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Diphenylmethyl and Tetrahydropyranyl Protecting Groups in the Synthesis of 3-Substituted 5-Amino- and 5-Hydrazino-1,2,4-triazoles

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Abstract — The use of hydrazine as reagent in nucleophilic substitution and reduction in the 1,2,4-triazole series in combination with introduction of labile protecting groups makes it possible to synthesize 5-hydrazino-3-nitro-1*H*-1,2,4-triazole and 3-chloro-5-hydrazino-1*H*-1,2,4-triazol-5-ylhydrazine which were difficultly accessible previously, as well as to extend the series of 3-substituted 5-amino-1*H*-1,2,4-triazoles.
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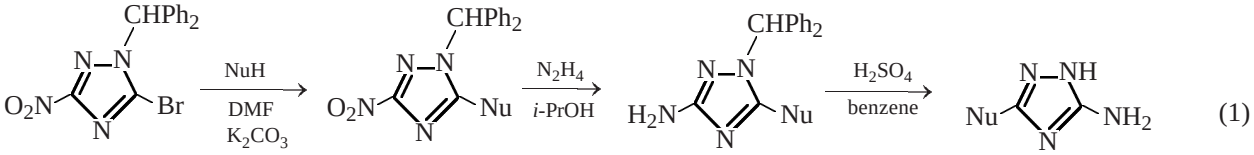
3-Substututed 5-amino-1*H*-1,2,4-triazoles (R = Alk, Ar) can be successfully synthesized via cyclization of acylated aminoguanidines. However, 5-amino-1,2,4-triazoles having a phenoxy, phenylsulfanyl, azolyl, or some other substituent in the 3-position can be prepared only from N-cyano iminocarbonates. In particular, 5-amino-3-phenoxy-1*H*-1,2,4-triazole was obtained in such a way [1, 2]. 5-Amino-3-phenylsulfanyl-1*H*-1,2,4-triazole was synthesized by arylation of 5-amino-2*H*-1,2,4-triazole-3(4*H*)-thione [3].

We now propose an alternative procedure for the synthesis of such compounds, which is based on nucleophilic replacement of the halogen atom in 5-halo-3-nitro-1,2,4-triazoles with preliminary protection of the N^1H group to avoid its deprotonation in basic medium (which sharply reduces the nucleophilicity of the substrate). This is achieved by introduction of a readily removable diphenylmethyl substituent and subsequent reduction and deprotection [scheme (1)].



(1)

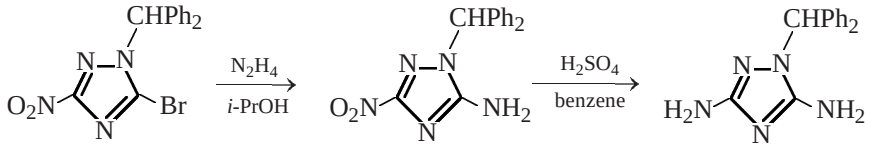
I **II–V** **VI–IX** **X–XIII**

II, VI, X, Nu = PhO; **III, VII, XI**, Nu = PhS; **IV, VIII, XII**, Nu = 1*H*-imidazol-1-yl; **V, IX, XIII**, Nu = 5-amino-1,2,4-triazol-1-yl.

The syntheses of a series of 1-diphenylmethyl-3-nitro-5-R-1,2,4-triazoles **II**–**V** were reported by us previously [4]. The nitro group therein is smoothly reduced with hydrazine hydrate in propan-2-ol to produce the corresponding amines without using Raney nickel catalyst. In this case, removal of the diphenylmethyl protecting group by treatment with 96% sulfuric acid in benzene [4] is quite admissible.

It seems obvious that the bromine atom in 5-bromo-1-diphenylmethyl-3-nitro-1*H*-1,2,4-triazole (**I**) can be replaced in a selective fashion by hydrazine and that the subsequent deprotection of the N^1 atom could produce 5-hydrazino-3-nitro-1*H*-1,2,4-triazole. However, when the reaction was carried out in propan-2-ol with excess 98% hydrazine hydrate (2.5 h under reflux), we isolated 5-amino-1-diphenylmethyl-3-

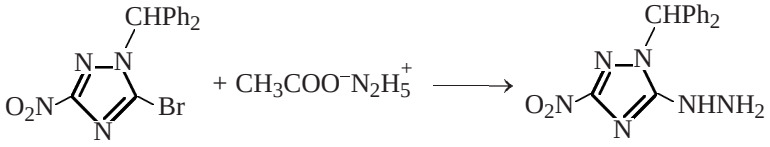
nitro-1*H*-1,2,4-triazole (**XIV**), and increase in the reaction time to 6 h resulted in the formation of 3,5-diamino-1-diphenylmethyl-1*H*-1,2,4-triazole (**XV**) [scheme (2)].



I **XIV** **XV** (2)

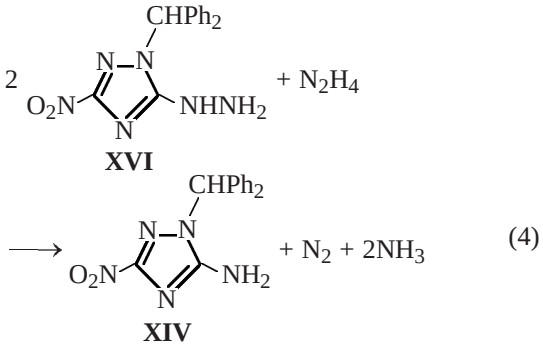
Analogous result was obtained in the reaction of 1-diphenylmethyl-5-methylsulfonyl-3-nitro-1*H*-1,2,4-triazole with excess hydrazine hydrate at room temperature in a shorter time.

The ability of hydrazine to act not only as nucleophile but also as reducing agent became apparent while attempting to perform nucleophilic substitution in 1,2,4-triazoles having reducible groups. As shown in [5], the reaction of 4-amino-3,5-bis(methylsulfanyl)-4*H*-1,2,4-triazole with hydrazine hydrate leads to 4-amino-5-methylsulfanyl-2*H*-1,2,4-triazole-3(4*H*)-thione; 1-methyl-3,5-dinitro-1*H*-1,2,4-triazole reacted with hydrazine [6] to give a mixture of the expected substitution product (1-methyl-3-nitro-1*H*-1,2,4-triazol-5-ylhydrazine, 70%) and minor reduction product (5-amino-1-methyl-3-nitro-1*H*-1,2,4-triazole, 30%). We succeeded in partially lowering the contribution of the redox reaction by (1) converting hydrazine into hydrazinium acetate (whose ability to transfer an electron is much weaker) and (2) using a smaller excess of the reagent (molar ratio hydrazine–substrate 3 : 1). Under these conditions we obtained the desired 1-diphenylmethyl-3-nitro-1,2,4-triazol-5-ylhydrazine (**XVI**) [scheme (3)].



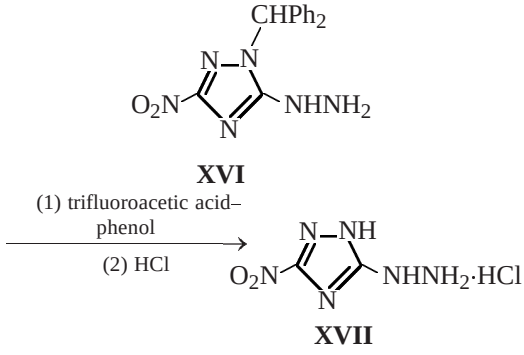
I **XVI** (3)

The result of the reaction of compound **XVI** with hydrazine hydrate confirmed the assumption that the hydrazino group in 1,2,4-triazoles having electron-withdrawing substituents can be reduced to amino group with excess hydrazine [scheme (4)].



(4)

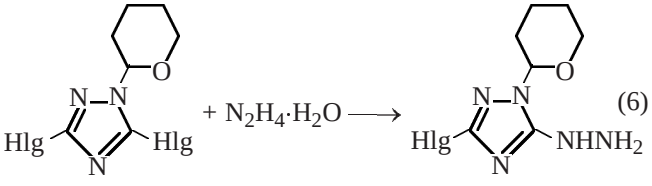
Removal of the diphenylmethyl protecting group from compound **XVI** can be performed in the system sulfuric acid–benzene, but treatment with trifluoroacetic acid in the presence of phenol is more advantageous due to smaller loss of the product during isolation [scheme (5)].



(5)

Obviously, the ability of 1,2,4-triazole heteroring to capture an electron from hydrazine molecule and

hence the probability of redox reaction should decrease when less electron-withdrawing substituents are present in the 1,2,4-triazole ring. 3,5-Dichloro-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazole (**XVIII**) and 3,5-dibromo-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazole (**XIX**) were synthesized by reaction of the corresponding dihalotriazoles with 3,4-dihydro-2*H*-pyran [8]. Compounds **XVIII** and **XIX** reacted with excess hydrazine hydrate in ethanol at 95–100°C, following exclusively the nucleophilic halogen replacement path [scheme (6)].

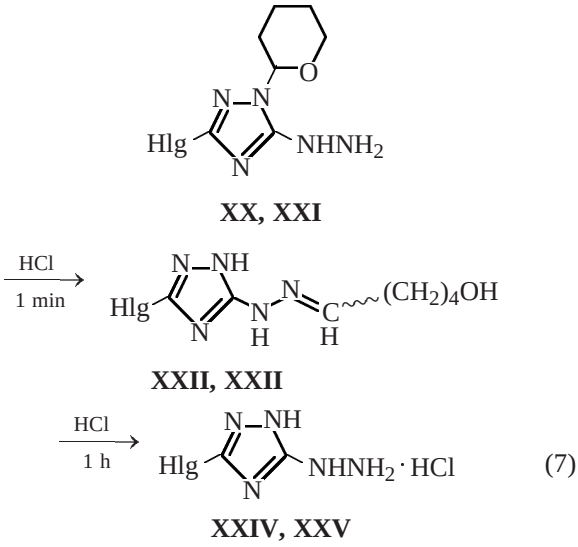


(6)

XVIII, XIX **XX, XXI**

XVIII, XX, Hlg = Cl; **XIX, XXI**, Hlg = Br.

Elimination of the tetrahydropyranyl group from molecules **XX** and **XXI** required more severe conditions (heating in an acidic aqueous solution at the boiling point for 1 h) than those reported in [7]. Presumably, hydrolysis of the tetrahydropyran ring is accompanied by formation of Schiff bases **XXII** and **XXIII** via reaction at the hydrazino group. This reaction occurs within 1–2 min after dissolution of compounds **XX** and **XXI** in a hot 20% aqueous solution of hydrochloric acid; Schiff bases **XXII** and **XXIII** separate from the mixture, and they can be isolated in almost quantitative yield. Prolonged heating leads initially to dissolution of **XXII** and **XXIII**, and (after heating for 1 h), hydrazino derivatives **XXIV** and **XXV** precipitate as the corresponding hydrochlorides [scheme (7)].



(7)

XX, XXII, XXIV, Hlg = Cl; **XXI, XXIII, XXV**, Hlg = Br.

The yields, melting points, and elemental analyses of compounds **VI**–**XXV** are given in Table 1. The structure of compounds **XVII**, **XXIV**, and **XXV** was confirmed by the ^{13}C NMR spectra, the other products were characterized by ^{1}H NMR spectroscopy (Table 2). The mass spectra of **VII**, **XIV**–**XVII**, **XXI**, and **XXIII**–**XXV** are presented in Table 3.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM-200 instrument (200 MHz) using DMSO-d_6 as solvent. The ^{13}C NMR spectra were measured on a Bruker DPX-300 spectrometer at 75 MHz from solutions in D_2O. The progress of reactions was monitored by TLC on Silufol UV-254 plates (carbon tetrachloride–propan-2-ol, 4:1; detection under UV light).

Table 1. Yields, melting points, and elemental analyses of substituted triazoles **VI**–**XXV**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VI	72.0	169	73.69	4.92	16.24	$C_{21}H_{18}N_4O$ (342.4)	73.67	5.30	16.36
VII	89.1	123	71.06	4.96	15.73	$C_{21}H_{18}N_4S$ (358.5)	70.36	5.06	15.63
VIII	68.2	199	68.15	5.13	25.83	$C_{18}H_{16}N_6$ (316.4)	68.34	5.10	26.56
IX	58.6	205	61.14	5.02	34.12	$C_{17}H_{16}N_8$ (332.4)	61.43	4.85	33.71
X	58.4	120	55.18	4.21	31.17	$C_8H_8N_4O$ (176.2)	54.54	4.58	31.80
XI	60.3	145	50.09	4.43	28.64	$C_8H_8N_4S$ (192.2)	49.98	4.19	29.14
XII	58.5	263	39.35	4.20	55.14	$C_5H_6N_6$ (150.1)	40.00	4.03	55.97
XIII	79.2	281	29.12	4.09	66.86	$C_4H_6N_8$ (166.1)	28.92	3.64	67.44
XIV	74.5, 80.1, 95.1 [a]	210	61.16	4.79	23.50	$C_{15}H_{13}N_5O_2$ (295.3)	61.01	4.44	23.72
XV	63.4	195	68.35	5.36	26.78	$C_{15}H_{15}N_5$ (265.3)	67.90	5.70	26.40

Table 1. (Contd.)

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
XVI	40.6	191	57.76	4.37	26.85	$C_{15}H_{14}N_6O_2$ (310.3)	58.06	4.55	27.08
XVII	36.6	215	13.08	3.34	46.38	$C_2H_5ClN_6O_2$ (180.6)	13.30	2.79	46.55
XVIII	77.6	80	38.41	4.23	19.05	$C_7H_9Cl_2N_3O$ (222.1)	37.86	4.08	18.92
XIX	81.3	117	27.22	2.83	13.29	$C_7H_9Br_2N_3O$ (311.0)	27.04	2.92	13.51
XX	72.6	125	38.52	5.43	32.11	$C_7H_{12}ClN_5O$ (217.7)	38.36	5.56	32.18
XXI	95.6	110	31.71	5.84	26.82	$C_7H_{12}BrN_5O$ (262.1)	32.08	4.61	26.72
XXII	92.4	184	39.24	5.45	32.03	$C_7H_{12}ClN_5O$ (217.7)	38.63	5.56	32.18
XXIII	94.2	185	31.83	5.08	26.83	$C_7H_{12}BrN_5O$ (262.1)	32.08	4.61	26.72
XXIV	35.3	215	14.49	2.75	40.90	$C_2H_5Cl_2N_5$ (170)	14.13	2.96	41.20
XXV	40.5	226	10.80	2.07	33.27	$C_2H_5BrClN_5$ (214.5)	11.20	2.35	32.66

[a] Methods *a*, *b*, and *c*, respectively.

Table 2. ^{1}H NMR spectra of substituted triazoles **VI**–**XVI** and **XVIII**–**XXIII** and ^{13}C NMR spectra of triazoles **XVII** and **XVI**–**XXV** [a]

Comp. no.	δ, δ_C, ppm
VI	5.23 s (2H), 6.62 s (1H), 7.19–7.42 m (15H)
VII	4.20 s (2H), 6.87 s (1H), 7.09–7.43 m (15H)
VIII	5.54 s (2H), 6.42 s (1H), 7.10 s (1H), 7.17–7.46 m (11H), 7.83 s (1H)
IX	5.46 s (2H), 7.17–7.47 m (12H), 7.61 s (1H), 7.81 s (1H)
X	5.96 s (2H), 7.01–7.17 m (3H), 7.24–7.38 m (2H), 11.34 s (1H)
XI	6.01 s (2H), 7.19–7.38 m (5H), 12.09 s (1H)
XII	6.24 s (2H), 6.97 s (1H), 7.47 s (1H), 8.01 s (1H), 11.90 s (1H)
XIII	6.22 s (2H), 6.96 s (2H), 7.36 s (1H), 11.97 s (1H)
XIV	6.96 s (1H), 7.21–7.44 m (12H)
XV	6.21 s (2H), 6.52 s (1H), 7.14–7.42 m (12H)
XVI	4.42 m (2H), 7.02 s (1H), 7.21–7.43 m (10H), 8.37 s (1H)
XVII	155.93, 160.27
XVIII	1.53–2.25 m (6H), 3.61–3.75 m (1H), 3.86–3.98 m (1H), 5.49–5.60 m (1H)
XIX	1.53–2.23 m (6H), 3.61–3.73 m (1H), 3.87–3.98 m (1H), 5.46–5.56 m (1H)
XX	1.49–2.16 m (6H), 3.58–3.71 m (1H), 3.84–3.94 m (1H), 4.03–4.49 m (2H), 5.23–5.34 m (1H), 7.92–8.14 m (1H)
XXI	1.36–2.09 m (6H), 3.50–3.65 m (1H), 3.75–3.87 m (1H), 4.16–4.66 m (2H), 5.22–5.37 m (1H), 7.88–8.22 m (1H)
XXII	Isomer mixture (ratio 1 : 4.3): 1.37–1.51 m (4H), 2.13–2.31 m (2H), 3.32–3.51 m (2H), 4.03–4.42 m (1H), 6.58 s (1H), 10.43 s (1H), 12.91 s (1H) and 1.37–1.51 m (4H), 2.13–2.31 m (2H), 3.32–3.51 m (2H), 4.03–4.42 m (1H), 7.26 s (1H), 10.82 s (1H), 12.75 s (1H)
XXIII	Isomer mixture (1 : 4.5): 1.38–1.55 m (4H), 2.14–2.29 m (2H), 3.37–3.57 m (2H), 4.03–4.72 m (1H), 6.59 s (1H), 10.49 s (1H), 13.16 s (1H) and 1.38–1.55 m (4H), 2.14–2.29 m (2H), 3.37–3.57 m (2H), 4.03–4.72 m (1H), 7.28 s (1H), 10.91 s (1H), 12.99 s (1H)
XXIV	146.275, 158.037
XXV	131.858, 159.107

[a] The spectra of **VI**–**XVI** and **XVIII**–**XXIII** were recorded in DMSO-d_6, and those of **XVII, XVI**, and **XXV**, in D_2O.

Table 3. Mass spectra of substituted triazoles **VII, XIV**–**XVII, XXI**, and **XXIII**–**XXV**

Comp. no.	m/z (I_{rel}, %)
VII	358 [M^+] (18), 167 (100), 152 (20), 136 (4), 121 (3), 109 (8), 77 (13)
XIX	295 [M^+] (2), 167 (100), 152 (17), 115 (4), 77 (5), 45 (5)
XV	265 [M^+] (10), 250 (2), 167 (100), 152 (20), 128 (2), 77 (5), 43 (14)
XVI	310 [M^+] (2), 263 (5), 233 (5), 167 (100), 152 (24), 139 (5), 115 (7), 77 (12), 53 (21)
XVII	144 [M^+] (36), 127 (58), 114 (1), 98 (11), 68 (36), 53 (40), 36 (100)
XXI	261 [M^+] (18), 214 (5), 179 (80), 106 (6), 85 (95), 67 (40), 57 (55), 41 (100)
XXIII	263 [M^+] (7), 216 (5), 205 (7), 190 (11), 177 (12), 162 (30), 148 (9), 100 (30), 85 (100), 67 (22), 53 (85), 41 (93)
XXIV	133 [M^+] (78), 117 (7), 103 (10), 88 (29), 76 (10), 68 (20), 62 (59), 53 (78), 43 (85), 36 (100)
XXV	177 [M^+] (25), 161 (2), 147 (2), 133 (9), 106 (25), 93 (3), 81 (12), 68 (40), 53 (80), 43 (85), 36 (100)

Compounds **XVIII** and **XIX** were synthesized according to the procedure described in [7]. The data for compounds **X**, **XI**, **XVIII**, and **XXIV** were in agreement with those given in [1–3, 8, 9].

1-Diphenylmethyl-5-phenoxy-1*H*-1,2,4-triazol-5-amine (VI). A solution of 1.58 g of triazole **II** and 20 ml of 98% hydrazine hydrate in 50 ml of propan-2-ol was heated for 1 h under reflux. The mixture was cooled and poured into 200 ml of water, and the precipitate was filtered off and recrystallized from ethanol.

1-Diphenylmethyl-5-phenylsulfanyl-1*H*-1,2,4-triazol-5-amine (VII). A solution of 1.44 g of triazole **III** and 20 ml of 98% hydrazine hydrate in 50 ml of propan-2-ol was heated for 2 h under reflux. The product was isolated and purified as described above for compound **VI**.

5-(1*H*-Imidazol-1-yl)-1-diphenylmethyl-1*H*-1,2,4-triazol-3-amine (VIII) was synthesized from 1.14 g of triazole **IV** and 15 ml of 98% hydrazine hydrate in 40 ml of propan-2-ol as described above for compound **VI**. After heating, the mixture was evaporated to dryness on a rotary evaporator under reduced pressure, and the residue was recrystallized from ethanol.

5-(5-Amino-1*H*-1,2,4-triazol-1-yl)-1-diphenylmethyl-1*H*-1,2,4-triazol-3-amine (IX) was synthesized from 1.72 g of triazole **V** and 25 ml of 98% hydrazine hydrate in 50 ml of propan-2-ol as described above for compound **VI**; reaction time 4 h. When the reaction was complete, the solvent was distilled off to dryness under reduced pressure on a rotary evaporator, and the residue was recrystallized from aqueous ethanol (1 : 1).

3-Phenoxy-1*H*-1,2,4-triazol-5-amine (X). A mixture of 0.38 g of compound **VI**, 15 ml of benzene, and 3 ml of 96% sulfuric acid was vigorously stirred for 12 h at 20°C. During that time, the organic phase was replaced twice (a solution of diphenylmethanol in benzene was separated by decanting, and a fresh portion of benzene was added). When the reaction was complete, the organic layer was separated, and the residue was poured into 20 ml of water on cooling. The mixture was neutralized with an aqueous solution of potassium hydroxide and extracted with ethyl acetate (4 × 25 ml). The extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was recrystallized from aqueous ethanol (1 : 1).

3-Phenylsulfanyl-1*H*-1,2,4-triazol-5-amine (XI) was obtained from 0.68 g of triazole **VII** using 20 ml of benzene and 4 ml of 96% sulfuric acid according to the procedure described above for compound **X**.

3-(1*H*-Imidazol-1-yl)-1*H*-1,2,4-triazol-5-amine (XII) was synthesized from 0.55 g of triazole **VIII** using 20 ml of benzene and 4 ml of 96% sulfuric acid, following the procedure described above for compound **X**. The reaction time was 14 h, and the benzene layer was replaced four times. When the reaction was complete, the organic layer was separated, the residue was diluted with 10 ml of water on cooling and neutralized with aqueous potassium hydroxide. The mixture was poured onto a Petri dish and allowed to evaporate to dryness on exposure to air. The dry residue was extracted with propan-2-ol in a Soxhlet apparatus. The extract was evaporated, and the residue was recrystallized from ethanol.

3-(5-Amino-1*H*-1,2,4-triazol-1-yl)-1*H*-1,2,4-triazol-5-amine (XIII) was obtained from 0.715 g of triazole **IX** using 20 ml of benzene and 5 ml of 96% sulfuric acid. The procedure was the same as described above for the synthesis of compound **XII**. The product was recrystallized from water.

1-Diphenylmethyl-3-nitro-1*H*-1,2,4-triazol-5-amine (XIV). *a*. A solution of 4 g of compound **I** and

10 ml of 98% hydrazine hydrate in 60 ml of propan-2-ol was heated for 2.5 h under reflux. After cooling, the precipitate was filtered off and recrystallized from ethanol.

b. A mixture of 0.36 g of 1-diphenylmethyl-5-methylsulfonyl-3-nitro-1,2,4-triazole [4], 5 ml of 98% hydrazine hydrate, and 18 ml of propan-2-ol was stirred for 3 h at 18–20°C.

c. Compound **XVI**, 0.1 g, was dissolved in 12 ml of ethanol, 0.6 ml of 98% hydrazine hydrate was added, and the mixture was kept for 60 h at 20°C and evaporated to dryness. The residue was recrystallized from ethanol.

1-Diphenylmethyl-1*H*-1,2,4-triazole-3,5-diamine (XV). A mixture of 4 g of compound **I** and 10 ml of 98% hydrazine hydrate in 60 ml of propan-2-ol was heated for 6 h under reflux. It was then cooled and poured into 150 ml of water, and the precipitate was filtered off and recrystallized from aqueous ethanol (1 : 1).

1-(1-Diphenylmethyl-3-nitro-1*H*-1,2,4-triazol-5-yl)hydrazine (XVI). Hydrazinium acetate, 7.5 g, was added to a solution of 10 g of triazole **I** in 150 ml of propan-2-ol, and the mixture was heated for 3 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed with water, and recrystallized twice from methanol.

3-Nitro-1*H*-1,2,4-triazol-5-ylhydrazine (XVII). *a*. A mixture of 0.85 g of compound **XVI**, 0.51 g of phenol, and 15 ml of trifluoroacetic acid was heated for 3 h at 60–65°C. It was then evaporated to dryness, the residue was kept for 20 h in a vacuum desiccator and dissolved in 50 ml of benzene, and the solution was extracted into 20% hydrochloric acid (2×10 ml). The acid solution was concentrated until crystals of **XVII** hydrochloride separated. The product was filtered off and dried in air.

b. Compound **XVI**, 0.85 g, was treated with 3 ml of 96% sulfuric acid in 80 ml of benzene as described above for triazole **XII**. The benzene layer was separated, and 5–10 ml of ethanol was added dropwise to the solution of compound **XVII** in sulfuric acid on cooling to –5 to 0°C until **XVII** sulfate separated. The product was filtered off, washed in succession with diethyl ether and ethanol, dried in a vacuum desiccator, and recrystallized from 1,4-dioxane.

3,5-Dichloro-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazole (XVIII). 3,4-Dihydro-2*H*-pyran, 15 g, was added over a period of 1 h to a solution of 10 g of 3,5-dichloro-1,2,4-triazole and 0.2 g of *p*-toluenesulfonic acid in 100 ml of ethyl acetate, heated to 50°C. The mixture was heated to the boiling point and was maintained boiling for 2 h. It was then cooled, diluted with 50 ml of ethyl acetate, washed with 50 ml of a 5% aqueous solution of sodium hydrogen carbonate, and evaporated. The product was recrystallized twice from propan-2-ol.

3,5-Dibromo-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazole (XIX) was synthesized in a similar way from 17 g of 3,5-dibromo-1,2,4-triazole and 15 g of 3,4-dihydro-2*H*-pyran in 100 ml of ethyl acetate in the presence of 0.3 g of *p*-toluenesulfonic acid.

3-Chloro-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazol-5-ylhydrazine (XX). A mixture of 6.9 g of triazole **XIII** and 25 ml of 98% hydrazine hydrate in 150 ml of ethanol was heated for 3 h under reflux. The mixture was evaporated to dryness, and the residue was recrystallized from toluene.

3-Bromo-1-(tetrahydropyran-2-yl)-1*H*-1,2,4-triazol-5-ylhydrazine (XXI) was synthesized in a similar way from 15 g of compound **XIX** and 30 ml of 98% hydrazine hydrate in 150 ml of ethanol. The product was purified by recrystallization from toluene.

1-(3-Chloro-1*H*-1,2,4-triazol-5-yl)-2-(5-hydroxypentylidene)hydrazine (XXII). Compound **XX**, 3 g, was dissolved in 10 ml of 20% hydrochloric acid on heating to 95–100°C. After 1–2 min, compound **XXII** separated. The mixture was cooled, and the precipitate was filtered off and recrystallized twice from water.

1-(3-Bromo-1*H*-1,2,4-triazol-5-yl)-2-(5-hydroxypentylidene)hydrazine (XXIII) was synthesized in a similar way from 3 g of compound **XXI**.

5-Chloro-1*H*-1,2,4-triazol-3-ylhydrazine hydrochloride (XXIV). A mixture of 3 g of compound **XX** and 75 ml of 10% hydrochloric acid was heated for 1 h at the boiling point in an open vessel. During that time, the volume of the mixture decreased to 30 ml. The mixture was cooled, and the precipitate was filtered off and recrystallized from 10% hydrochloric acid.

5-Bromo-1*H*-1,2,4-triazol-3-ylhydrazine hydrochloride (XXV) was synthesized in a similar way from 3 g of compound **XXI**.

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