Aromatic Systems with 10 π Electrons Derived from 3a-Azapentalene. XXIV. Synthesis of Pyrazolo[1,5-*d*]tetrazoles.

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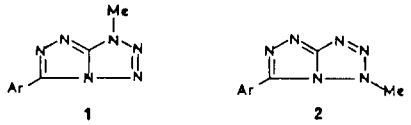
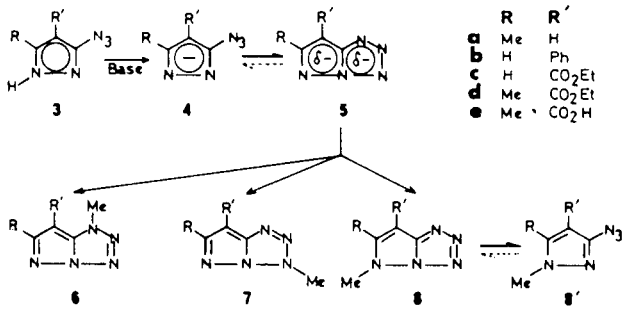
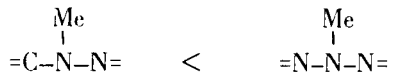
Fused tetrazoles with nitrogen-containing five membered rings can only be isolated if the tetrazole ring is *N*-substituted, as in the *s*-triazolo[4,3-*d*]tetrazoles **1** and **2** described by Butler (2,3).



Until now it has not been possible to build stable azolotetrazoles from the corresponding azoles (4). However, the methylation of the bicyclic anions **5** (5) afforded three monomethyl derivatives: 1-methylpyrazolo[1,5-*d*]-tetrazoles (**6**), 3-methylpyrazolo[1,5-*d*]tetrazoles (**7**) and 1-methyl-3-azidopyrazoles (**8′**).



The azides **8′** were characterized by infrared spectroscopy ($\nu_{as}N_3$ = 2140-2130 cm^{-1}) (6) and the structures of the two pyrazolo[1,5-*d*]tetrazole isomers **6** and **7** assigned on the basis of proton nmr spectroscopy using the relationship indicated by Butler (7) that the chemical shift (δ) of the *N*-methyl groups increases in the following order for the structure units **A** and **B**.



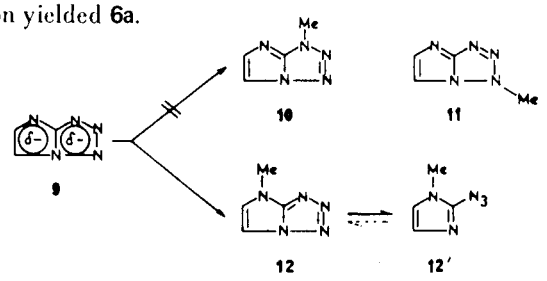
Because this relationship has been applied with success to compounds **1** and **2** (7) we extended the correlation to the products **6** and **7**. Data summarized in Table I shows that the signal of the 1-methyl isomer **6** is 0.30-0.35 ppm upfield from that of the corresponding 3-methyl isomer **7**. In the cases **c** and **d** in deuteriochloroform this signal is only 0.15 or 0.18 ppm upfield because of the effect of the carbethoxy group in the 7 position on the 1-methyl group of compounds **6**.

TABLE I

Values of the *N*-Methyl Chemical Shifts for the Derivatives Obtained by Methylation of the Bicyclic Anions **5**

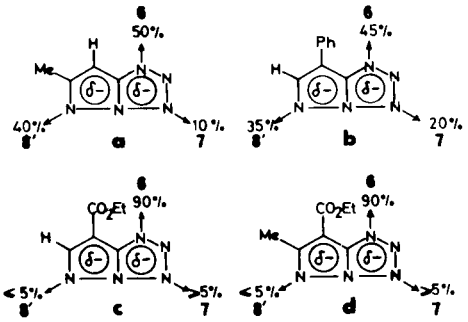
Compounds		**6**	**7**	**8′**
a	$CDCl_3$	4.04	4.37	3.65
R = Me, R′ = H	DMSO-d_6	4.08	4.40	3.64
b	$CDCl_3$	4.12	4.42	3.79
R = H, R′ = Ph	DMSO-d_6	4.21	4.54	3.80
c	$CDCl_3$	4.39	4.57	3.82
R = H, R′ = CO_2Et	DMSO-d_6	4.32	4.60	3.83
d	$CDCl_3$	4.34	4.49	3.70
R = Me, R′ = CO_2Et	DMSO-d_6	4.26	4.55	3.72

The difficult separation of the monomethyl derivatives **6**, **7** and **8′** was realized by column chromatography and fractional crystallisation. Only the following *N*-methylpyrazolo[1,5-*d*]tetrazole derivatives have been isolated as pure isomers: 1,6-dimethyl (**6a**), 3-methyl-7-phenyl (**7b**), 1-methyl-7-carbethoxy (**6c**) and 1,6-dimethyl-7-carbethoxy (**6d**). The compound **6d** gave by saponification the corresponding acid **6e**, which after decarboxylation yielded **6a**.



We also tried to apply this method to the preparation of imidazo[1,2-*d*]tetrazole derivatives **10** and **11**, but in this case the methylation of the bicyclic anion **9** (8) gave 1-methyl-2-azidoimidazole (**12'**).

The proportion of monomethyl derivatives obtained in all cases was determined by running the nmr of the mixture of the reaction in DMSO-d_6 (9).



EXPERIMENTAL

All melting points are uncorrected. The ir spectra were taken in potassium bromide on a Perkin Elmer Model 577 spectrometer. The nmr spectra were obtained in 10% solutions of deuterated dimethylsulfoxide or in deuteriochloroform with TMS as an internal standard, on a Varian T-60 instrument.

Methylation of Bicyclic Anions (**5**). General Procedure.

A mixture of compounds **3** (0.01 mole) and sodium ethoxide (0.1 mole) in dry ethanol was kept at room temperature until formation of the bicyclic anions (**5**) [the disappearance of the azido band was checked by infrared spectroscopy (3)]. Then, a solution of methyl iodide (0.1 mole) in absolute ethanol was added and the reaction mixture refluxed (5-10 hours) with stirring. After cooling, the mixture was concentrated under reduced pressure and the residual mass taken up in 200 ml. of cold water and neutralized with hydrochloric acid. The solution was extracted with ether several times, the ether extracts washed with sodium thiosulfate, dried, concentrated and the residue (80% yield) chromatographed (Silicagel 60 Merck, 70-230 mesh ASTM) using petroleum ether 50-70°, benzene and ether as eluents (cases **a** and **b**) or fractionally crystallized in methanol-water (cases **c** and **d**).

1,6-Dimethylpyrazolo[1,5-*d*]tetrazole (**6a**).

This compound was obtained in 40% yield, m.p. 88-91°; nmr (deuteriochloroform) δ: 2.41 (s, C-CH_3); 4.03 (s, N-CH_3); 5.60 (s, H_7); (DMSO-d_6) δ: 2.33 (s, C-CH_3); 4.08 (s, N-CH_3); 5.87 (s, H_7); ir (potassium bromide) ν max cm^{-1}: 1605, 1465, 1445, 1440, 1380, 1370, 1320, 1265, 1008, 1003, 770, 658 and 650.

Anal. Calcd. for $C_5H_7N_5$: C, 43.8; H, 5.1; N, 51.1. Found: C, 43.7; H, 5.0; N, 51.1.

3-Methyl-7-phenylpyrazolo[1,5-*d*]tetrazole (**7b**).

This compound was obtained in 15% yield, m.p. 139-140°; nmr (deuteriochloroform) δ: 4.45 (s, N-CH_3); 8.23 (s, H_6), 7.2-7.8 (m, phenyl protons); (DMSO-d_6) δ: 4.54 (s, N-CH_3); 8.50 (s, H_6), 7.15-7.8 (m, phenyl protons); ir (potassium bromide) ν max cm^{-1}: 1608, 1440, 1190, 988, 762, 695 and 662.

Anal. Calcd. for $C_{10}H_9N_5$: C, 60.3; H, 4.5; N, 35.2. Found: C, 60.3; H. 4.4; N, 35.0.

1-Methyl-7-carbethoxypyrazolo[1,5-*d*]tetrazole (**6c**).

This compound was obtained in 70% yield, m.p. 67-68°; nmr (deuteriochloroform) δ: 1.39 (t, CH_3); 4.32 (q, CH_2); 4.40 (s, N-CH_3); 8.14 (s, H_6): (DMSO-d_6) δ: 1.33 (t, CH_3): 4.28 (q, CH_2): 4.32 (s, N-CH_3); 8.25 (s, H_6); ir (potassium bromide) ν max cm^{-1}: 1680, 1620, 1490, 1480, 1380, 1280, 1240, 1180, 1120, 1080, 770 and 740.

Anal. Calcd. for $C_7H_9N_5O_2$: C, 43.1; H, 4.6; N, 35.9. Found: C, 42.9; H, 4.5; N, 36.0.

1,6-Dimethyl-7-carbethoxypyrazolo[1,5-*d*]tetrazole (**6d**).

This compound was obtained in 70% yield, m.p. 97-98°; nmr (deuteriochloroform) δ: 1.40 (t, CH_3); 4.34 (q, CH_2); 2.58 (s, C-CH_3); 4.36 (s, N-CH_3); (DMSO-d_6) δ: 1.33 (t, CH_3); 4.24 (q, CH_2); 2.46 (s, C-CH_3); 4.26 (s, N-CH_3); ir (potassium bromide) ν max cm^{-1}: 1690, 1615, 1470, 1460, 1300, 1290, 1250, 1168, 1140, 1100, 1030, 1008, 775 and 668.

Anal. Calcd. for $C_8H_{11}N_5O_2$: C, 31.5; H, 3.6; N, 22.9. Found: C, 31.4; H, 3.5; N, 22.8.

1,6-Dimethylpyrazolo[1,5-*d*]tetrazole-7-carboxylic Acid (**6e**).

Compound **6d** (0.002 mole) and sodium hydroxide (0.02 mole) in 10 ml. of water were refluxed during 2 hours. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in 40 ml. of water and acidified with 6*N* hydrochloric acid until the product **6e** precipitates. The solid was filtered, washed with water and dried (yield 90%), m.p. 224-225°; nmr (DMSO-d_6) δ: 2.48 (s, C-CH_3); 4.28 (s, N-CH_3); ir (potassium bromide) ν max cm^{-1}: 3020-2920, 1725, 1715, 1600, 1490, 1235, 1120, 1108, 932, 780 and 660.

Anal. Calcd. for $C_6H_7N_5O_2$: C, 39.8; H, 3.9; N, 38.7. Found: C, 39.2; H, 3.8; N, 39.0.

Compound **6e** heated in a sand bath (T ~ 270°) afforded **6a**.

Methylation of the Imidazo[1,5-*d*]tetrazole Anion (**9**).

A mixture of 2-azidoimidazole (0.01 mole) and sodium hydride (0.1 mole) in dimethylsulfoxide was kept at room temperature until formation of the bicyclic anion **9** [nmr (DMSO-d_6/HNa) δ: 7.21 (d, 1H); 7.43 (d, 1H), J = 1.2 Hz]. Then an excess of methyl iodide (0.12 mole) was added and the reaction mixture stirred at room temperature for 6 hours; 200 ml. of cold water were added carefully and, after neutralization with hydrochloric acid, the solution was extracted with ether. After evaporation of the ether extracts 1-methyl-2-azidoimidazole was obtained (liquid); nmr (DMSO-d_6) δ: 3.43 (s, N-CH_3): 6.76 (d, 1H); 6.96 (d, 1H), J_{45} = 1.5 Hz.

REFERENCES AND NOTES

(1) Present address: Laboratoire de Chimie Moléculaire, Université d'Aix-Marseille III, 13397 Marseille Cedex, France.

(2) R. N. Butler, *Chem. Ind.* (London), 371 (1973).

(3a) E. Alcalde, J. de Mendoza, and J. Elguero, *J. Chem. Soc., Chem. Commun.*, 411 (1974); (b) E. Alcalde, J. de Mendoza, and J. Elguero, *J. Heterocyclic Chem.*, **11**, 921 (1974).

(4) *s*-Triazolo[4,3-*d*]tetrazoles **1** and **2** were obtained by cyclization of arylidene-*N*-methyltetrazol-5-yl-hydrazidic bromides

(2).

(5) In previous papers (3) we described that the anions of 3-azidopyrazoles (**4**) cyclises to the bicyclic anions **5**.

(6) The methylation of *N*-unsubstituted 3-azidopyrazoles (**3**) in neutral conditions afforded only compounds **8'** (3).

(7) R. N. Butler, *Can. J. Chem.*, **51**, 2315 (1973).

(8) E. Alcalde and R. M. Claramunt, *Tetrahedron Letters*, 1523 (1975).

(9) There is a 20% of unidentified products.

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