Synthesis of New 1,2,3-Triazolo[1,2-*a*]benzotriazoles or 2,3-Benzo-1,3a,6,6a-tetraazapentalenes

Giuliana Biagi, Irene Giorgi, Oreste Livi*, and Valerio Scartoni

Dipartimento di Scienze Farmaceutiche, Università di Pisa, 56126 Pisa, Italy

Pier Luigi Barili

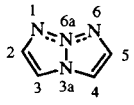
Dipartimento di Bioorganica, Università di Pisa, 56126 Pisa, Italy

Received June 12, 1995

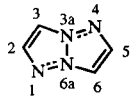
Some new *v*-triazolo[1,2-*a*]benzotriazoles or 2,3-benzo-1,3a,6,6a-tetraazapentalenes were prepared according to previously employed synthetic routes concerning deoxycyclization reactions of appropriate nitrophenyl-1,2,3-triazole derivatives and/or thermal decompositions of appropriate azidophenyl-1,2,3-triazoles. The nitration of 9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazoles allowed the isolation of some mononitro- and trinitro-derivatives, whose structures were assigned by chemical and spectroscopic methods.

J. Heterocyclic Chem., **32**, 1709 (1995).

The heterocyclic system constituted by two 1,2,3 triazole rings, fused through two nitrogen atoms, was named tetraazapentalene and may be described by two isomeric structures (Figure 1). When these heterocycles are fused



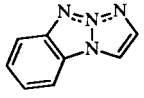
1,3a,6,6a-Tetraazapentalene (T form)



1,3a,4,6a-Tetraazapentalene (S form)

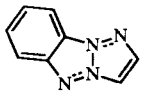
Figure 1.

with a benzene ring, the new structures obtained were named benzotetraazapentalenes or *v*-triazolobenzotriazoles (Figure 2). The first synthesis of a tetraazapentalene



2,3-Benzo-1,3a,6,6a-tetraazapentalene

1,2,3-Triazolo[1,2-*a*]benzotriazole



2,3-Benzo-1,3a,4,6a-tetraazapentalene

1,2,3-Triazolo[2,1-*a*]benzotriazole

Figure 2.

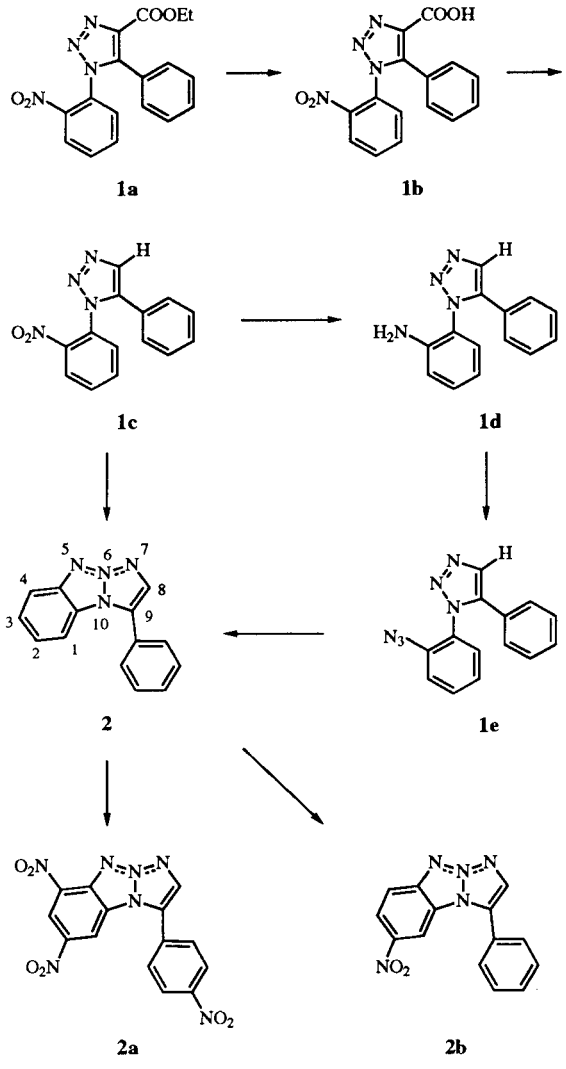
derivative was performed in 1962 when Carboni and Castle [1] prepared the dibenzo-1,3a,4,6a-tetraazapentalene by thermal decomposition of 2,2'-diazidoazobenzene. The same authors and/or their coworkers, in a series of papers published in 1967 [2-6], prepared also the isomeric dibenzo-1,3a,6,6a-tetraazapentalene [2] and brought evidence for the structure of the two new heterocyclic systems, by thermal and photochemical decomposition of the appropriate 2-azidophenylbenzotriazoles. The benzo-1,3a,4,6a-tetraazapentalene (or 1,2,3-triazolo[2,1-*a*]-benzotriazole) [3] was also prepared and several reactions were examined to evaluate the chemical behaviour of these new heterocyclic rings and their influence toward the electrophilic substitution on the phenyl ring. A new ring-closure reaction based upon the trialkyl phosphite deoxygenation of *o*-nitrophenyltriazole derivatives [4] together with theoretical and practical studies based on heats of combustion [5] and new synthetic routes [6] were then described. Analogous thermal decomposition reactions of *o*-azidobenzenes to give dibenzotetraazapentalenes [7] and related proton nmr-analyses [8] confirmed the previous considerations. Successively, in 1983 [9] and 1984 [10], Albini *et al.* studied the behavior of 1,2,3-triazolobenzotriazoles in photooxydation and thermal addition to dimethyl acetylendicarboxylate reactions respectively. Finally, a paper published in 1989 [11] reports ^{14}N-nmr data and semiempirical molecular orbital calculations for the dibenzo-1,3a,4,6a-tetraazapentalene.

Since the biological properties of these structures are unknown and we have been dealing with 1,2,3-triazole derivatives for several years, we thought it would be interesting to synthesize new tricyclic compounds corresponding to *v*-triazolobenzotriazoles, bearing substituents on the 1,2,3-triazole and/or benzene ring, to submit them to biological assays.

Thus by 1,3-dipolar cycloaddition reaction of *o*-nitrophenylazide [12] to ethyl benzoylacetate (Scheme I), the expected triazole ester **1a** was isolated in 21% yield only, being the corresponding acid **1b**, the main reaction product. This reaction was carried out adding an equimolar mixture of azide and activated methylenic compound to an ethanolic sodium ethoxyde solution at 0-5° and stirring the mixture at room temperature for 24 hours.

In the next reactions the ester **1a** was not isolated, but the reacted mixture was hydrolyzed with sodium hydrox-

Scheme I



ide solution to obtain directly the acid **1b** in 80% yield. The triazole acid **1b** easily decarboxylated by refluxing in toluene to give the 1-(2-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole (**1c**) which underwent a deoxycyclization reaction by heating with triethyl phosphite in cumene (150°) under nitrogen atmosphere. The expected 9-phenyl-1,2,3-triazolo[1,2-*a*] benzotriazole (**2**) was isolated in ≈24% yield by silica-gel column chromatography. The reaction yield, although corresponding to that of analogous reactions described, was moderated, therefore another synthetic route, based upon the photolysis or pyrolysis of the suitable azide, was engaged.

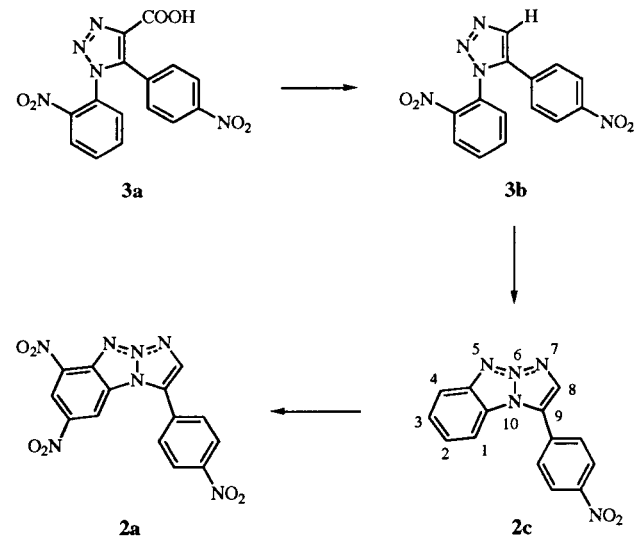
The nitrophenyltriazole **1c**, by catalytic hydrogenation, was reduced to the corresponding amino derivative **1d** which was then converted into the azide **1e** *via* diazonium salt and nitrogen displacement by azide ion.

Irradiation of **1e** in trifluoroacetic acid solution with ultraviolet light (70-W high pressure mercury lamp, Hanau Model TQ 81), as well as the pyrolysis of **1e** in toluene solution gave a negative result, but the thermal decomposition in *o*-dichlorobenzene solution (180°) [2] caused a quick and complete nitrogen evolution and provided **2** in 35-40% yield.

In order to functionalize this structure and, at the same time, to examine the orientation of the aromatic electrophilic substitution, the triazolobenzotriazole **2** underwent a nitration. Treatment of **2** in concentrated sulphuric acid with potassium nitrate at 0-5° then at 70°, allowed the isolation of the trinitro derivative **2a**, while working in acetic acid solution at 45-50°, the mononitro derivative **2b** was isolated; attempts at obtaining a dinitro compound failed.

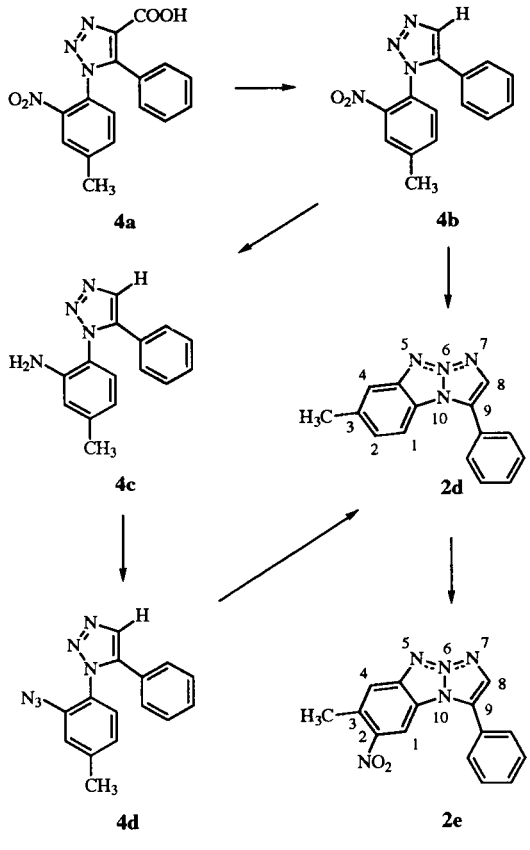
A mononitro derivative **2c** (Scheme II), isomer of **2b**, was synthesized using *o*-nitrophenylazide and ethyl *p*-nitrobenzoylacetate as an activated methylenic compound. Thus, under the same experimental conditions described above, after saponification of the reaction mixture, the triazole acid **3a** was obtained, which was decarboxylated to give the 1-(2-nitrophenyl)-5-(4-nitrophenyl)-1*H*-1,2,3-triazole (**3b**). Deoxycyclization of **3b**, performed under experimental conditions analogous to those employed for the preparation of **2**, but lengthening the reaction time, gave the expected 9-(4-nitrophenyl)-1,2,3-triazolo[1,2-*a*]-benzotriazole (**2c**) in 27% yield. Treatment of **2c** with 65% nitric acid at 0-5° then at room temperature for two hours [4] gave the trinitro derivative **2a**; this result showed that a nitro group was placed on the *para* position of the 9-substituted phenyl ring while the other two nitro groups were on the benzotetraazapentalene ring, which clearly was strongly activated toward the electrophilic substitution.

Scheme II



However to unequivocally assign the position of the two nitro groups, an analogous triazolobenzotriazole derivative, bearing a substituent in a settled position of the ring, was prepared (Scheme III).

Scheme III



The 2-nitro-4-methylphenylazide [13] reacted with ethyl benzoylacetate and, according to the usual synthetic route, the triazole acid **4a** was obtained and decarboxylated to **4b**. The latter, by deoxycyclization reaction with triethyl phosphite, gave the expected 3-methyl-9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazole **2d**. The same compound **2d** was also obtained by thermal decomposition of the suitable azide **4d**, prepared from the amino derivative **4c**, coming from the catalytic hydrogenation of **4b**. Nitration of **2d** under mild conditions provided a reaction mixture from which the mononitro derivative **2e** was isolated and characterized.

The structures of all the new 1,2,3-triazole derivatives prepared were assigned according to the known reaction mechanisms (1,3-dipolar cycloaddition and other common reactions) and were confirmed by analytical and spectroscopic data (see experimental). Instead, the structure determination of the nitro-*v*-triazolobenzotriazole derivatives required a more accurate nmr analysis. For this purpose, the ^1H and ^{13}C spectra of **2**, **2a**, **2b**, **2c**, **2d** and **2e** were recorded in DMSO-d_6 as solvent and the temperature was raised to 50° to improve resolution and sample solubility.

For the proton spectra, first order analysis could be performed satisfactorily, except for compound **2**, in which a large signal crowding was present. This spectrum was analyzed by means of a well-resolved COSY experiment. The resonances of carbons bearing hydrogen were assigned by heteronuclear correlation experiments *via* ^1J coupling constants (HETCOR), performed on compounds **2**, **2b**, **2c** and **2d**; the signal attributions of **2a** and **2e**, not soluble enough, were made by analogy. The quaternary carbons were identified by means of a heteronuclear correlation experiment *via* ^2J and ^3J coupling constants (COLOC), recorded for **2d**.

From the nmr data reported in Tables I and II, the nitro-group positions in the compounds **2a**, **2b** and **2e** could be determined: in fact in the ^1H nmr spectrum of **2e** two sharp singlets were present to indicate a *para* relationship unequivocally attributable to the H-1 and H-4 positions, therefore the nitro-group had to be in the 2-position of the heterocycle.

Table I

^1H NMR Data for Compounds **2**, **2a-e** in DMSO

	2	**2a**	**2b**	**2c**	**2d**	**2e**
H-1	7.79	8.94	8.55	7.99	7.69	8.47
H-2	7.18	—	—	7.31	7.02	—
H-3	7.50	9.15	8.26	7.58	—	—
H-4	7.73	—	7.44	7.82	7.53	7.63
H-8	8.13	8.75	8.31	8.39	8.12	8.27
H-2'	7.81	8.26	7.88	8.10	7.80	7.86
H-3'	7.61	8.55	7.69	8.43	7.62	7.64
H-4'	7.53	—	7.62	—	7.51	7.62
Me	—	—	—	—	2.46	2.66
J1,2	8.42	—	—	8.50	8.62	—
J1,3	1.12	2.05	2.22	1.09	—	—
J1,4	0.7	—	0.0	0.77	0.0	0.0
J2,3	7.13	—	—	7.11	—	—
J2,4	1.1	—	—	1.13	1.58	—
J3,4	8.50	—	9.36	8.52	—	—

Table II

^{13}C NMR Data for Compounds **2**, **2a-e** in DMSO

	2	**2a**	**2b**	**2c**	**2d**	**2e**
C-1a	118.4	123.6	122.9	119.0	116.7	122.6
C-1	110.4	112.6	107.6	111.0	110.1	108.9
C-2	118.6	135.8	137.5	119.7	129.5	139.1
C-3	125.8	119.1	121.2	126.2	135.7	131.7
C-4	114.2	129.9	113.7	114.9	113.5	115.6
C-4a	143.9	140.3	147.3	144.0	144.4	146.4
C-8	129.6	133.4	130.6	131.9	129.6	130.4
C-9	119.6	121.7	117.3	117.9	119.5	117.8
Me	—	—	—	—	20.6	20.2
C-1'	125.0	130.8	124.0	131.6	125.2	124.2
C-2'	126.2	127.9	126.5	126.3	126.1	126.4
C-3'	128.5	124.1	128.7	123.8	128.6	128.7
C-4'	128.0	147.6	129.2	146.0	128.0	129.0

In the proton spectrum of **2b**, the J coupling values of the ABX system limited the possibilities for the nitro-substitution to the positions 2 or 3, but only the first was compatible with the carbon spectrum; in fact, considering the substituent effect, a good agreement between the spectra of **2b** and **2e** or of **2b** and **2** could be obtained for a nitro-group substituted in the 2 position. In the proton spectrum of the trinitro derivative **2a**, the presence of an AA'BB' system indicated a 4'-nitro substitution, while the J value of the remaining AB system indicated a *meta* relationship between the hydrogens of the benzotriazole ring and necessarily also between the two nitro-groups. Hence the 2,4,4'-trinitro structure was assigned to **2a** by comparison with the carbon spectra as above for **2b**.

The preference of an electrophilic attack toward the 2 and 4 positions suggested a major contribution to the resonance hybrid of structures with negative charge delocalized in those positions of the benzene ring; on the other hand, the upfield resonance of the C-2 and C-4 carbon atoms and of the H-2 proton were agreed with this hypothesis.

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 **2** and **2a-e** were recorded with a Bruker AC 200 instrument, operating at 200 Mhz for the ^{1}H and 50 Mhz for the ^{13}C. In all cases the chemical shifts were in δ units from TMS as internal standard. The correlation spectroscopy experiments were performed by using the standard Bruker programs. The COLOC experiment was optimized for a J value of 5 Hz (100 ms delay). 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-carboethoxy-5-phenyl-1*H*-1,2,3-triazole (**1a**).

To an ice-cooled and stirred solution of sodium ethoxide (0.138 g, 6.0 mmoles of sodium in 10 ml of absolute ethanol), a mixture of *o*-nitrophenylazide [12] (0.625 g, 4.0 mmoles) and ethyl benzoylacetate (0.921 g, 4.8 mmoles) in 10 ml of absolute ethanol was added dropwise. After 30 minutes, the ice-bath was removed and stirring continued at room temperature for 21 hours. The reaction mixture was concentrated *in vacuo*, treated with water and extracted with chloroform. Evaporation of the combined extracts gave a semisolid residue which, after treatment with 40-60° petroleum ether and crystallization from ethanol, resulted in **1a**, 0.287 g, yield 21%; mp 131-134°; ir: ν 1710 (C=O), 1510, 1340 (NO_2), 1200 (C-O) cm^1; ^{1}H nmr (chloroform-d): δ 1.35 (t, 3H, CH_3), 4.45 (q, 2H, CH_2), 7.40 (s, 5H, phenyl), 7.4-8.3 (m, 4H, phenyl).

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.19; 3.90; N, 16.25.

Acidification of the alkaline aqueous mother liquors precipitated the corresponding acid **1b** which was isolated by extraction with chloroform, 0.523 g, yield 42%.

1-(2-Nitrophenyl)-4-carboxy-5-phenyl-1*H*-1,2,3-triazole (**1b**).

A solution of *o*-nitrophenylazide (1.97 g, 12 mmoles) and ethyl benzoylacetate (2.3 ml, 14.4 mmoles) in 25 ml of absolute ethanol was dropped slowly into an ice-cooled and stirred solution of sodium ethoxide (0.414 g, 18 mmoles of sodium in 10 ml of absolute ethanol). After 2 hours the ice-bath was removed and stirring was continued for 21 hours at room temperature. A little water was added to the reaction mixture which was heated on a boiling water-bath for 1 hour. The solution was concentrated *in vacuo*, diluted with water and washed with chloroform. The aqueous layer was acidified to precipitate **1b** as a yellow solid which was isolated by filtration: 2.98 g, yield 80%; mp 155-156° from ethanol; ir: ν 3200 (OH), 1700 (C=O), 1500, 1350 (NO_2) cm^{-1}; ^{1}H nmr (chloroform-d + dimethyl sulphoxide-d_6): δ 7.40 (s, 5H, phenyl), 7.4-8.4 (m, 4H, phenyl).

Anal. Calcd. for $C_{15}H_{10}N_4O_4$: C, 58.07; H, 3.25; N, 18.06. Found: C, 58.25; H, 3.27; N, 18.04.

1-(2-Nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole (**1c**).

A solution of **1b** (9.25 g, 29.8 mmoles) in 200 ml of toluene was heated under reflux for 4 hours. After cooling, the solution was washed with 6% sodium hydrogen carbonate solution, then evaporated under reduced pressure to give **1c** as a solid residue, 7.20 g, yield 91%; mp 76-80°. The compound could be purified by short distillation at 220°/0.7 mm Hg; ir: ν 1500, 1350 (NO_2) cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.40 (s, 5H, phenyl), 7.3-8.3 (m, 4H, phenyl), 7.96 (s, 1H, C4-H).

Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.05. Found: C, 63.41; H, 3.70; N, 20.91.

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

A solution of **1c** (4.52 g, 17 mmoles) in 300 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.800 g). The catalyst was filtered off, washed with boiling ethanol and the combined filtrates were evaporated to give **1d** as a white solid: 3.80 g, yield 95%; mp 145-147° from 60-80° petroleum ether; ir: ν 3460, 3350 (NH_2) cm^{-1}; ^{1}H nmr (chloroform-d): 4.00 (broad, 2H, NH_2), 6.76-7.40 (m, 4H, C_6H_4), 7.41 (s, 5H, C_6H_5), 8.05 (s, 1H, C4-H).

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.37; H, 4.98; N, 23.46.

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

To an ice-cooled and stirred solution of **1d** (3.50 g, 14.8 mmoles) in 36% hydrochloric acid (25 ml) and water (42 ml), a solution of sodium nitrite (1.13 g, 16.3 mmoles in 15 ml of water) was added drop by drop. After 1 hour of stirring a solution of sodium azide (0.980 g, 15 mmoles) in 18 ml of water was added dropwise and the title compound precipitated as a pale yellow solid. After 2 hours of stirring at room temperature the precipitate was collected by filtration and washed with water repeatedly, 3.65 g, yield 94%, mp 117-119° from benzene/60-80° petroleum ether; ir: ν 2100 (N_3) cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.2-7.7 (m, 9H, phenyl), 8.00 (s, 1H, C4-H).

Anal. Calcd. for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04. Found: C, 63.95; H, 3.89; N, 32.30.

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

A) To a solution of 1-(2-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole (**1c**) (2.66 g, 10 mmoles) in 20 ml of cumene, 4.5 ml of triethyl phosphite was added and the mixture was heated at 150° for 21 hours, under a nitrogen stream. The solvent was distilled off under reduced pressure and the residue, dissolved in benzene/ethyl acetate 9:1, was chromatographed through a silica gel column (18 x 2.5 cm). Elution with the same solvent mixture provided 1.140 g of crude compound **2** which was crystallized from cyclohexane, 0.560 g, yield 24%, mp 157-159°.

B) A solution of the triazoleazide **1e** (2.59 g, 9.9 mmoles) in 7 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 washed, by decantation, with ethyl acetate portionwise, 1.0 g, yield 43%, mp 155-157°; ^{1}H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 234 (M^+), 179, 103, 76.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.96; H, 4.32; N, 24.03.

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

A) To an ice-cooled and stirred solution of **2** (0.340 g, 1.45 mmoles) in 5 ml of 96% sulphuric acid, 0.350 g (3.46 mmoles) of potassium nitrate was added portionwise (≈ 1 hour). The ice-bath was removed and after 4 hours at room temperature, the reaction mixture was heated at 70° for 1 hour. After cooling the mixture was poured into crushed ice, the crude trinitro derivative **2a** precipitated and was collected by filtration, 0.520 g, yield 97%. The compound, purified by extraction with boiling benzene and crystallization of the soluble material from acetone/ethanol 1:1, melted at 288-291°.

B) To an ice-cooled and stirred solution of 65% nitric acid (7 ml), 0.230 g (0.86 mmole) of the mononitro triazolobenzotriazole **2c** was added portionwise (≈ 15 minutes). After 20 minutes the ice-bath was removed and the reaction mixture was stirred for an additional 2 hours at room temperature. Crushed ice was added and the precipitated solid was collected by filtration and crystallized from acetone/ethanol 2:1 to give **2a** (0.070 g, yield 22%) with mp 290-292°; ir: ν 1470, 1350 (NO_2) cm^{-1}; ^{1}H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 369 (M^+), 268, 222, 120, 74.

Anal. Calcd. for $C_{14}H_7N_7O_6$: C, 45.54; H, 1.91; N, 26.55. Found: C, 45.89; H, 1.99; N, 26.27.

2-Nitro-9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**2b**).

To an ice-cooled and stirred solution of **2** (0.800 g, 3.4 mmoles) in 85 ml of acetic acid, potassium nitrate (0.815 g, 8.0 mmoles) was added portionwise (≈ 2 hours). The ice-bath was removed and after ≈ 2 hours the monitro derivative **2b** began to precipitate as a yellow solid. The reaction mixture was stirred at room temperature for an additional 19 hours, then it was diluted with water and the solid precipitated was collected by filtration, 0.810 g, yield 85%, mp 206-209° from benzene; ir: ν 1460, 1360 (NO_2) cm^{-1}; ^{1}H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 279 (M^+), 224, 178, 104, 75.

Anal. Calcd. for $C_{14}H_9N_5O_2$: C, 60.21; H, 3.25; N, 25.08. Found: C, 60.54; H, 3.04; N, 24.77.

1-(2-Nitrophenyl)-4-carboxy-5-(4-nitrophenyl)-1*H*-1,2,3-triazole (**3a**).

To an ice-cooled and stirred solution of sodium ethoxide (0.280 g, 12 mmoles in 20 ml of absolute ethanol), a solution of *o*-nitrophenylazide (1.320 g, 8.0 mmoles) and ethyl *p*-nitrobenzoylacetate (2.280 g, 9.6 mmoles) in 150 ml of absolute ethanol was added dropwise during ≈ 2 hours. After 6 hours the ice-bath was removed and stirring was continued at room temperature for 62 hours. The reaction mixture was diluted with water and heated on a boiling water-bath for 1.5 hours. The solution obtained was concentrated *in vacuo*, diluted with water, washed with chloroform and acidified to give **3a** as a precipitate which was collected by filtration, 2.75 g, yield 97%, mp 160-162° from ethanol/water; ir: ν 3400 (OH), 1700 (C=O), 1520, 1350 (NO_2) cm^{-1}; ^{1}H nmr (chloroform-d + dimethyl sulphoxide-d_6): δ 7.65-8.45 (m, 8H, phenyl).

Anal. Calcd. for $C_{15}H_9N_5O_6$: C, 50.71; H, 2.55; N, 19.71. Found: C, 50.55; H, 2.47; N, 19.85.

1-(2-Nitrophenyl)-5-(4-nitrophenyl)-1*H*-1,2,3-triazole (**3b**).

A solution of **3a** (2.70 g, 7.6 mmoles) in 150 ml of toluene was heated under reflux for 4 hours. The solvent was evaporated *in vacuo* and the solid residue was treated with 6% sodium hydrogen carbonate solution. The insoluble material, consisting of **3b**, was collected by filtration and washed with water, 2.10 g, yield 85%, mp 199-201° from ethanol; ir: ν 1510, 1350 (NO_2) cm^{-1}; ^{1}H nmr (chloroform-d + dimethyl sulphoxide-d_6): δ 7.53-8.48 (m, 8H, aromatics), 8.26 (s, 1H, C4-H).

Anal. Calcd. for $C_{14}H_9N_5O_4$: C, 54.02; H, 2.91; N, 22.50. Found: C, 54.06; H, 2.91; N, 22.38.

9-(4-Nitrophenyl)-1,2,3-triazolo[1,2-*a*]benzotriazole (**2c**).

To a solution of **3b** (0.934 g, 3.0 mmoles) in 30 ml of cumene, 1.4 ml of triethyl phosphite were added and the mixture was heated at 150° for 19 hours, under a nitrogen stream. The solvent was distilled off under reduced pressure and the crude residue, dissolved in benzene, was chromatographed through a silica gel column (11 x 2.5 cm). Elution with the same solvent mixture allowed the isolation of **2c** which, after purification from dimethylformamide/water, appeared as an orange powder, 0.230 g, yield 27%, mp 283-285°; ir: ν 1490, 1360 (NO_2) cm^{-1}; ^{1}H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 279 (M^+), 224, 172, 151, 76.

Anal. Calcd. for $C_{14}H_9N_5O_2$: C, 60.21; H, 3.25; N, 25.08. Found: C, 60.48; H, 3.17; N, 25.26.

1-(2-Nitro-4-methyl-phenyl)-4-carboxy-5-phenyl-1*H*-1,2,3-triazole (**4a**).

To an ice-cooled and stirred solution of sodium ethoxide (0.600 g, 26.3 mmoles of sodium in 15 ml of absolute ethanol), a solution of 2-nitro-4-methylphenylazide [13] (2.600 g, 14.7 mmoles) and ethyl benzoylacetate (3.0 ml, 17.6 mmoles) in 15 ml of absolute ethanol was added dropwise. The reaction mixture was stirred at room temperature for 15 hours until a soft suspension was obtained which was diluted with water and heated on a boiling water-bath for 1 hour. The solution was concentrated *in vacuo*, washed with chloroform and acidified to precipitate **4a** as a yellow solid: 2.95 g, yield 62%, mp 158-161° from ethanol; ir: ν 1710 (C=O), 1460, 1360 (NO_2) cm^{-1}; ^{1}H nmr (chloroform-d + dimethyl sulphoxide-d_6): δ 2.53 (s, 3H, CH_3), 7.30-8.00 (m, 3H, C_6H_3), 7.41 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.25; H, 3.70; N, 17.28.

1-(2-Nitro-4-methyl-phenyl)-5-phenyl-1*H*-1,2,3-triazole (**4b**).

A solution of **4a** (1.90 g, 5.86 mmoles) in 30 ml of toluene was heated under reflux for 4 hours. The solvent was evaporated *in vacuo* and the solid residue was treated with 10% sodium hydroxide solution. The insoluble material, consisting of **4b**, was collected by filtration, 1.51 g, yield 92%, mp 158-161° from benzene; ir: ν 1490, 1350 (NO_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.56 (s, 3H, CH_3), 7.23-8.13 (m, 8H, aromatics), 7.96 (s, 1H, C4-H).

Anal. Calcd. for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 63.97; H, 4.42, N, 20.06.

1-(2-Amino-4-methylphenyl)-5-phenyl-1*H*-1,2,3-triazole (**4c**).

A solution of **4b** (1.51 g, 5.39 mmoles) in 50 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.300 g). The catalyst was filtered off, washed with boiling ethanol and the combined filtrates were evaporated to give a solid residue which was treated with 18% hydrochloric acid and extracted with ether. From the aqueous layer, by alkalinization with 20% sodium hydroxide, precipitated **4c** which was collected by filtration, 0.765 g, yield 57%, mp 126-128° from 60-80° petroleum ether; ir: ν 3450, 3360 (NH_2) cm^{-1}; ^1H nmr (chloroform-d): δ 2.33 (s, 3H, CH_3), 3.93 (broad, 2H, NH_2), 6.50-7.00 (m, 3H, C_6H_3), 7.40 (s, 5H, C_6H_5), 8.03 (s, 1H, C4-H).

Anal. Calcd. for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.94; H, 5.76; N, 22.68.

1-(2-Azido-4-methylphenyl)-5-phenyl-1*H*-1,2,3-triazole (**4d**).

To an ice-cooled and stirred solution of **4c** (1.0 g, 4.0 mmoles) in 18% hydrochloric acid (20 ml), a solution of sodium nitrite (0.3 g, 4.4 mmoles in 10 ml of water) was added drop by drop. After 30 minutes of stirring, a solution of sodium azide (0.33 g, 5.0 mmoles in 10 ml of water) was added dropwise and the title compound precipitated as a pale yellow solid. After 2 hours of stirring at room temperature the precipitate was collected by filtration and washed with water repeatedly: 1.06 g, yield 96%; mp 143-147° from benzene/40-60° petroleum ether; ir: ν 2100 (N_3) cm^{-1}; ^1H nmr (chloroform-d): δ 2.46 (s, 3H, CH_3), 7.06-7.66 (m, 3H, C_6H_3), 7.36 (s, 5H, C_6H_5), 7.96 (s, 1H, C4-H).

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.33; H, 4.46; N, 30.28.

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

A) To a solution of **4b** (1.41 g, 5.0 mmoles) in 10 ml of cumene, 2.5 ml of triethyl phosphite was added and the mixture was heated at 150° for 6 hours, under a nitrogen stream. The title compound **2d** precipitated as a brown solid which was collected by filtration and washed with benzene: 0.37 g, yield 30%, mp 155-158° from cyclohexane. An additional amount of **2d** (0.108 g) was obtained from the filtrate after evaporation *in vacuo* and crystallization of the crude brown residue from cyclohexane: total yield 38%.

B) A solution of the triazoloazide **4d** (0.79 g, 2.86 mmoles) in 2.5 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 washed with 60-80° petroleum ether portionwise, 0.588 g, yield 83%, mp 155-156°; ^1H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 248 (M^+), 192, 165, 102, 89.

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.83; H, 4.75; N, 22.61.

2-Nitro-3-methyl-9-phenyl-1,2,3-triazolo[1,2-*a*]benzotriazole (**2e**).

To an ice-cooled and stirred solution of **2d** (0.280 g, 1.12 mmoles) in 30 ml of acetic acid, potassium nitrate (0.288 g, 2.85 mmoles) was added portionwise (≈ 1 hour). The ice-bath was removed and after ≈ 1.5 hours the reaction mixture was heated at 60° for 1 hour then poured into crushed ice. A solid, consisting of a mixiure of products, precipitated and was collected by filtration and washed with water (0.290 g). Accurate crystallization of this mixture from benzene allowed the isolation of the pure mononitro derivative **2e**, 0.101 g, yield 31%, mp 234-237°; ir: ν 1500, 1340 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulphoxide-d_6): see Table I; ^{13}C nmr (dimethyl sulphoxide-d_6): see Table II; ms: m/z 293 (M^+), 238, 192, 89.

Anal. Calcd. for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88. Found: C, 61.16; H, 3.84; N, 23.62.

Acknowledgements.

This work was supported by Italian M.U.R.S.T.

REFERENCES AND NOTES

[1] R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962).

[2] R. A. Carboni, J. C. Kauer, J. E. Castle and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 2618 (1967).

[3] R. A.Carboni, J. C. Kauer, W. R. Hatchard and R. J. Harder, *J. Am. Chem. Soc.*, **89**, 2626 (1967).

[4] J. C. Kauer and R. A.Carboni, *J. Am. Chem. Soc.*, **89**, 2633 (1967).

[5] Y. T. Chia and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 2638 (1967).

[6] R. J. Harder, R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **89**, 2643 (1967).

[7] J. H. Hall, J. G. Stephanie and D. K. Nordstrom, *J. Org. Chem.*, **33**, 2951 (1968).

[8] J. H. Hall, *J. Org. Chem.*, **36**, 217 (1971).

[9] A. Albini, G. F. Bettinetti and G. Minoli, *J. Org. Chem.*, **48**, 1080 (1983).

[10] A. Albini, G. F. Bettinetti and G. Minoli, *J. Org. Chem.*, **49**, 2670 (1984).

[11] M. Witanowsky, J. Sicinska, S. Biernat and G. A. Webb, *Magn. Reson. in Chem.*, **27**, 88 (1989).

[12] P. A. S. Smith and J. H. Boyer in Organic Syntheses, Vol **31**, R. S. Screiber, ed, John-Wiley & Sons, New York, 1951, pp 14-16.

[13] Y. Tanaka, S. R. Velen and S. I. Miller, *Tetrahedron*, **29**, 3271 (1973).