Synthesis of New 1,2,3-Triazolo[1,2-*a*]benzotriazole Derivatives or Substituted 2,3-Benzo-1,3a,6,6a-tetraazapentalenes. II

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This paper continues the synthesis of new 1,2,3-triazolo[1,2-*a*]benzotriazoles or 2,3-benzo-1,3a,6,6a-tetrazapentalenes to submit to biological assays. The derivatives were obtained by deoxycyclization reactions of appropriate nitrophenyl-1,2,3-triazole derivatives and by thermal decomposition of appropriate azidophenyl-1,2,3-triazoles (Schemes 1 and 2). Some attempts to extend these synthetic routes to the preparation of 1,2,4-triazolo[1,2-*a*]benzotriazoles (Scheme 3) and 1,2,3-triazolo[1,2-*b*]-4*H*-1,2,3-benzotriazines (Scheme 4) completely failed.

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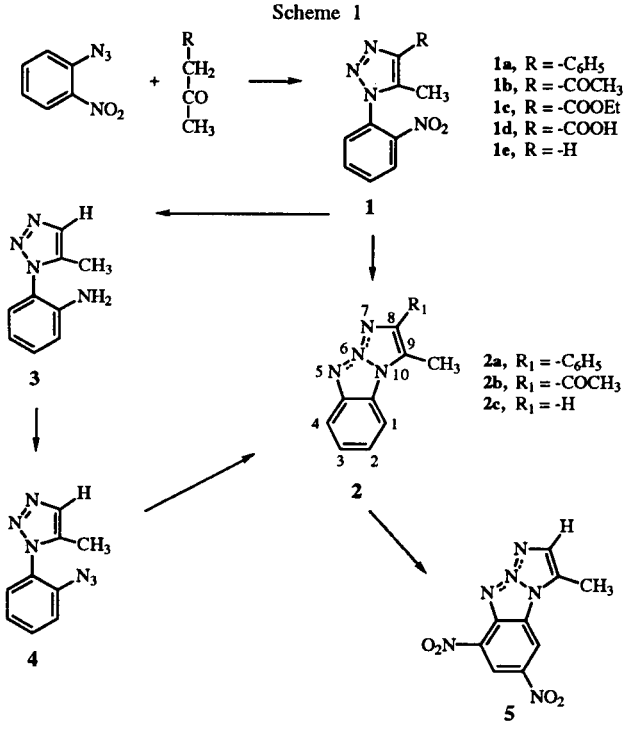
In a previous paper [1] we took into consideration the chemistry of the tetraazapentalenes, the synthesis of new 9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazole derivatives, and the nitration of these compounds.

This study continued by the preparation of other analogous compounds, differently substituted, *via* the known reactions of deoxycyclization of the appropriate nitrophenyl-1,2,3-triazole and/or of thermal decomposition of the appropriate azidophenyl-1,2,3-triazoles (Schemes 1 and 2).

Scheme 1



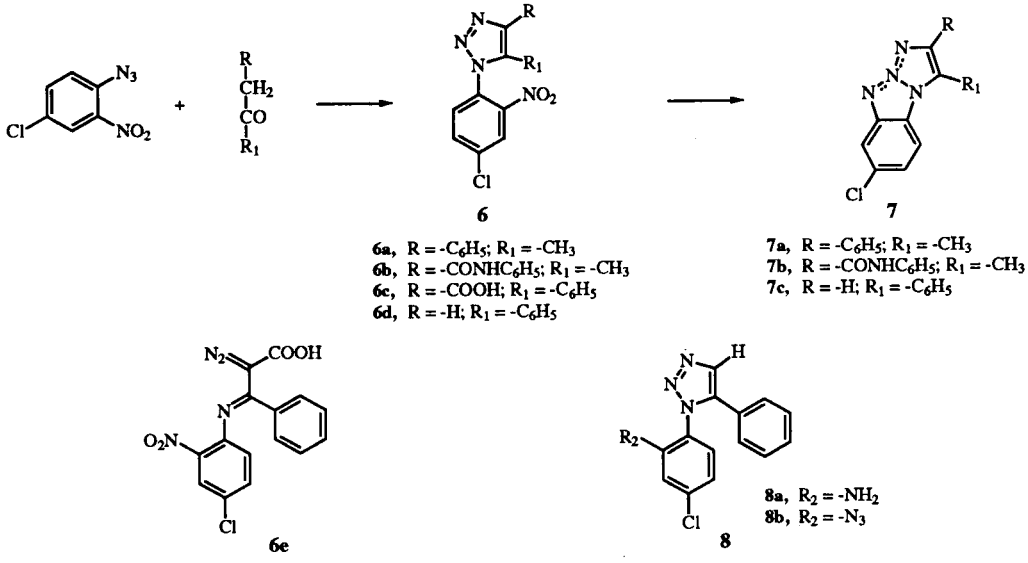
Some attempts to extend these synthetic routes to the preparation of 1,2,4-triazolo[1,2-*a*]benzotriazoles (Scheme 3) as well as 1,2,3-triazolo[1,2-*b*]-4*H*-1,2,3-benzotriazines (Scheme 4) completely failed.

As reported in Scheme 1, the 2-nitrophenylazide [2], by 1,3-dipolar cycloaddition reaction at 0° with phenylacetone, acetylacetone and ethyl acetoacetate respectively, provided the corresponding 1,2,3-triazole derivatives **1a, 1b** and **1c** in good yield. Together with the ester **1c**, the corresponding acid **1d** was also isolated in variable yields; **1d** represented the final reaction product when the mixture of the cycloaddition reaction with ethyl acetoacetate underwent alkaline hydrolysis. The acid **1d** easily decarboxylated by refluxing in toluene to give 1-(2-nitrophenyl)-5-methyl-1*H*-1,2,3-triazole (**1e**).

Compounds **1a, 1b** and **1e** submitted to deoxycyclization reaction by prolonged heating in triethyl phosphite [3] gave the corresponding 1,2,3-triazolo[1,2-*a*]benzotriazoles **2a, 2b** and **2c** in 33% yield. These compounds were isolated as pure solids from the crude reaction mixtures by column chromatographies. Compound **2c** was also prepared in 65% yield by thermal decomposition of the appropriate azido intermediate **4**; the latter was obtained, *via* diazonium salt and displacement with sodium azide, from the corresponding amine **3**, in its turn prepared by catalytic hydrogenation of **1e**. Nitration of **2c** with potassium nitrate in concentrated sulphuric acid at 0-5°, stirring at room temperature and then heating at 70°, provided the 2,4-dinitro derivative **5** in moderate yield.

Similarly, starting from the 2-nitro-4-chlorophenylazide [4] (Scheme 2), by 1,3-cycloaddition reaction to activated methylenic compounds (phenylacetone, acetoacetoanilide and ethyl benzoylacetate), the 1,2,3-triazole derivatives **6a, 6b** and **6c** were obtained in high yields.

Scheme 2



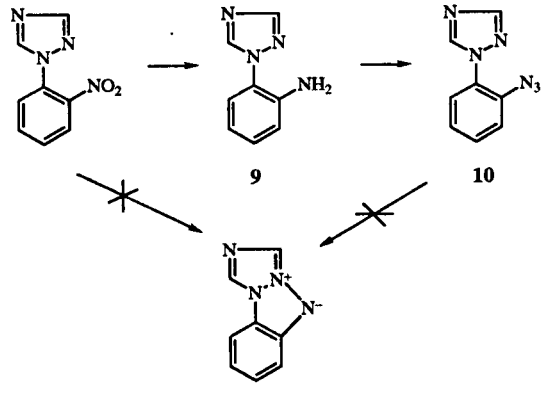
The acid **6c** was isolated at the end of the cycloaddition reaction with ethyl benzoylacetate, by adding a little 10% sodium hydroxide and heating it on a water-bath, to accomplish hydrolysis of the intermediate triazolester. Purification of **6c** by fractional crystallization allowed the isolation of low amounts (0.6-2.8%) of the isomer **6e**. Decarboxylation of **6c** by heating in toluene-dimethylformamide gave **6d**.

Compounds **6a**, **6b** and **6d** heated under reflux in triethyl phosphite for 5 hours underwent the expected nitro reduction and intramolecular cyclization, to give the corresponding substituted 3-chloro-1,2,3-triazolo[1,2-*a*]benzotriazoles **7a**,**7b** and **7c** in 45%, 45% and 35% yields respectively.

Compound **7c** was also obtained by the alternative route involving the amino derivative **8a** and the corresponding azide **8b**.

Utilization of the 1,2,4-triazole ring to synthesize analogous tricyclic derivatives as well as to examine the behaviour of the deoxycyclization reactions and of the azido group thermal decomposition with regard to a different heterocyclic system [5] is reported in Scheme 3.

Scheme 3



Thus 1,2,4-triazole was reacted with 2-nitrofluorobenzene in refluxing dimethylformamide in the presence of anhydrous sodium carbonate to give the 1-(2-nitrophenyl)-1*H*-1,2,4-triazole [6] in 79% yield. Treatment of this compound with triethyl phosphite provided a tarred mixture which did not allow the isolation of the expected 1,2,4-triazolo[1,2-*a*]benzotriazole. This compound was not obtained even by thermal decomposition of the azide **10**, prepared from the

Scheme 4

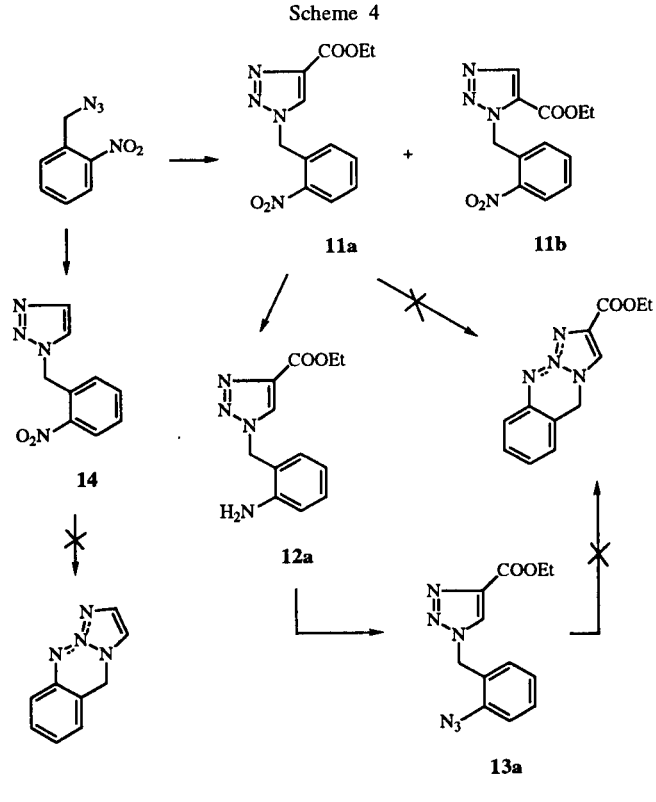


Table I

Chemical and Physical Properties of Compounds **1-5**

Compound	Crystallization Solvent	Yield %	Mp °C	Elemental Analysis	Calcd./Found C	H	N
1a	EtOH	33	105-107	$C_{15}H_{12}N_4O_2$	64.26	4.32	20.00
					64.17	4.53	20.13
1b	EtOH	43	110-111	$C_{11}H_{10}N_4O_3$	53.64	4.10	22.76
					53.85	3.98	23.05
1c	EtOH-H_2O	56	81-83	$C_{12}H_{12}N_4O_4$	52.16	4.38	20.29
					51.98	4.09	20.29
1d	[a]	77	137-138	$C_{10}H_8N_4O_4$	48.38	3.25	22.58
					47.99	3.03	22.39
1e	EtOH	91	114-115	$C_9H_8N_4O_2$	52.92	3.95	27.45
					53.18	3.93	27.65
3	[b]	98	[b]	$C_9H_{10}N_4$	62.05	5.79	32.17
					61.78	6.04	32.27
4	60-80 Petroleum ether	66	74-78	$C_9H_8N_6$	53.98	4.03	41.99
					54.06	3.89	41.81
2a	EtOH	33	183-185	$C_{15}H_{12}N_4$	72.55	4.87	22.58
					72.81	4.79	22.81
2b	EtOH	33	210-212	$C_{11}H_{10}N_4O$	61.66	4.71	26.16
					61.76	4.79	26.08
2c	Cyclohexane	34	135-137	$C_9H_8N_4$	62.77	4.69	32.55
					62.76	4.64	32.32
5	Benzene	12	265-267	$C_9H_6N_6O_4$	41.21	2.31	32.06
					41.46	1.94	32.24

[a] Purified through its sodium salt. [b] Liquid compound see Experimental.

corresponding amine **9**, probably as a consequence of the low stability of **10**.

Two failed attempts to obtain a 1,2,3-triazolo[1,2-*b*]-1,2,3-benzotriazine structure [7], starting from the 2-nitrobenzylazide [8], are reported in Scheme 4.

The azide reacted with an excess of ethyl propiolate in refluxing benzene to give the expected mixture of the 1,2,3-triazole isomers, 4-carbethoxy- **11a** and 5-carbethoxy-substituted **11b** [9] in high yield (isomer ratio 3:1). The 1-(2-nitrobenzyl)-4-carbethoxy-1*H*-1,2,3-triazole (**11a**), isolated by crystallization and flash chromatography, gave by catalytic hydrogenation at room temperature and pressure the amino derivative **12a** which was converted to the corresponding azide **13a**. This compound

Table II

Chemical and Physical Properties of Compounds **6-8**

Compound	Crystallization Solvent	Yield %	Mp °C	Elemental Analysis	Calcd./Found C	H	N
6a	EtOH	41	178-182	$C_{15}H_{11}N_4O_2Cl$	57.31	3.53	17.84
					57.43	3.24	18.17
6b	EtOH	80	187-189	$C_{16}H_{12}N_5O_3Cl$	53.77	3.39	19.61
					53.63	3.09	19.55
6c	EtOH-H_2O	88	144-146	$C_{15}H_9N_4O_4Cl$	52.32	2.64	16.28
					52.68	2.58	16.28
6e	EtOH-H_2O	3	178-180	$C_{15}H_9N_4O_4Cl$	52.32	2.64	16.28
					52.20	2.30	15.94
6d	EtOH	86	147-149	$C_{14}H_9N_4O_2Cl$	55.99	3.02	18.67
					56.36	3.02	18.69
7a	Toluene	45	224-226	$C_{15}H_{11}N_4Cl$	63.81	3.93	19.86
					63.54	3.92	19.59
7b	Cumene	37	299-300	$C_{16}H_{12}N_5OCl$	59.06	3.72	21.54
					59.39	3.94	21.82
7c	Cyclohexane	35	153-156	$C_{14}H_9N_4Cl$	62.67	3.38	20.90
					62.63	3.30	20.78
8a	EtOH-H_2O	63	134-136	$C_{14}H_{11}N_4Cl$	62.21	4.10	20.74
					62.34	4.30	21.09
8b	EtOH-H_2O	63	119-123	$C_{14}H_9N_6Cl$	56.75	3.06	28.38
					56.93	3.16	28.29

Table III

Chemical and Physical Properties of Compounds **9-14**

Compound	Crystallization Solvent	Yield %	Mp °C	Elemental Analysis	Calcd./Found C	H	N
9	[a]	96	[a]	$C_8H_8N_4$	59.97	5.04	34.99
					59.75	4.86	35.13
10	60-80 Petroleum ether	90	72-73	$C_8H_6N_6$	51.59	3.25	45.16
					51.32	3.34	44.98
12a	Benzene	95	97-99	$C_{12}H_{14}N_4O_2$	58.51	5.73	22.76
					58.85	5.69	22.59
13a	Benzene	84	94-96	$C_{12}H_{12}N_6O_2$	52.92	4.44	30.88
					52.98	4.60	30.75
14	AcOEt	47	114-115	$C_9H_8N_4O_2$	52.92	3.95	27.45
					53.07	3.75	27.21

[a] Liquid compound, see Experimental.

underwent thermal decomposition reactions under different experimental conditions (140°,160°,180°) or photochemistry decomposition (70-W high pressure mercury lamp, Hanau Model TQ 81), but the expected 1,2,3-triazolo[1,2-*b*]-4*H*-1,2,3-benzotriazine was never obtained.

Also deoxycyclization reactions carried out on the 1-(2-nitrobenzyl)-1*H*-1,2,3-triazole (**14**), prepared from 2-nitrobenzylazide and vinyl acetate in a closed tube at 110°, did not provide the analogous 1,2,3-triazolo-1,2,3-benzotriazine structure.

The structures of all the new prepared compounds were assigned according to reaction mechanisms and were confirmed by analytical and spectroscopic data (Table IV). Regarding the dinitro compound **5**, the presence of the triazole proton in position 8 was confirmed by ^{1}H- and ^{13}C nmr spectroscopy (see Table IV and V) while the position of the two nitro groups on the benzotriazole moiety was assigned by comparison with analogous nitro compounds previously prepared [1]. These results suggested the 2 and 4 positions are preferred under an electrophilic attack.

Table IV

^{1}H NMR Data of 1,2,3-Triazolo[1,2-*a*]benzotriazole Derivatives in DMSO

	2a	**2b**	**2c**	**5**	**7a**	**7b**	**7c**
H-1	8.01	8.04	8.02	9.09	8.12	8.14	7.75
H-2	7.16	7.23	7.19	----	7.20	7.27	7.14
H-3	7.45	7.50	7.47	9.15	----	----	----
H-4	7.64	7.67	7.65	----	7.74	7.82	7.78
H-8	----	----	7.72	8.13	----	----	8.16
Me	2.88	2.96	2.76	2.92	2.93	3.06	----
$J_{1,2}$	8.28	8.30	8.27	----	8.78	8.77	8.79
$J_{1,3}$	1.16	1.12	1.17	2.10	----	----	----
$J_{1,4}$	0.72	0.7	0.77		0.0	0.0	0.0
$J_{2,3}$	7.09	7.10	7.09	----	----	----	----
$J_{2,4}$	1.11	1.10	1 11	----	1.93	1.93	2.04
$J_{3,4}$	8.50	8.50	8.51	----	----	----	----
$J_{8,Me}$	----	----	1.00	0.8	----	----	----

Other signals: **2a**: 7.75 (2H), 7.50 (3H); **2b**: 2.59 (s, COMe); **7a**: 7.79 (2H), 7.51 (3H); **7b**: 7.84 (2H), 7.35 (2H), 7.12 (1H); **7c**: 7.79 (2H), 7.61 (3H).

Several compounds together with previously prepared analogs [1] were tested for their affinity to the benzodiazepine and/or adenosine receptors, but they resulted in a lack of biological activity.

Table V

^{13}C NMR Data of 1,2,3-Triazolo[1,2-*a*]benzotriazole Derivatives in DMSO

	2a	**2b**	**2c**	**5**	**7a**	**7b**	**7c**
C-1a	118.6	118.6	119.0	123.5	118.4	118.2	117.7
C-1	110.3	111.0	111.2	113.7	112.6	113.0	112.4
C-2	118.3	119.1	118.8	135.8	118.8	119.6	119.1
C-3	127.5	126.5	126.4	119.6	131.0	131.5	131.0
C-4	113.5	113.9	114.1	130.1	113.2	113.5	113.7
C-4a	143.5	144.4	144.4	141.6	144.8	145.4	145.1
C-8	111.6	136.1	129.9	132.6	111.8	134.2	130.4
C-9	129.7	131.1	116.0	122.1	129.9	120.3	121.0
Me	8.3	8.2	8.6	8.6	8.8	8.5	------

Other signals: **2a**: 139.9, 128.1, 126.7, 125.7; **2b**: 174.2, 27.0; **7a**: 141.0, 128.7, 128.3, 127.4; **7b**: 158.5, 138.1, 128.3, 123.8, 120.5; **7c**: 129.1, 128.8, 126.8, 125.2.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are uncorrected. The ir spectra in nujol mulls were recorded on a Perkin-Elmer Mod. 1310 spectrometer. The ^{1}H-nmr spectra were recorded with a Varian EM 360 spectrometer operating at 60 MHz. The spectra of compounds **2a-c**, **5** and **7a-c** were recorded with a Bruker AC 200 instrument, operating at 200 MHz for the ^{1}H and 50 MHz for the ^{13}C. Assignments were confirmed, when necessary, with the aid of homo and hetero correlation spectroscopy, performed by using the standard Bruker programs. In all cases the chemical shifts were in δ units from TMS as internal standard. Mass spectra were performed with a Hewlett Packard MS/System 5988. Elemental analyses (C,H,N) were performed on a Carlo Erba Elemental Analyzer Mod. 1106

apparatus. Short distillations were performed in a Buchi GKR 50 tubular oven.

1-(2-Nitrophenyl)-4-phenyl-5-methyl-1*H*-1,2,3-triazole (**1a**) and 1-(2-Nitrophenyl)-4-acetyl-5-methyl-1*H*-1,2,3-triazole (**1b**).

A solution of *o*-nitrophenylazide (1.97 g, 12 mmoles) and 14.4 mmoles of phenylacetone or 2,4-pentanedione in 150 ml of absolute ethanol was dropped during 2 hours into an ice-cooled and stirred solution of sodium ethoxide (0.414 g, 18 mmoles of sodium in 45 ml of absolute ethanol). After 2 hours the ice-bath was removed and the solution was concentrated *in vacuo* to 2/3 of the volume (temperature <40°) and kept for 40 hours at 4°. Compound **1a** precipitated as a yellow solid which was collected by filtration and washed with ethanol (Table I); ir: ν 1470, 1345 (NO_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.40 (s, 3H, CH_3), 8.32-7.30 (m, 9H, aromatics). For compound **1b** the reaction mixture was further concentrated *in vacuo*, diluted with water and extracted with chloroform. The combined extracts, washed with 18% hydrochloric acid and water, were evaporated *in vacuo* to give a solid residue which was purified by crystallization (Table I); ir: ν 1675 (C=O), 1460, 1340 (NO_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.40 (s, 3H, CH_3), 2.70 (s, 3H, $COCH_3$), 8.40-7.43 (m, 4H, aromatics).

1-(2-Nitrophenyl)-4-carboethoxy-5-methyl-1*H*-1,2,3-triazole (**1c**) and 1-(2-Nitrophenyl)-4-carboxy-5-methyl-1*H*-1,2,3-triazole (**1d**).

A solution of *o*-nitrophenylazide (3.68 g, 22.4 mmoles) and ethyl acetoacetate (3.4 ml, 26.92 mmoles) in 140 ml of absolute ethanol was slowly dropped into an ice-cooled, stirred solution of sodium ethoxide (0.733 g, 33.6 mmoles of sodium in 19 ml of absolute ethanol). After 30 minutes, the ice-bath was removed and stirring continued at room temperature for 15-20 hours. The reaction mixture was concentrated *in vacuo*, treated with water and extracted with chloroform. Evaporation of the combined extracts gave a semisolid residue of crude **1c** which was purified by crystallization (Table I); ir: ν 1720 (C=O), 1460, 1345 (NO_2), 1210 (C-O) cm^{-1}; ^1H nmr (chloroform-d): δ 1.16 (t, 3H, J 7.0 Hz, CH_3), 2.56 (s, 3H, CH_3), 4.53 (q, 2H, CH_2), 8.50-7.43 (m, 4H, aromatics). For isolation of **1d**, after concentration *in vacuo*, 5 ml of 10% sodium hydroxide were added to the reaction mixture heating in a boiling water-bath for 1 hour. The solution was washed with chloroform and the aqueous layer was acidified with 18% hydrochloric acid to precipitate **1d** as a yellow solid which was isolated by filtration (Table I); ir: ν 3300 (OH), 1695 (C=O), 1465, 1355 (NO_2) cm^{-1}; ^1H nmr (chloroform-d + dimethyl sulfoxide d_6): δ 2.55 (s, 3H, CH_3), 8.50-7.66 (m, 4H, aromatics).

1-(2-Nitrophenyl)-4-carboxy-5-methyl-1*H*-1,2,3-triazole (**1d**).

A solution of **1c** (6.40 g, 23.2 mmoles) in 30 ml of 10% sodium hydroxide and 10 ml of ethanol were refluxed for 45 minutes. After cooling, the reaction mixture was washed with chloroform and acidified with 10% hydrochloric acid to precipitate the title compound which was collected by filtration and washed with water, 4.22 g, yield 74%.

1-(2-Nitrophenyl)-5-methyl-1*H*-1,2,3-triazole (**1e**).

A solution of **1d** (1.11 g, 4.47 mmoles) in 20 ml of toluene was heated under reflux for 4 hours. After cooling, the solution was washed with 10% sodium hydroxide solution, then evaporated under reduced pressure to give **1e** as a solid residue (Table I); ir: ν 1455, 1365 (NO_2) cm^{-1}.

1-(2-Aminophenyl)-5-methyl-1*H*-1,2,3-triazole (**3**).

A solution of **1e** (1.68 g, 8.22 mmoles) in 118 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.118 g). The catalyst was filtered off, washed with boiling ethanol and the combined filtrates were evaporated to give a semisolid residue which was dissolved in 18% hydrochloric acid and washed with ethyl ether. Alkalinization of the aqueous layer gave an oil which was extracted with chloroform. Evaporation of the combined extracts gave **3** as an oil which was purified by short distillation at 195-200°/0.1 mm Hg (Table I); ir: ν 3420, 3320, 3190 (NH_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.26 (s, 3H, CH_3), 3.93 (bs, 2H, NH_2), 7.56-6.76 (m, 4H, aromatics), 7.73 (s, 1H, H-4); ms: m/z 174 (M^+), 145, 118.

1-(2-Azidophenyl)-5-phenyl-1*H*-1,2,3-triazole (**4**).

To an ice-cooled, stirred solution of **3** (0.940 g, 5.40 mmoles) in 13 ml of 18% hydrochloric acid, a solution of sodium nitrite (0.484 g, 7.02 mmoles in 15 ml of water) was added drop by drop. After 30 minutes of stirring, a solution of sodium azide (0.456 g, 7.02 mmoles) in 15 ml of water was added dropwise and after 30 minutes of stirring at 0°, the reaction mixture was extracted with ethyl ether. Evaporation of the combined extracts afforded a semisolid residue, which was purified by crystallization (Table I); ir: ν 2090 (N_3) cm^{-1}; ms: m/z 200 (M^+) 172, 117.

8-Phenyl-9-methyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**2a**) and 8-Acetyl-9-methyl-1,2,3-triazolo[1,2-*a*]benzatriazole (**2b**).

To a solution of 4.0 mmoles of **1a** or **1b** in 18 ml of cumene, 1.9 ml of triethyl phosphite were added and the mixture was heated at 150° for 5 hours, then stirred for 14 hours at room temperature under a nitrogen stream. The solid precipitated was collected by filtration and washed with ethyl acetate (Table I); **2a**: ^1H and ^{13}C nmr see Table IV and V; **2b**, ir: ν 1690 (C=O) cm^{-1}; ^1H and ^{13}C nmr see Table IV and V.

9-Methyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**2c**).

A) To a solution of **1e** (1.457 g, 7.14 mmoles) in 14 ml of cumene, 3.2 ml of triethyl phosphite were added and the mixture was heated at 150° for 5 hours, under a nitrogen stream. The solvent was distilled off under reduced pressure and the residue, dissolved in 30-50° petroleum ether/ethyl acetate 1:2, was filtered through a silica gel column (11 x 3.5 cm). Elution with the same solvent mixture provided the crude compound **2c** which was purified by crystallization (Table I).

B) A solution of the triazole azide **4** (0.890 g, 4.45 mmoles) in 6 ml of 1,2-dichlorobenzene was heated at 180° until the evolution of nitrogen ceased (≈ 30 minutes). The solvent was distilled off under reduced pressure and the crude solid residue was dissolved in 40-60° petroleum ether/ethyl acetate 1:2 and filtered through a silica gel column (8.5 x 3 cm). Elution with the same solvent mixture provided 0.490 g (yield 64%) of the compound **2c**; ^1H and ^{13}C nmr see Table IV and V; ms: m/z 172 (M^+), 117, 76.

2,4-Dinitro-9-methyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**5**).

To an ice-cooled and stirred solution of **2c** (0.120 g, 0.7 mmole) in 2 ml of 96% sulphuric acid, 0.124 g (1.5 mmoles) of potassium nitrate were added portionwise (≈ 1 hour). The ice-bath was removed and the reaction mixture was maintained at room temperature for 4 hours and then heated at 70° for 1 hour. After cooling, the mixture was poured into crushed ice and the precipitated dinitro derivative **5** was collected by filtration and

washed with water. The compound was purified by fractional crystallization from benzene (Table I); ir: ν 1470, 1350 (NO_2) cm^{-1}; ^1H and ^{13}C nmr see Table IV and V; ms: m/z 262 (M^+), 216, 170, 161.

1-(2-Nitro-4-chlorophenyl)-4-phenyl-5-methyl-1*H*-1,2,3-triazole (**6a**) and 1-(2-Nitro-4-chlorophenyl)-4-(*N*-phenylcarboxamido)-5-methyl-1*H*-1,2,3-triazole (**6b**).

To an ice-cooled and stirred solution of sodium ethoxide (0.680 g, 29.5 mmoles of sodium in 18 ml of absolute ethanol), a solution of 2-nitro-4-chlorophenylazide (3.42 g, 19.7 mmoles) and 23.65 mmoles of phenylacetone or acetoacetanilide in 40 ml of absolute ethanol was added dropwise. After 2 hours the ice-bath was removed and stirring continued at room temperature for 18 hours. The reaction mixture was concentrated *in vacuo* and diluted with water to precipitate the title compounds which were collected by filtration and washed with water (Table II); **6a**: ir: ν 1460, 1355 (NO_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.43 (s, 3H, CH_3), 8.32-7.36 (m, 8H, aromatics); ms: m/z 315 (M^+), 240, 105; **6b**: ir: ν 3360 (NH), 1675 (C=O), 1460, 1360 (NO_2) cm^{-1}; ^1H nmr (chloroform-d + dimethyl sulfoxide d_6): δ 2.32 (s, 3H, CH_3), 8.07-7.06 (m, 8H, aromatics), 10.4 (bs, 1H, NH); ms: m/z 359 (M+2), 357 (M^+), 268, 105.

1-(2-Nitro-4-chlorophenyl)-4-carboxy-5-phenyl-1*H*-1,2,3-triazole (**6c**) and 2-Diazo-3-phenyl-3-(4-chloro-2-nitrophenylimino)propionic Acid (**6e**).

A solution of 2-nitro-4-chlorophenylazide (0.675 g, 3.4 mmoles) and ethyl benzoylacetate (0.7 ml, 4.07 mmoles) in 6 ml of absolute ethanol was dropped slowly into an ice-cooled and stirred solution of sodium ethoxide (0.156 g, 6.8 mmoles of sodium in 4 ml of absolute ethanol). After 2 hours, the ice-bath was removed and stirring continued at room temperature for 15 hours. The reaction mixture was concentrated *in vacuo;* the semisolid residue was suspended in water, and heated in a boiling water-bath for 1 hour. After cooling, the solution was acidified with 10% hydrochloric acid to precipitate crude **6c** as a yellow solid which was isolated by filtration. Purification by fractional crystallization from ethanol-water first provided a little fraction of **6e** as a yellow solid (Table II); ir: ν 2110 (C≡N), 1660 (C=O), 1450, 1335 (NO_2) cm^{-1}; ms: m/z 344 (M^+), 270, 228, 145, 105. The further fraction consisted of **6c** (Table II); ir: ν 3300 (OH), 1710 (C=O), 1460, 1345 (NO_2) cm^{-1}; ^1H nmr (chloroform-d + dimethyl sulfoxide d_6): δ 7.47 (m, 5H, phenyl), 7.57 (d, 1H, J 8.0 Hz, H-6'), 7.88 (dd, 1H, H-5'), 8.18 (d, 1H, J 2.0 Hz, H-3'); ms: m/z 344 (M^+), 300, 138, 105.

1 -(2-Nitro-4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole (**6d**).

A solution of **6c** (6.67 g, 19.4 mmoles) in 120 ml of toluene and 6 ml of dimethylformamide was heated under reflux for 4 hours. After cooling, the solvent was evaporated *in vacuo* and the residue was dissolved in chloroform and washed with 10% sodium hydroxide solution. Evaporation of the solvent gave crude **6d**, which was purified by crystallization (Table II); ir: ν 1460, 1350 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide d_6, 200 MHz): δ 7.44-7.30 (m, 5H, phenyl), 7.78 (d, 1H, J 8.60 Hz, H-6'), 8.02 (dd, 1H, H-5'), 8.23 (d, 1H, J 2.33 Hz, H-3'); ^{13}C nmr (dimethyl sulfoxide d_6, 50 MHz): δ 125.1 (C-5), 126.0 (C-3'), 127.7 (C-1'), 128.2 and 129.1 (C-2" and C-3"), 129.7 (C-4"), 131.1 (C-4), 132.8 (C-6'), 134.6 (C-5'), 135.9 (C-4'), 139.0 (C-1"), 145.5 (C-2'); ms: m/z 344 (M^+), 270, 228, 105.

3-Chloro-8-phenyl-9-methyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**7a**) and 3-Chloro-8-(*N*-phenylcarboxamido)-9-methyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**7b**).

To a solution of **6a** or **6b** (6.36 mmoles) in 12 ml of cumene, 3.9 ml (22.3 mmoles) of triethyl phosphite were added and the mixture was heated at 150° for 5 hours under a nitrogen stream. For compound **7a** the mixture was further stirred at room temperature for 15 hours. After cooling, the title compounds crystallized pure and were collected by filtration. The filtrates were evaporated under reduced pressure and the semisolid residue was purified by flash-chromatography through a silica gel (230-400 mesh) column eluting with ethyl acetate/ 30°-50° petroleum ether 1:6 to obtain a further amount of products (Table II); **7a**: ^1H and ^{13}C nmr see Table IV and V; ms: m/z 284 (M+2), 282 (M^+), 151, 110; **7b**: ir: ν 3360 (NH), 1680 (C=O) cm^{-1}; ^1H and ^{13}C nmr see Table IV and V; ms: m/z 327 (M+2), 325 (M^+), 205, 177, 151.

3-Chloro-9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**7c**).

A) A solution of **6d** (1.50 g, 4.98 mmoles) and triethyl phosphite (3.0 ml, 17.5 mmoles) in 10 ml of cumene was heated at 150° for 5 hours, under a nitrogen stream. The solvent was distilled off under reduced pressure and the black semisolid residue was purified by flash-chromatography through a silica gel (230-400 mesh) column eluting with ethyl acetate/ 30-50° petroleum ether 1:6 to obtain pure **7c** as a white crystalline solid (Table II); ^1H and ^{13}C nmr see Table IV and V; ms: m/z 270 (M+2), 268 (M^+), 213, 178, 151.

B) A solution of the triazoloazide **8b** (0.65 g, 2.18 mmoles) in 3 ml of 1,2-dichlorobenzene was heated at 180° until the evolution of nitrogen ceased (≈ 30 minutes). The solvent was distilled off under reduced pressure and the crude solid residue was portionwise extracted with boiling cyclohexane. The title compound crystallized after concentration of the combined extracts: 0.275 g (47%).

1-(2-Amino-4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole (**8a**).

A suspension of **6d** (0.836 g, 2.78 mmoles) and tin (II) chloride dihydrate (1.87 g, 8.31 mmoles) in 20 ml of 36% hydrochloric acid and 10 ml of water was refluxed for 2-3 hours, then stirred at room temperature for 2 hours. Alkalinization of the reaction mixture with 10% sodium hydroxide precipitated **8a** which was collected by filtration (Table II); ir: ν 3450, 3300, 3150 (NH_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide d_6, 200 MHz): δ 6.60 (dd, 1H, H-5'), 6.90 (d, 1H, J 2.32 Hz, H-3'), 7.01 (d, 1H, J 8.17 Hz, H-6'), 7.37 (m, 5H, phenyl); ^{13}C nmr (dimethyl sulfoxide d_6, 50 MHz): δ 114.9 (C-3'), 115.3 (C-5'), 119.7 (C-1'), 126.3 (C-5), 127.6 and 128.7 (C-2" and C-3"), 129.1 (C-4"), 129.9 (C-4), 132.6 (C-6'), 135.1 (C-4'), 138.3 (C-1"), 146.2 (C-2').

1-(2-Azido-4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole (**8b**).

To an ice-cooled and stirred solution of **8a** (4.38 g, 1.62 mmoles) in 10 ml of 36% hydrochloric acid, a solution of sodium nitrite (0.135 g, 1.94 mmoles in 5 ml of water) was added drop by drop. After 30 minutes of stirring, the reaction mixture was quickly filtered and a solution of sodium azide (0.126 g, 1.94 mmoles) in 5 ml of water was dropwise added to the filtrate (0-5°). After 2 hours of stirring at room temperature the precipitated **8b** was collected by filtration and washed repeatedly with water (Table II); ir: ν 2100 (N_3) cm^{-1}; ^1H nmr (chloroform-d): δ 7.58-7.33 (m, 8H, aromatics), 8.11 (s, 1H, H-4); ms: m/z 296 (M^+), 268, 102.

1-(2-aminophenyl)-1*H*-1,2,4-triazole (**9**).

A solution of nitrophenyl-1,2,4-triazole [6] (1.00 g, 5.26 mmoles) in 55 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.140 g). The catalyst was filtered off, washed with boiling ethanol and the combined filtrates were evaporated to give **9** as an oil which could be purified by short distillation at 175°/0.8 mmHg (Table III); ir: ν 3420, 3320, 3200 (NH_2) cm^{-1}; ^1H nmr (chloroform-d): δ 4.32 (bs, 2H, NH_2), 6.95 (m, 2H, aromatics), 7.30 (m, 2H, aromatics); ms: m/z 160 (M^+), 133, 106.

1-(2-Azidophenyl)-1*H*-1,2,4-triazole (**10**).

To an ice-cooled, stirred solution of **9** (0.480 g, 3.0 mmoles) in 10 ml of 18% hydrochloric acid, a solution of sodium nitrite (0.230 g, 3.30 mmoles) in 5 ml of water was added drop by drop. After 1 hour a solution of sodium azide (0.195 g, 3.0 mmoles) in 6 ml of water was added dropwise under vigorous stirring. After 2 hours the ice-bath was removed and the solution was extracted with chloroform. The title compound was obtained by evaporation of the solvent and purified by crystallization (Table III); ir: ν 2100 (N_3) cm^{-1}; ms: m/z 186 (M^+), 158, 103.

1-(2-Aminobenzyl)-4-carbethoxy-1*H*-1,2,3-triazole (**12a**).

To a solution of **11a** [9] (2.10 g, 7.59 mmoles) in 260 ml of ethanol, 0.185 g of 5% palladium on activated charcoal was added and the mixture was hydrogenated at room temperature and pressure. The catalyst was filtered off, washed with ethanol and evaporation of the solvent afforded **12a** as a white solid (Table III); ir: ν 3450, 3360, 3250 (NH_2), 1710 (C=O), 1220 (C-O) cm^{-1}; ^1H nmr (chloroform-d): δ 1.36 (t, 3H, J 7.0 Hz, CH_3), 4.10 (bs, 2H, NH_2), 4.43 (q, 2H, CH_2), 5.56 (s, 2H, benzylic CH_2), 7.46-6.63 (m, 4H, aromatics), 8.13 (s, 1H, H-5); ms: m/z 246 (M^+), 106.

1-(2-Azidobenzyl)-4-carbethoxy-1*H*-1,2,3-triazole (**13a**).

To an ice-cooled, stirred solution of **12a** (0.20 g, 0.80 mmole) in 5 ml of 18% hydrochloric acid, a solution of sodium nitrite (0.11 g, 1.60 mmoles) in 8 ml of water was added drop by drop. After 30 minutes a solution of sodium azide (0.104 g, 1.60 mmoles) in 8 ml of water was added dropwise under vigorous stirring. The ice-bath was removed and the reaction mixture was stirred for 1 hour at room temperature.The precipitate, consisting of **13a**, was collected by filtration and washed with water (Table III); ir: ν 2070 (N_3), 1710 (C=O), 1210 (C-O) cm^{-1}; ^1H nmr (chloroform-d): δ 1.38 (t, 3H, J 7.0 Hz, CH_3), 4.46 (q, 2H, CH_2), 5.63 (s, 2H, benzylic CH_2), 7.70-7.16 (m, 4H, aromatics), 8.16 (s, 1H, H-5); ms: m/z 272 (M^+), 170, 142, 115.

1-(2-Nitrobenzyl)-1*H*-1,2,3-triazole (**14**).

A solution of 2-nitrobenzylazide (2.42 g, 13.6 mmoles) and vinyl acetate (11 ml, 119 mmoles) was heated in a closed tube at 110° for 23 hours. The reaction mixture was evaporated and the tarred residue was dissolved in chloroform and chromatographed through a silica gel column (7 x 3 cm) eluting with ethylacetate. Evaporation of the central eluates provided **14**, which was purified by crystallization (Table III); ir: ν 1460, 1350 (NO_2) cm^{-1}; ^1H nmr (chloroform-d): δ 6.10 (s, 2H, benzylic CH_2), 7.22 (m, 1H, aromatic), 7.75 (m, 2H, aromatics), 7.92 (s, 2H, H-4 and H-5), 8.31 (m, 1H, aromatic); ms: m/z 204 (M^+), 174, 135, 128.

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