Aromatic Systems with 10π Electrons derived from 3a-Azapentalene. Part 37.[1] Cyclization of the Anion of Azido-*s*-triazole into the Anion of *s*-Triazolo[2,3-*d*]tetrazole

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Two *N*-methyl derivatives of a novel bicyclic system with 10π electrons derived from 3a-azapentalene, *s*-triazolo-[2,3-*d*]tetrazole, have been synthesized and their structures established by comparison with known isomeric systems using ^1H and ^{13}C n.m.r., i.r., and mass spectra. Isomerization of the anion of azido-*s*-triazole to the anion of *s*-triazolo[2,3-*d*]tetrazole is confirmed.

In previous papers we showed that the azidoazomethine–tetrazole equilibrium was shifted completely to the azido-form in neutral molecules of several 3-azidopyrazoles [2] and 2-azidoimidazole,[3] and to the tetrazole form in the corresponding anions. Herein we report the more complex case of azido-*s*-triazoles.

RESULTS AND DISCUSSION

I.r. and n.m.r. spectra of 3-azido-*s*-triazoles (3) showed only the azido-form in solution in agreement with the literature.[4,5] In the basic medium, sodium hydride in dimethyl sulphoxide, we have now detected, for the first time, a mixture of the anions of the azide (5) and the bicyclic tetrazole, (6) or (7), in a ratio depending on the nature of the substituent R.†

Our principal aim was to determine whether the structure of the bicyclic tetrazole anion was of the *s*-triazolo[4,3-*d*]tetrazole type (6) or the *s*-triazolo[2,3-*d*]-tetrazole type (7). As previously with pyrazolo[1,5-*d*]-tetrazoles [2] we tried to trap the bicyclic *s*-triazolo-tetrazoles as the *N*-methyl derivatives. Methylation of the anion (6) could give a mixture of the compounds (4a and b), (8), and (9), whilst that of the anion (7) would yield compounds (4b and c), (10), and (11) (Scheme). The *N*-methyl-azides could not be used to distinguish between the two possibilities because of the presence of the anion (5) in the equilibrium mixture, since its methylation could afford products (4a—c) (Scheme). However, compounds (8) and (9) had been previously prepared unequivocally by one of us [6] by cyclisation of tetrazol-5-ylhydrazonyl bromides.

Results for methylation of the species (1), (3), and (5)—(7), are in Table 1. Alkylations of amino-*s*-triazoles gave different results when affected on the neutral molecule and the anion.[7] The 4-*N*-alkyl isomer (2c) was particularly difficult to obtain since it was only formed in appreciable proportions in the methylation of the neutral molecule and the overall reaction yield was poor in this case. Similar results were obtained for the azido-*s*-triazoles. When compound (3) was methylated in sodium hydroxide and methyl iodide, the derivatives (4a and b) were obtained suggesting the presence of the anion (5) only under these conditions and in order to obtain derivatives of the fused *s*-triazolotetrazole anion it was necessary to use the stronger aprotic medium sodium hydride in dimethyl sulphoxide.[2,3] Methylation of the mixture of anions in this latter medium gave five compounds, the azides (4a—c) and two *s*-triazolotetrazoles (10) and (11) (Scheme). The compounds (10) and (11) were different to the known [6] compounds (8) and (9),‡ and their presence confirms that the anion (5) is in equilibrium with the *s*-triazolo[2,3-*d*]tetrazole species (7). §

The bicyclic system with 10π electrons derived from 3a-azapentalene, *s*-triazolo[2,3-*d*]tetrazole, is described here for the first time. The anion of the azido-*s*-triazole (5) may cyclize on N(1) rather than N(4) because of

TABLE 1

Reactions (Scheme)

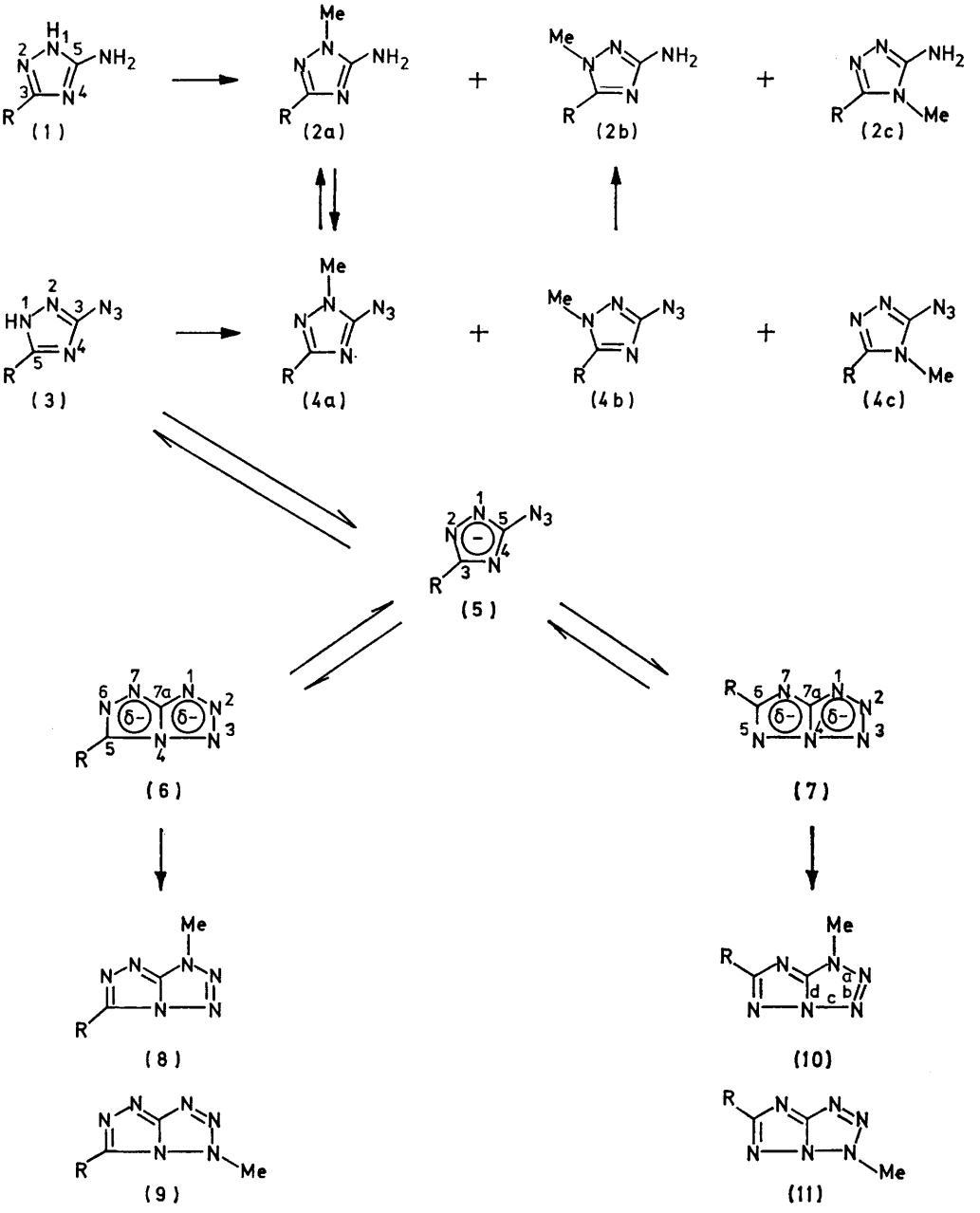
Substrate	Reagent, conditions	Overall product yield (%)	Isomer distribution (%)
(1)	CH_3I	30	(2a) 35; (2b) 20; (2c) 45
(1) anion	CH_3I	70	(2a) 55; (2b) 40; (2c) 5
(5)	CH_3I–NaOH	80	(4a) 40; (4b) 25; (4c) trace
(5) + (7)	CH_3I–NaH–DMSO	95	(4a) 35; (4b) 25; (4c) 5; (10) 25; (11) 10
(2a)	$NaNO_2$ NaN_3	40	(4a)
(4a)	$LiAlH_4$	46	(2a)
(4b)	$LiAlH_4$	65	(2b)

† Unless otherwise specified, R = Ph.

‡ We thank Mr. M. Cunningham for assistance with the preparation of a sample of compound (9).

§ For R = H the anion (5) also cyclized to the fused tetrazole (7) and the azido–tetrazole equilibrium constant in [$^2H_6$]DMSO at 27 °C was 0.45 (K = [(5)]/[(7)] = 0.45). For R = Ph the constant was 0.78 at 23 °C and 1.60 at 80 °C [determined from the intensities of the *o*-phenyl protons at 250 MHz (Table 2)].

the more nucleophilic character of N(1) which has the adjacent N(2), a type of α-effect which also appears in the methylation results. However, since the anions (5)—(7) are in equilibrium, a more desirable explanation might be based on the relative stability of the two bicyclic anions (6) and (7). Lack of theoretical data does not allow an assessment of the relative energies of these systems at the present time.



SCHEME

Structural Assignments.—All the compounds described gave satisfactory elemental analysis and for the bicyclic compounds the mass spectra eliminated any possible dimeric structures. Compounds (8) and (9) have been synthesized unequivocally,[6] and therefore the two new bicyclic compounds must have structures (10) and (11) (distinguished by n.m.r.). The structures of the isomeric azides (4a and b) and the amines (2a and b) were established by the n.m.r. data (Tables 2 and 3) and confirmed by the chemical reduction reactions (Table 1) which allowed compound (4a) to be directly related to the known compound (2a) (see Experimental section) and which allowed compound (4b) to be related to the other amine isomer (2b). These reductions of the azido- to the amino-group were achieved using lithium aluminium hydride in anhydrous ether.[8] The new method of Stanovnik *et al.*,[9] using acetylacetone and triethylamine for the reduction of heterocyclic azides to amines failed

TABLE 2

^{1}H N.m.r. data (δ; Me_4Si as standard) [a]

Compound	$CDCl_3$		$[^2H_6]DMSO$		CF_3CO_2H	
	C_6H_5	NCH_3	C_6H_5	NCH_3	C_6H_5	NCH_3
(1)	Insoluble		7.37 (*m,p*), 7.87 (*o*) (Δ = 0.50)		7.72 (*o,m,p*)	
(2a)	7.35 (*m,p*), 7.97 (*o*) (Δ = 0.62)	3.67	7.38 (*m,p*), 7.88 (*o*) (Δ = 0.50)	3.60	7.75 (*o,m,p*)	3.90
(2b)	7.47 (*o,m,p*) (Δ = 0.2)	3.76	7.57 (*o,m,p*) (Δ < 0.2)	3.71	7.67 (*o,m,p*) (s)	4.03
(2c)	Insoluble		7.60 (*o,m,p*) (s) (Δ = 0.0)	3.48	7.66 (*o,m,p*) (s)	3.73
(3)	7.52 (*m,p*), 7.93 (*o*) (Δ = 0.41)		7.55 (*m,p*), 7.97 (*o*) (Δ = 0.42)		7.83 (*o,m,p*)	
(4a)	7.33 (*m,p*), 7.95 (*o*) (Δ = 0.62)	3.61	7.43 (*m,p*), 7.90 (*o*) (Δ = 0.47)	3.60		
(4b)	7.51 (*o,m,p*) (s) (Δ = 0.0)	3.87	7.43 (*o,m,p*) (s) (Δ = 0.0)	3.86		
(4c)	7.37 (*o,m,p*) (s) (Δ = 0.0)	3.58	7.43 (*o,m,p*) (s) (Δ = 0.0)	3.54		
(5)			7.99 (*o*), 7.36 (*m*), 7.23 (*p*) [b]			
(7)			8.14 (*o*), 7.49 (*m*), 7.44 (*p*) [b]			
(8)	7.52 (*m,p*), 8.22 (*o*), (Δ = 0.70)	4.20	7.60 (*m,p*), 8.12 (*o*) (Δ = 0.52)	4.15		
(9)	7.51 (*m,p*), 8.20 (*o*) (Δ = 0.69)	4.60	7.58 (*m,p*), 8.08 (*o*) (Δ = 0.50)	4.64		
(10)	7.46 (*m,p*), 8.15 (*o*) (Δ 0.69)	4.20	7.50 (*m,p*), 8.13 (*o*) (Δ 0.63)	4.18	7.70 (*m,p*), 8.10 (*o*) 0.40	4.49
(11)	7.50 (*m,p*), 8.15 (*o*) (Δ 0.65)	4.53	7.55 (*m,p*) 8.20 (*o*) (Δ = 0.65)	4.56	7.75 (*m,p*), 8.18 (*o*) 0.43	4.80

[a] The phenyl signals are multiplets unless indicated as a singlet (s). [b] Measured at 250 MHz.

TABLE 3

Carbon n.m.r. shifts (p.p.m. from Me_4Si) of *s*-triazoles ($[^2H_6]DMSO$)

Compound	R = Ph Series							R = H Series		
	C-R	C-N	*ipso*-C	*ortho*-C	*meta*-C	*para*-C	N-Me	CR	CN	NMe
(1) [a]	158.4	158.5	131.5	125.7	128.4	128.5		148.0	158.4	
(2a)	157.1	156.5	132.2	125.5	128.6	128.6	33.6	148.0	155.4	33.3
(2b)	152.1	162.6	(129.3) [b]	128.1	128.6	129.3	36.0	143.0	164.2	35.3
(2c)	149.8	156.3	132.0	127.8	128.8	129.0	30.4	140.9	155.2	29.4
(3)	155.5	157.0	127.0	126.2	129.2	130.6		145.1	156.9	
(4a)	158.7	148.9	130.4	125.5	128.7	129.2	34.1	149.6	148.5	33.9
(4b)	154.7	155.7	131.9	128.6	128.8	130.4	37.2	145.5	157.8	36.6
(4c)	*c*							142.9	*b*	30.5
(5)	160.7	155.1	134.2	125.2	128.4	129.2		154.4	161.0	

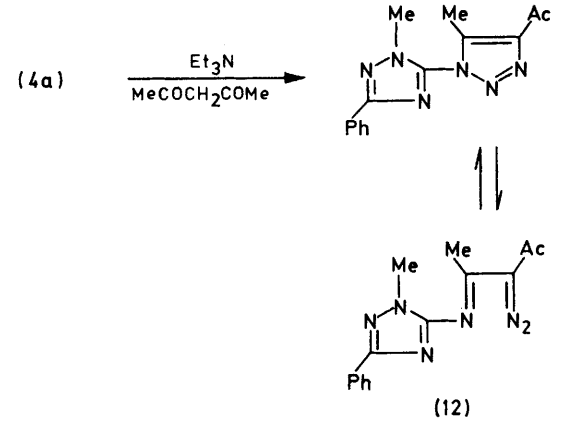
[a] Compound (1; R = Ph) recorded at 70 °C. At normal conditions (27 °C) signals of the heterocycle and *ipso*-C were broadened possibly due to slow proton exchange between N(1) and N(2). [b] Not observed. [c] The small quantities of this compound encountered were insufficient for a ^{13}C n.m.r. spectrum.

in the case of the azide (4a) and only the intermediate *v*-triazole (12) was isolated under the recommended [9] conditions. Possibly, the necessary *v*-triazole ⇌ diazoimine equilibrium is shifted appreciably to the diazoimine form only for azides of π-deficient heterocycles (all examples cited [9] are of this latter type).

^{1}H *and* ^{13}C *N.m.r. Spectra.*—^{1}H N.m.r. spectra for the series with R = phenyl are in Table 2. Derivatives of type a (Me group β to phenyl substituent) showed the phenyl signal as two complex multiplets (0.4 < Δ < 0.7 p.p.m.) due to coplanarity of the rings and extensive interannular conjugation.[10] In structures of type b and c (Me group α to phenyl substituent) the phenyl protons appeared at a singlet or a sharp multiplet (0.0 < Δ < 0.2 p.p.m.) due to decreased conjugation arising from steric interaction of the phenyl substituent and the α-methyl group.[10] A similar phenomenon [10] is observed for the carbon spectra (Table 3) in the shifts of C(2′) and C(3′). The shifts of the *N*-methyl groups on the *s*-triazolotetrazole ring system were δ 4.2 for derivatives (8) and (10) and δ 4.6 for compounds (9) and (11), corresponding respectively to the structural units =C–N(Me)–N= and =N–N(Me)–N≺,[11] and they allow a distinction of the

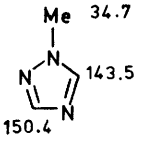
isomers (10) and (11) using this correlation as previously noted.[11]

^{13}C N.m.r. data for the amino- and azido-*s*-triazoles are in Table 3. It has been noted previously [11b] that the

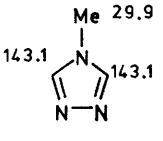


(12)

N-methyl shift permits a distinction between compounds of type c [=C–N(Me)–C= unit; δ(N–CH_3) *ca.* 30 p.p.m.] and types a and b [C–N(Me)–N= unit; δ(N–CH_3) *ca.* 33, series a, and *ca.* 36 p.p.m., series b]. Comparison of these values with the chemical shifts of the two parent *N*-methyl-*s*-triazoles (13) and (14) [12] ([$^2H_6$]DMSO) demonstrates that the substituent effects are effectively constant. On the *ipso*-carbon the amino-NH_2 group produced a shift of δ *ca.* +12 p.p.m., the azido-group a shift of δ *ca.* +6 p.p.m. and the phenyl group δ +9 p.p.m.



(13)



(14)

Comparison of the chemical shifts of the *N*-unsubstituted compounds with those of the *N*-methyl derivatives suggests that for the triazole series with R = Ph or H, the predominant tautomers have the structures (1) and (3) (Scheme). These results agree with those obtained from dipole-moment measurements on 5-amino- (1) [13] and 3-azido-1,2,4-triazole (3).[14]

^{13}C N.m.r. measurements for *s*-triazolotetrazoles are in Table 4. The *N*-methyl chemical shifts here follow the pattern of the proton shifts and they confirm the differentiation between compounds (8) and (10) [=C–N(Me)–N=; δ(N–CH_3) *ca.* 35 p.p.m.] and (9) and (11) [=N–N(Me)–N<; δ(N–CH_3) *ca.* 43.5 p.p.m.] by complying with the correlation previously applied to ^{13}C spectra of other azapentalenes [15] and tetrazoles.[11b] The chemical shifts of C(7a) also allowed such a distinction. In both cases the C(7a) shift paralleled that of the C(5) of monocyclic tetrazoles,[16] appearing at significantly lower field for isomers containing the '2-substituted tetrazole' moiety, *e.g.* (9) and (11), as against the '1-substituted tetrazole' moiety in compounds (8) and (10). Also of interest was the large difference in the C(5) [C(6)] shift (*ca.* 30 p.p.m.) depending on its location in the *s*-triazolo[4,3-*d*]tetrazole or *s*-triazolo[2,3-*d*]-tetrazole systems.

TABLE 4

Carbon n.m.r. shifts (p.p.m. from Me_4Si) of *s*-triazolotetrazoles ([$^2H_6$]DMSO)

Compound	R = Ph Series							R = H Series		
	C(5)[C(6)]	C(7a)	*ipso*-C	*ortho*-C	*meta*-C	*para*-C	N-Me	C(5)[C(6)]	C(7a)	N-Me
(7)	153.5	165.5	133.4	126.3	128.8	128.8		159.5	164.4	
(8)	139.7	154.5	128.4	124.8	129.3	130.0	34.4			
(9)	136.9	164.6	125.6	124.2	129.3	129.3	43.7			
(10)	168.4	150.2	132.6	126.6	128.9	130.6	35.1	159.3	*a*	35.2
(11)	169.0	156.2	133.1	126.9	129.0	130.8	43.2	159.9	*a*	43.3

[a] Signals not observed.

50 spectrometers, respectively. T.l.c. was carried out on Merck F_{254} silica gel plates. For column chromatography, silica gel 60 Merck, 70—230 mesh ASTM was used. Results of elemental analyses are given in Supplementary Publication No. SUP 22496 (12 pp.).*

The starting material (1; R = H) is commercially available and the following compounds were prepared according to literature procedures: (1; R = Ph), m.p. 191—193° (from water) (lit.,[17] 186—187°); (3; R = Ph), m.p. 193—194° (from methanol–water) (lit., 181—182,[5] 190—193° [18]).

Methylation of Compound (1; R = Ph).—The procedure used was similar to that described for 3(5)-amino-*s*-triazole (1; R = H) [7] in neutral and basic media with heating for 25 and 50 h respectively, in this case. The relative proportions of methyl derivatives obtained are in Table 1.

Separation of the three isomers (2a—c) was achieved by column chromatography using chloroform and chloroform–ethanol (1 : 1) as eluants. The elution order was (2b), (2a), and finally (2c). *5-Amino-1-methyl-3-phenyl-1,2,4-triazole* (2a) had m.p. 195—196° (from water) (lit.,[19] 190—191°); $\nu_{max.}$ (KBr) 3 460 and 3 360 cm^{-1} (NH_2); *3-amino-1-methyl-5-phenyl-1,2,4-triazole* (2b), m.p. 177—179°, $\nu_{max.}$ (KBr) 3 340 and 3 185 cm^{-1} (NH_2); and *2-amino-1-methyl-5-phenyl-1,3,4-triazole* (2c), m.p. 268—269° (decomp.), $\nu_{max.}$ (KBr) 3 260 and 3 100 cm^{-1} (NH_2).

Methylation of Compound (3; R = Ph).—(a) *Sodium*

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

EXPERIMENTAL

M.p.s were determined on a Buchi apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on Varian EM-360 and JEOL JNM-MH-100 spectrometers. ^{13}C N.m.r. spectra were obtained with a Varian CFT-20 instrument and a JEOL FX-60 machine. I.r. and mass spectra were taken with Perkin-Elmer model 577 and A.E.I. MS-

hydroxide in aqueous alcohol. When a mixture of the azide (3) (400 mg), ethanol (10 ml), water (10 ml), acetone (8 ml), 10% sodium hydroxide (1 ml), and methyl iodide (1 ml) was heated under reflux for 1 h, and treated with water while hot, compound (4a) (124 mg) separated. Fractional evaporation of the filtrate gave a 2 : 1 mixture (65 mg) of compounds (4a and b) which was separated by fractional crystallization. Further evaporation of the mother-liquor gave compound (4b) (99 mg crude). Ether extraction of the remaining mother liquor gave a brown gum (60 mg) showing *N*-methyl n.m.r. signals at δ 3.32, 3.38, and 3.44, one of which may be due to traces of compound (4c). Careful column chromatography of these gums failed to isolate compound (4c) but gave further small quantities of compounds (4a and b). *5-Azido-1-methyl-3-phenyl-1,2,4-triazole* (4a) had m.p. 93—95° (from ethanol), $\nu_{max.}$ (Nujol) 2 160 cm^{-1} (N_3); *3-azido-1-methyl-5-phenyl-1,2,4-triazole* (4b), m.p. 60.5—62° from aqueous ethanol), $\nu_{max.}$ (Nujol) 2 140 cm^{-1} (N_3).

(b) *Sodium hydride in DMSO.* A solution of compound (3) (1.86 g, 0.01 mol) and sodium hydride (50% in oil; 0.72 g, 0.015 mol) in the minimal amount of DMSO was kept at room temperature until the equilibrium between the azido (5) and tetrazole (7) forms was attained (checked by ^1H n.m.r. spectroscopy). Methyl iodide (3 ml, 0.05 mol) was then added and the mixture stirred for 24 h at ambient temperatures. The solution was cooled and treated with water until a precipitate was obtained (2.3 g, quantitative yield).

The insoluble residue was a mixture of isomers (4a and b), (10), (11), and (4c) whose relative proportions are indicated in Table 1. Chromatography through silica gel in benzene and benzene–chloroform yielded in the following order: (4a and b) identical with samples obtained previously by methylation of the anion (5); *1-methyl-6-phenyl-s-triazolo*[2,3-d]*tetrazole* (10), m.p. 150–152°, $\nu_{max.}$ ($CHCl_3$) 1 615, 1 600, 1 460, 1 450, 1 425, 1 365, 1 320, 1 275, 1 235, and 1 200 cm^{-1}, *m/e* 200 (M^+, 39%), 149 (11), 104 (12), 103 (100), and 77 (25); and *3-methyl-6-phenyl-s-triazolo*-[2,3-d]*tetrazole* (11), m.p. 182—184°, $\nu_{max.}$ ($CHCl_3$) 1 565, 1 445, 1 420, 1 400, and 1 350 cm^{-1}, *m/e* 200 (M^+, 26%), 129 (14), 103 (55), 78 (10), and 77 (100). The last product eluted was *2-azido-1-methyl-5-phenyl-1,3,4-triazole* (4c).

Compound (4a).—Compound (4a) was obtained by treating the corresponding amine (2a) (174 mg) in acetic acid (1.5 ml) with sodium nitrite in water (1M; 1.1 ml) at −10 °C for 10 min, followed by dropwise addition of aqueous sodium azide (1M; 1.3 ml) at 0 °C until gas evolution ceased. The mixture was neutralized with sodium hydrogencarbonate and the products extracted into chloroform. After evaporation of the chloroform, the mixture was separated by chromatography with benzene–chloroform to afford (4a) (40%) and the starting material (2a) (60%).

Reduction of Azides (4).—*Triazole* (2b). A solution of the azide (4b) (120 mg) in dry diethyl ether (20 ml) was treated with dropwise addition of an excess of lithium aluminium hydride also in dry diethyl ether (30 ml) and the mixture, which boiled during the mixing, was heated under reflux for 2 h, cooled, and treated with moist diethyl ether then dropwise addition of water. Insoluble salts were removed and the ether layer separated and evaporated to give plates of compound (2b), (72 mg, 67%) m.p. 177—179°, identical (mixed m.p. and i.r. spectra) with an authentic sample.

A similar reduction of compound (4a), using a larger excess of lithium aluminium hydride and a longer reflux time (4 h) gave *triazole* (2a) (46%) some of which separated with the insoluble salts and was extracted from them by leaching with diethyl ether. Attempted reduction of compound (2a) with acetylacetone and triethylamine as described [9] gave *1-(1-methyl-3-phenyl-1,2,4-triazol-5-yl)-4-methoxycarbonyl-5-methyl-1,2,3-triazole* (12) (90%), m.p. 136—137° (from chloroform) (Found: C, 59.7; H, 5.2; N, 29.2. $C_{14}H_{14}N_6O$ requires C, 59.6; H, 5.0; N, 29.75%), $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (C=O); δ($CDCl_3$) 2.74 (CH_3CO), 2.84 (CCH_3), 4.08 (NCH_3), 7.38—7.46 (3 H, *m*-, *p*-H), and 8.00—8.16 (2 H, *o*-H).

All compounds with R = H were prepared [20] by reaction similar to those described for the series with R = Ph.

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