV*2	174—175 (175 [14])	0,78 (B)	266 (4,3), 330 (4,4)	—	—	—	—	—	—	—	50
XV	181—182	0,62 (B)	240 (4,3), 314 (4,2), 360 (4,1)	68,2	4,6	26,4	$C_{12}H_{10}N_4$	68,6	4,8	26,7	85
XVI*3	173—175	0,49 (A)	242 (4,2), 328 (4,3)	67,9	4,0	19,7	$C_{12}H_9N_3O$	68,2	4,3	19,9	76
XVII	176—178 (dec.)	0,37 (C)	286 (4,4), 390 (3,4)*4	59,8	3,2	23,5	$C_{12}H_8N_4O_2$	60,0	3,3	23,3	96
XVIIIa	156—158	0,53 (A)	288 (4,3)	59,6	3,1	23,5	$C_{12}H_8N_4O_2$	60,0	3,3	23,3	75
XVIIIb	181—182	0,36 (A)	296 (4,3)	59,6	3,1	23,1	$C_{12}H_8N_4O_2$	60,0	3,3	23,3	62

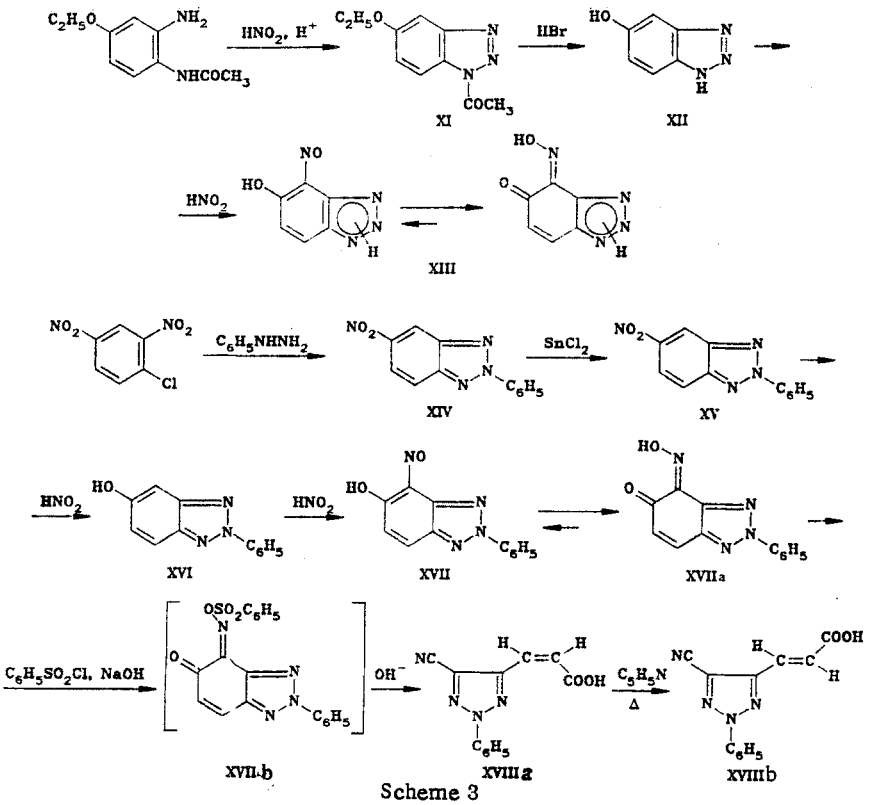
*1System A: ethanol — 12% aqueous ammonia, 4:1; B — benzene-ethanol, 30:1; C — acetone — 12% ammonia, 20:3.
*2PMR spectrum: 3.74 (1H, s, NH), 6.84 (1H, d, 4-H, J_{46} = 2 Hz); 7.0 ppm (1H, d.d, 6-H, J_{67} = 10, J_{64} = 2 Hz) 7.77 ppm (1H, d, 7-H, J_{76} = 10 Hz).
*3PMR spectrum: 7.15 (1H, d, 4-H, J_{46} = 2 Hz); 7.06 (1H, d.d, 6-H, J_{67} = 10, J_{64} = 2 Hz); 7.83 (1H, d, 7-H, J_{76} = 10 Hz); 7.4-7.6 and 8.1-8.3 ppm (5H, m, C_6H_5).
*4In ethanol solution of KOH: 228 (4.2), 258 (4.0), 324 (4.4), 418 nm (4.1).

boiled for 30 min in dry pyridine, it was converted into the trans-isomer XVIIIb (6.74 and 7.37 ppm, J = 16 Hz). In the mass spectra of compounds XIII, XVII, XVIIIa, b (Table 2), intense peaks of molecular ions are observed. The character of their further fragmentation in the case of compounds XIII and XVII differs sharply from the paths of the fragmentation of unsaturated acids in a mass spectrometer. While in the mass spectra of the first two compounds the peaks of the fragmentary ions $[M-OH]^+$ are most intense (Table 4), and the further elimination of the CO molecule is less probable (especially in the case of compound XVII), in the mass spectra of the unsaturated acids the most intense peaks are those of the $[M-CO_2H]^+$ ions, and the stability of the $[M-OH]^+$ ions is extremely low. It can thus be asserted that, up to fragmentation, the molecular ion of the hydroxy-nitroso compound XVII does not undergo a rearrangement into the $M^{+\cdot}$ ion of the acid. All our attempts to split compound XIII into the triazole derivative were unsuccessful.

TABLE 2. Mass Spectra* of Compounds I-V, VIII-Xa, b, XIII, XVII, XVIIIa, b

Compound	m/z values (relative intensity, %)
I	177 (100), 160 (98), 149 (11), 132 (86), 120 (11), 119 (15), 105 (15), 92 (17), 91 (15), 79 (11), 78 (17), 77 (12), 76 (14), 65 (30), 64 (25), 51 (20); W_M 14,8
II	177 (93), 160 (100), 132 (41), 106 (10), 105 (16), 92 (10), 78 (15), 65 (10), 64 (12), 51 (13); W_M 19,6
III	163 (100), 133 (11), 117 (37), 105 (13), 90 (82), 63 (36), 57 (19); W_M 33,5
IV	177 (100), 131 (33), 116 (20), 104 (21), 90 (19), 77 (10), 63 (24); W_M 41,0
V	177 (100), 131 (36), 119 (14), 104 (15), 90 (29), 77 (27), 63 (15), 148 (100), 147 (58), 120 (16), 119 (10), 91 (90), 65 (15); W_M 38,8
VIII	148 (100), 147 (58), 120 (16), 119 (10), 91 (10), 65 (15); W_M 41,0
IX	148 (11), 121 (31), 106 (32), 105 (19), 93 (100), 79 (12), 65 (12), 57 (11); W_M 5,0
Xa	177 (100), 160 (74), 132 (61), 131 (39), 105 (11), 78 (12), 67 (17), 66 (11), 64 (19), 51 (11); W_M 19,3
Xb	177 (100), 160 (40), 132 (34), 131 (23), 67 (10), 64 (11); W_M 26,0
XIII	164 (100) M, 147 (76), 136 (36), 119 (47), 91 (43), 79 (16), 77 (14), 67 (11), 65 (19), 52 (48), 51 (50); W_M 14,1
XVII	240 (83) M, 223 (100), 140 (21), 115 (10), 91 (14), 77 (67), 64 (20), 51 (28); W_M 17,7
XVIIIa	240 (75) M, 195 (46), 118 (11), 91 (100), 78 (59), 77 (51), 64 (32), 63 (11), 52 (17), 51 (31), 50 (13); W_M 13,3
XVIIIb	240 (76), 195 (46), 118 (11), 91 (100), 77 (37), 64 (29), 63 (10), 51 (20); W_M 16,2

*Ion peaks with an intensity ≥10% are given.



Scheme 3

TABLE 3. Peak Intensities of Characteristic Ions in Mass Spectra of Compounds I, II, X ($\%\Sigma_{30}$)

Compound	W_M	Φ_1	Φ_2	Φ_3	Φ_4
I	14,8	14,6	12,1	0,8	0,4
II	19,6	20,8	8,8	1,9	0,4
X	19,3	13,5	11,3	1,1	6,5

TABLE 4. Peak Intensities of Characteristic Ions in Mass Spectra of Compounds XIII, XVII, XVIIIa, b ($\%\Sigma_{30}$)

Compound	W_M	$[M-OH]^+$	$[M-OH-CO]^+$	$C_6H_5N^+$, m/z 91	$C_6H_5^+$, m/z 77
XIII	14,1	10,7*	6,5	6,1	2,1
XVII	17,7	21,8	0,8	2,5	12,2
XVIIIa	13,3	0,6	7,0	15,2	7,7
XVIIIb	16,2	0,9	8,4	15,7	6,9

*In addition, there is also a $[M-N_2]^{+\cdot}$ ion (5.0).

EXPERIMENTAL

The UV spectra were recorded on a SF-16 spectrophotometer in 95% ethanol, and the PMR spectra in DMSO on a Hitachi Perkin-Elmer spectrometer (90 MHz), using HMDS as internal standard. The mass spectra were recorded on Varian MAT-212 and 111 mass spectrometers, with a direct introduction of the material into the ionic source, and at ionization energies of 70 and 80 eV, respectively. The individual state and the purity of the compounds obtained was controlled by TLC on Al_2O_3, grade II of activity. The spots were developed in iodine vapors.

The quantum-chemical calculation was carried out by the CNDO/2 method according to a program in [10], using model geometrical structures, calibrated for the reproduction of UV spectra, tautomeric equilibria and dipole moments of the 1H- and 2H-benzotriazoles.

TABLE 5. Quantum-Chemical Parameters of Benzotriazole Derivatives ($\times 10^3$)*

Compound	atom	$-q_i$	$\rho_{i,HOMO}$	$-S^E_{i,HOMO}$	$-S_i^E$	$W_{3a,4}$	$W_{4,5}$	$W_{5,6}$	$W_{6,7}$	$W_{7,7a}$
XVII	4	−63	123	13	223					
	5	−216	189	20	199					
	6	22	6	1	230	**1194**	1430	1301	1568	1235
	7	32	117	12	222					
XVIIa	4	−171	4	0	198					
	5	−299	6	1	184					
	6	23	221	24	234	1069	**1044**	1165	1704	1136
	7	−48	48	5	217					
XVIIb	4	−202	1	0	196					
	5	−302	4	0	184					
	6	23	225	24	235	1077	**1036**	1163	1705	1134
	7	48	50	6	219					

*q_i – charge on atom; $\rho_{i,HOMO}$ – atomic population; $S^E_{i,HOMO}$ – atomic electrophilic superdelocalization; S_i^E – total electrophilic superdelocalization; W – bonding index.

The starting 6-nitroindazole (III) was obtained by the method [8], mp 182-183°C (from water) (according to the data in [8], mp 181,°C), R_f 0.67 (benzene-ethanol), 6:1). UV spectrum, λ_{max} (log ε): 250 (4.16), 286 nm (3.99). PMR spectrum: 8.24 (s, 3-H); 8.39 (d, 7-H, J_{15} = 1.5 Hz); 7.96 (q, 5-H, J_{57} = 1.5, J_{54} = 10 Hz); 7.86 (d, 4-H, J_{45} = 10 Hz); 3.5 ppm (br. s, NH).

1-Methyl-6-nitro- (IV) and 2-Methyl-6-nitroindazole (V). Dimethyl sulfate (56 g, 450 mmoles) is added in portions, with vigorous stirring, to a warm solution of 65.2 g (400 mmoles) of indazole III in 1 liter of water containing 24 g (600 mmoles) of NaOH. The mixture is stirred for another 15-20 min, and then is cooled, the precipitate is filtered, washed with water, and dried to yield 65 g (92%) of a mixture of indazoles IV and V. After recrystallization of this mixture from benzene, 30 g (43%) of compound V are obtained, mp 161.5-162.5°C (according to the data in [12]. mp 159°C), R_f 0.74 (benzene-ethanol, 15:1). UV spectrum, λ_{max} (log ε): 264 (4.32), 350 nm (3.40). Evaporation of the benzene filtrate gave 30 g (43%) of crude nitroindazole IV. After successive recrystallizations from a minimal amount of benzene and from a benzene–carbon tetrachloride mixture (1:1), a chromatographically pure compound IV is obtained, mp 125-126°C (according to the data in [12], mp 107-109°C, according to the data in [13], 122°C). R_f 0.86 (benzene-ethanol, 15:1), UV spectrum, λ_{max} (log ε): 454 (4.19), 390 (4.00), 346 nm (3.49).

1-Methyl-6-aminoindazole (VI). Nitroindazole IV 8.85 g (50 mmoles) is added in portions to a hot solution of 50 g (260 mmoles) of $SnCl_2$, in such a way that the mixture does not boil too vigorously. The mixture is cooled, the precipitate is separated, dissolved in 150 ml of hot water, and the solution is poured with stirring, into a hot solution of 25 g of NaOH in 350 ml of water. The mixture is boiled for 5-10 min, and filtered hot. The filtrate is cooled, the precipitate is filtered, washed with cold water, and dried. Yield, 57 g (78%), mp 173-174°C (from water). R_f 0.56 (benzene–ethanol, 6:1). UV spectrum, λ_{max} (log ε): 218 (4.42), 300 nm (3.86). Found: N 28.5%. $C_8H_9N_3$. Calculated: N 28.6%.

2-Methyl-6-aminoindazole (VII) is obtained in a similar way as VI from 53.1 g (300 mmoles) of nitroindazole V, 300 g (1.6 mole) of tin dichloride and 300 ml of concentrated HCl, to yield 35 g (79%) of aminoindazole VII, mp 157.5-158.5°C (from water). R_f 0.36 (benzene–ethanol, 6:1). UV spectrum, λ_{max} (log ε): 222 (4.40), 292 nm (3.84). Found: N 28.5%. $C_8H_9N_3$. Calculated: N 28.6%.

1-Methyl-6-hydroxyindazole (VIII). A solution of 2.76 g (40 mmoles) of sodium nitrite in 10 ml of water is added dropwise, with cooling (0-5°C) and stirring, to a solution of 5.88 g (40 mmoles) of the amino compound VI and 5 ml of concentrated H_2SO_4. A 3.5 g portion of boric acid and 5 ml of concentrated H_2SO_4 are added, the mixture is boiled for 10 min, then cooled, and an ammonia solution is added to a weakly alkaline reaction. The precipitate is separated, washed with cold water, and recrystallzied from water to yield 34 g (58%) of compound VIII, mp 221-222°C. R_f 0.63 (benzene-ethanol, 6:1). UV spectrum, λ_{max} (log ε): 214 (4.53), 288 nm (3.91). Found: N 19.0%. $C_8H_8N_2O$. Calculated: N 18.9%.

2-Methyl-6-hydroxyindazole (IX) is obtained in a similar way as VIII, from 5.88 g (40 mmoles) of aminoindazole VII. After recrystallization from water, yield 1.2 g (20%), mp 175.5-176.5°C, R_f 0.58 (benzene-ethanol, 6:1). Found: N 18.9%. $C_8H_8N_2O$. Calculated: N 18.9%. UV spectrum, λ_{max} (log ε): 208 (4.54), 288 nm (4.08).

1-Methyl-6-hydroxy-7-nitrosoindazole (I). A 20-ml portion of a 17% hydrochloric is added dropwise and with stirring, at 0-5°C, to a solution of 7.4 g (50 mmoles) of the hydroxy-derivative VIII, 3 g (75 mmoles) of NaOH and 3.3 g (50 mmoles) of sodium nitrite in 75 ml of water. The mixture is held for another 35 min, and the dark-pink precipitate is filtered, washed with cold water, and dried. Yield 7.7g (80%), mp 159°C (from ethanol). R_f 0.63 (propanol—water—25% aqueous ammonia, 20:5:2.5). UV spectrum, λ_{max} (log ε): 264 (4.12), 354 (3.48), 428 nm (3.28). Found: N 23.8%. $C_8H_7N_3O_2$. Calculated: N 23.7%.

2-Methyl-6-hydroxy-7-nitrosoindazole (II). A solution of 0.35 g (5 mmoles) of sodium nitrite in 2 ml of water is added dropwise and with stirring, at 0-5°C to a solution of 0.74 g (5 mmoles) of the hydroxy compound IX in 0.6 ml of concentrated HCl and 5 ml of water. The yellow-greenish crystals are filtered, washed with 2 ml of ice water, and dried. Yield 0.75 g (85%), mp 157°C (from water). R_f 0.28 (propanol-water-25% aqueous ammonia, 20:5:2.5). UV spectrum, λ_{max} (log ε): 246 (4.30), 324 (3.43), 394 nm (3.40). Found: N 23.9%. $C_8H_7N_3O_2$. Calculated: N 23.7%.

1-Methyl-4-carboxyvinyl-5-cyanopyrazole (X). A solution of 0.44 g of NaOH in 4.5 ml of water is added in portions, with stirring, to a hot solution of 0.57 g (3 mmoles) of compound I and 0.8 g (4.5 mmoles) of benzenesulfonyl chloride. At the end of the addition, the mixture boils spontaneously. It is boiled for another 10-15 min and the solvent is evaporated. The residue is made alkaline with 5 ml of 5% sodium bicarbonate, the mixture is boiled with activated charcoal, and filtered. The cold filtrate is acidified by dilute hydrochloric acid to pH 4, the precipitate is filtered, washed with water, and dried. After recrystallization from water with activated charcoal, mp 178-179.5°C, R_f 0.46 (propanol—water—25% aqueous ammonia, 20:5:2.5). UV spectrum, λ_{max} (log ε): 228 (3.83), 280 nm (4.14). Found: N 24.0%. $C_8H_7N_3O_2$. Calculated: N 23.7%.

1-Acetyl-5-ethoxybenzotriazole (XI). A solution of sodium nitrite (3.9 g in 20 ml of water) is added dropwise, in the course of 20 min, with stirring and cooling by cold water, to a solution of 9.7 g (50 mmoles) of 3-amino-4-acetaminophenetole in dilute hydrochloric acid (11 ml of 35% hydrochloric acid and 150 ml of water). The precipitate that formed is separated, washed with cold water, and dried (see Table 1).

5-Hydroxybenzotriazole (XII). A solution of 8.2 g (40 mmoles) of compound XI in 25 ml of concentrated hydrobromic acid is boiled for 24 h. Then 10 ml of water are added, and the mixture is cooled and made alkaline by 25% ammonia solution to pH 8. After 3 h, the precipitate is separated, washed with water, and dried.

4-Nitroso-5-hydroxybenzotriazole (XIII). A solution of 0.7 g (10 mmoles) of sodium nitrite in 20 ml of water is added dropwise, with stirring and cooling (0°C), to a solution of 1.35 g (10 mmoles) of hydroxy compound XII in 4 ml of 35% hydrochloric acid and 150 ml of water. The mixture is stirred for 20 min, the yellow precipitate is filtered, washed with water, and dried.

2-Phenyl-5-nitrobenzotriazole (XIV). A solution of 20.2 g (100 mmoles) of 2,4-dinitrochlorobenzene, 14.7 g (100 mmoles) of sodium acetate and 21.6 g (200 mmoles) of phenylhydrazine in 200 ml of ethanol is boiled for 1 h. The mixture is cooled, the precipitate is separated, washed with ethanol, water, once again with ethanol, and dried.

2-Phenyl-5-aminobenzotriazole (XV). A hot solution of 12 g (50 mmoles) of the nitro derivative XIV in 60 ml of DMFA is added to portions to a hot solution of 50 g of tin dichloride in 50 ml of concentrated HCl. At the end of the exothermal reaction, the mixture is diluted with 150-200 ml of 15% hydrochloric acid, cooled, and the precipitate is separated, dissolved with stirring in 50 ml of DMFA, and 500 ml of hot 25% KOH solution are cautiously added. The mixture is cooled, the precipitate is separated, washed with cold water, and crystallized from propanol.

2-Phenyl-5-hydroxybenzotriazole (XVI). A solution of 3.5 g (50 mmoles) of sodium nitrite in 20 ml of concentrated H_2SO_4 is added to a solution of 10.5 g (50 mmoles) of amine XV in 40 ml of concentrated H_2SO_4. The mixture is stirred for 10-15 min, 40 g of ice and a few drops of isoamyl alcohol are added, and the mixture is heated until nitrogen ceases

to evolve. The mixture is cooled, diluted with cold water, the residue is separated, washed with water, dried, and recrystallized from toluene.

2-Phenyl-4-nitroso-5-hydroxybenzotriazole (XVII). A 2-ml portion of water is added to a solution of 2.11 g (10 mmoles) of the hydroxy compound XVI in 25 ml of glacial acetic acid. The mixture is cooled to 0-5°C, and a solution of 0.7 g (10 mmoles) of sodium nitrite in 5 ml of water is added dropwise. The mixture is stirred for 1 h, diluted with 35 ml of water, the precipitate is filtered, washed with water, and dried.

cis-2-Phenyl-4-cyano-5-carboxyvinyl-1,2,3-triazole (XVIII). A warm solution of 2.8 g (70 mmoles) of NaOH in 28 ml of water is added in portions, with stirring, to a boiling solution of 4.8 g (20 mmoles) of compound XVII and 3.1 ml (24 mmoles) of benzene-sulfonyl chloride in 150 ml of acetone. The mixture is boiled for another 5 min, acetone is evaporated, the aqueous solution is stirred with activated charcoal and filtered. The cold filtrate is acidified with dilute hydrochloric acid (pH $\sim$ 3), the precipitate is filtered, washed with cold water, and dried.

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