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2*H*,5*H*-Triazolo[4,5-*d*]triazoles. A New Heteroaromatic System

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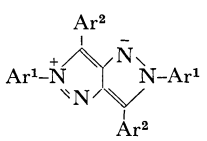
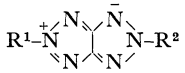
2-Aryl-5-phenyltriazolo[4,5-*d*]triazoles and related compounds, a new heteroaromatic system, have been prepared from 4,5-diamino-2-phenyl-1,2,3-triazole. The meso-ionic character of the new ring system is discussed on the basis of proton NMR shifts.

Syntheses of 2,3,5,6-tetraaryl-1,2,4,5-tetraazapentalenes (I), meso-ionic heteroaromatics, have recently been described.[1] A further replacement of the ring carbon atoms by nitrogen may yield another stable azapentalene. This paper presents the synthesis of 2-aryl-5-phenyl-1,2,3,4,5,6-hexaazapentalenes (2-aryl-5-phenyltriazolo[4,5-*d*]triazoles, II: $R^1=C_6H_5$, $R^2=Ar$) and related compounds.



I



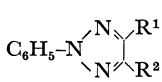
II: $R^1=C_6H_5$, $R^2=Ar$
XI: $R^1=C_6H_5$, $R^2=CH_3$
XII: $R^1=C_6H_5$, $R^2=$cyclo-C_6H_{11}
XIII: $R^1=R^2=$cyclo-C_6H_{11}

Condensation of 4,5-diamino-2-phenyl-1,2,3-triazole[2] (III) with nitrosobenzene in aqueous potassium hydroxide yielded 4-amino-2-phenyl-5-phenylazo-1,2,3-triazole, $C_{14}H_{12}N_6$ (IV, 72%), mp 206—208°C. Diazotization of the aminotriazole (IV) by means of sodium nitrite and hydrochloric acid followed by treatment with aqueous sodium azide precipitated 4-azido-2-phenyl-5-phenylazo-1,2,3-tri-

1) J. H. Lee, A. Matsumoto, O. Simamura and M. Yoshida, *Chem. Commun.*, **1969**, 1393.

2) J. Thiele and K. Schleussner, *Ann. Chem.*, **295**, 129 (1897).

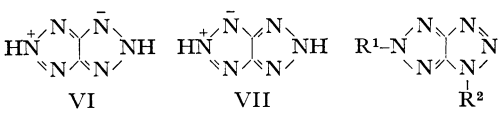
azole, yellow needles, $C_{14}H_{10}N_8$ (V, 76%), which did not show any definite melting point owing to gradual decomposition on heating, the structure being confirmed on the basis of its IR spectrum (ν_{N_3} 2120 cm^{-1}) and analytical data. On being heated gently in decahydronaphthalene until nitrogen evolution ceased, it gave an almost quantitative yield of colorless leaflets, $C_{14}H_{10}N_6$, mp 249°C, sparingly soluble in ordinary organic solvents. This compound shows ultraviolet absorption maxima at 231 and 342 nm (log ε 4.1 and 4.6, respectively) in ethanol. The mass spectrum shows a molecular ion at 262, which was 53% of the base peak at 77. Thus, the compound was assigned the structure of 2,5-diphenyltriazolo[4,5-*d*]triazole (II: Ar=C_6H_5) on the ground of its mode of formation and of its spectral and analytical data.



III: $R^1=R^2=NH_2$
IV: $R^1=C_6H_5N_2$, $R^2=NH_2$
V: $R^1=C_6H_5N_2$, $R^2=N_3$

The following triazolo[4,5-*d*]triazoles have been prepared in a similar way: II (Ar=*p*-$CH_3\cdot C_6H_4$), mp 233—234°C; II (Ar=*p*-$Cl\cdot C_6H_4$), mp 265.5—266.0°C; II (Ar=*p*-$(CH_3)_2N\cdot C_6H_4$), mp 285—286°C.

The parent structure underlying these compounds, 2*H*,5*H*-triazolo[4,5-*d*]triazole, comprises ten π-electrons distributed over the two rings and is satisfactorily represented only by the resonance of several charge-separated structures such as VI and VII, while its isomer, 1*H*,5*H*-triazolo[4,5-*d*]triazole, is represented by structure VIII without any charge-separation in the ground state. The effect of positive charge situated on positions 2 and 5 in derivatives of 2*H*,5*H*-isomer should be reflected in low field shift of proton NMR signals of substituents at positions 2 and 5. The following observations substantiate this view.



VI VII VIII

VIII: $R^1=R^2=H$
IX: $R^1=C_6H_5$, $R^2=H$
X: $R^1=C_6H_5$, $R^2=CH_3$

Treatment of the silver salt of 5-phenyl-1*H*-triazolo[4,5-*d*]triazole[2] (IX) with excess of methyl iodide in boiling benzene afforded two mono-methylated products, $C_9H_8N_6$ (X, 51%), mp 139.2—139.8°C and $C_9H_8N_6$ (XI, 27%), mp 149.0—149.8°C. The NMR spectrum of X shows a sharp singlet at τ 5.72 (3H) and two multiplets centered at τ 2.54 (3H) and 1.87 (2H) corresponding to methyl and phenyl protons, respectively. The NMR spectrum of XI exhibits three signals at τ 5.47, 2.48 and 1.69 quite similar in appearance to those of X. The fact that the signals from XI are all shifted to lower field regions relative to the corresponding ones of X leads to the assignment of the structure of 2-methyl-5-phenyltriazolo[4,5-*d*]triazole to XI and that of 1-methyl-5-phenyltriazolo[4,5-*d*]triazole to X, because the low field shift is attributable to positive charges at positions 2 and 5 due to the meso-ionic structure of XI causing deshielding of the relevant protons, while such a charge is absent from structure VIII. Analogous deshielding of protons due to positive nature of nuclear positions is found in the methyl protons (τ 5.99) of 1,3-dimethylimidazolium iodide[3] in comparison with those (τ 6.33) of 1-methylimidazole.[4]

Catalytic hydrogenation of II (Ar=C_6H_5) with platinum oxide in acetic acid at room temperature gave two products without ring-opening, $C_{14}H_{16}N_6$ (XII, 30%), mp 128.5—129.5°C, and $C_{14}H_{22}N_6$ (XIII, 15%), mp 171.0—171.2°C. XII was assigned the structure of 2-cyclohexyl-5-phenyltriazolo-[4,5-*d*]triazole, and XIII, that of 2,5-dicyclohexyltriazolo[4,5-*d*]triazole on the basis of spectral and analytical data. The NMR shifts of these compounds are recorded in Experimental part; the phenyl protons and the methine protons in a cyclohexyl group are found shifted more or less to lower field regions than the usual positions, obviously because of the deshielding effect of the positively charged nitrogen at positions 2 and 5.

Experimental

4-Amino-2-phenyl-5-phenylazo-1,2,3-triazole (IV). To a suspension of 4,5-diamino-2-phenyl-1,2,3-triazole[2] (8.5 g) in a mixture of 5 m*l* of benzene and 85 m*l* of 50% sodium hydroxide solution heated at 60°C was added nitrosobenzene (5.1 g) in small portions over a period of 10 minutes. The mixture was stirred for a further 10 minutes at 60°C. On pouring it into 900 m*l* of water it gave 4-amino-2-phenyl-5-phenylazo-1,2,3-triazole as brownish red precipitate (9.5 g, 72%), mp 206—208°C (from benzene).

Found: C, 63.64; H, 4.34; N, 31.96%. Calcd for $C_{14}H_{12}N_6$: C, 63.62; H, 4.58; N, 31.80%.

4-Azido-2-phenyl-5-phenylazo-1,2,3-triazole (V). 4-Amino-2-phenyl-5-phenylazo-1,2,3-triazole (4.3 g) was dissolved by heating in 70 m*l* of concentrated hydrochloric acid. A slurry of the amine hydrochloride formed upon cooling was diluted with 14 m*l* of water and diazotized by addition of a solution of sodium nitrite (1.2 g) in 15 m*l* of water over a period of 30 min at 0—5°C. The mixture was stirred for an additional hour to complete the reaction at 0—5°C. The resulting diazonium solution was filtered to remove a small amount of insoluble material. A solution of sodium azide (1.5 g) in 20 m*l* of water was added to the filtrate over a period

3) C. G. Overberger, J. C. Salamone and S. Yaroslavsky, *J. Org. Chem.*, **30**, 3580 (1965).

4) G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *J. Amer. Chem. Soc.*, **84**, 336 (1962).

of 30 min at 0—5°C, during which violent nitrogen evolution was observed. Stirring was continued for 10 min to complete the reaction at 0—5°C. The yellow solid deposited was collected to yield 3.6 g of 4-azido-2-phenyl-5-phenylazo-1,2,3-triazole (76%). This crude material was carefully recrystallized from methanol to give yellow needles, which softened at 159—161°C, but changed to infusible white crystals at elevated temperatures.

Found: C, 58.05; H, 3.20; N, 38.47%. Calcd for $C_{14}H_{10}N_8$: C, 57.93; H, 3.47; N, 38.60%.

2,5-Diphenyltriazolo[4,5-*d*]triazole (II: Ar=C_6H_5). 4-Azido-2-phenyl-5-phenylazo-1,2,3-triazole (2.5 g) in 300 m*l* of decahydronaphthalene was heated gently at 105—115°C with stirring. After vigorous evolution of nitrogen had ceased, the temperature was raised to 160°C to complete the decomposition. The reaction mixture, upon cooling to room temperature, deposited crystals of 2,5-diphenyltriazolo[4,5-*d*]triazole, which were filtered off, and the filtrate was concentrated to 20 m*l* under reduced pressure to give a second crop. The total yield of the crude products was almost quantitative. The combined products were recrystallized three times from benzene (with active charcoal) to give 1.74 g of colorless leaflets, mp 249°C.

Found: C, 64.39; H, 3.84; N, 32.14%. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.05%.

2-Phenyl-5-*p*-tolyltriazolo[4,5-*d*]triazole (II: Ar=*p*-$CH_3 \cdot C_6H_4$). This compound (Found: C, 65.04; H, 4.41; N, 30.50%. Calcd for $C_{15}H_{12}N_6$: C, 65.20; H, 4.38: N, 30.42%.), mp 233—234°C (from ligroin and benzene), was prepared from 4,5-diamino-2-phenyl-1,2,3-triazole and *p*-methylnitrosobenzene through 4-amino-2-phenyl-5-*p*-tolylazo-1,2,3-triazole, mp 208°C (Found: C, 64.88; H, 4.99; N, 30.26%. Calcd for $C_{15}H_{14}N_6$: C, 64.73; H, 5.03; N, 30.20%.), and 4-azido-2-phenyl-5-*p*-tolylazo-1,2,3-triazole, mp 115°C (dec.), in a way similar to the above.

5-*p*-Chlorophenyl-2-phenyltriazolo[4,5-*d*]triazole (II: Ar=*p*-Cl·C_6H_4). This compound (Found: C, 56.90; H, 3.48; N, 29.12%. Calcd for $C_{14}H_9N_6Cl$: C, 56.67; H, 3.06; N, 28.32%.), mp 265.5—266.0°C (from benzene), was prepared from 4,5-diamino-2-phenyl-1,2,3-triazole and *p*-chloronitrosobenzene, through 4-amino-5-*p*-chlorophenylazo-2-phenyl-1,2,3-triazole, mp 239°C (Found: C, 56.21; H, 4.03; Cl, 11.18%. Calcd for $C_{14}H_{11}N_6Cl$: C, 56.28; H, 3.71; Cl, 11.53%.), and 4-azido-5-*p*-chlorophenylazo-2-phenyl-1,2,3-triazole, in a way similar to the above except for the preparation of the azidoazotriazole.

This azidoazotriazole was prepared as follows: 4-Amino-5-*p*-chlorophenylazo-2-phenyl-1,2,3-triazole (0.71 g) in 15 m*l* of concentrated sulphuric acid was added to a solution of sodium nitrite (0.195 g) in 10 m*l* of concentrated sulphuric acid over a period of 10 min at room temperature. The mixture was stirred for 20 min at room temperature and poured into a large amount of ice water. It was treated with sodium azide (0.20 g) and left at room temperature with stirring for an hour. 4-Azido-5-*p*-chlorophenylazo-2-phenyl-1,2,3-triazole was obtained as yellow precipitate (0.70 g, 91%), which did not show any definite melting point owing to gradual decomposition on heating. The infrared spectrum showed a peak at 2130 cm^{-1} corresponding to the azido stretching vibration.

5-Dimethylaminophenyl-2-phenyltriazolo[4,5-*d*]-triazole (II: Ar=*p*-$(CH_3)_2N \cdot C_6H_4$). 4-Amino-5-*p*-dimethylaminophenylazo-2-phenyl-1,2,3-triazole[2] was converted, as described for the preparation of II (Ar=C_6H_5), into 5-dimethylaminophenyl-2-phenyltriazolo-[4,5-*d*]triazole (Found: C, 62.88; H, 4.72; N, 32.29%. Calcd for $C_{16}H_{15}N_7$: C, 62.94; H, 4.95; N, 32.11%.), mp 285—286°C (from benzene and dioxane).

1-Methyl- and 2-Methyl-5-phenyltriazolo[4,5-*d*]-triazole (X and XI). 5-Phenyl-1*H*-triazolo[4,5-*d*]-triazole[2] (0.50 g) was dissolved in 10 m*l* of concentrated ammonium hydroxide and treated with a solution of silver nitrate (0.60 g) in 5 m*l* of concentrated ammonium hydroxide. The mixture was stirred for 10 min at room temperature and the pale yellow precipitate was collected and washed with water to yield 0.79 g of the silver salt of 5-phenyl-1*H*-triazolo[4,5-*d*]triazole (92%). The silver salt (0.77 g) was heated in a mixture of benzene (15 m*l*) and methyl iodide (1.5 m*l*) under reflux for 3 hr. On cooling, the supernatant solution was separated from precipitate by decantation and the residue was treated with benzene—methyl iodide solution twice more as above. Then, the precipitate was separated by filtration and washed with benzene. The combined benzene solutions gave 0.495 g of a light yellowish brown solid on evaporation of the solvent under reduced pressure. The crude material (0.20 g) was subjected to purification by preparative thin-layer chromatography on silica gel. After development with dichloromethane, the bands having R_f values of 0.24—0.36 and 0.37—0.44 were scraped off the plates and eluted with ethanol. Evaporation of the eluants gave 0.118 g of X (51%) and 0.064 g of XI (27%).

1-Methyl-5-phenyltriazolo[4,5-*d*]triazole (Found: C, 53.92; H, 3.78; N, 42.05%. Calcd for $C_9H_8N_6$: C, 53.99; H, 4.03; N, 41.98%.), X: mp 139.2—139.8°C (from ethanol); UV max. (ethanol) 299, 223 nm (log ε=4.33, 3.86, respectively).

2-Methyl-5-phenyltriazolo[4,5-*d*]triazole (Found: C, 54.11; H, 4.11; N, 41.89%. Calcd for $C_9H_8N_6$: C, 53.99; H, 4.03; N, 41.98%.), XI: mp 149.0—149.8°C (from ethanol); UV max. (ethanol) 301, 226 nm (log ε=4.40, 3.79, respectively).

Catalytic Hydrogenation of 2,5-Diphenyltriazolo-[4,5-*d*]triazole. 2,5-Diphenyltriazolo[4,5-*d*]triazole (0.99 g) in 250 m*l* of acetic acid was hydrogenated over platinum oxide (0.206 g) for 58 hr at room temperature. Insoluble starting material (0.125 g) was recovered by filtration. The filtrate was concentrated to 20 m*l* and poured into a large volume of water. The precipitate formed was filtered off to yield 0.615 g of colourless material. The crude material (0.13 g) was subjected to purification by preparative thin-layer chromatography on silica gel. After development with benzene, the bands having R_f values of 0.08—0.16, 0.18—0.32 and 0.35—0.52 were scraped off the plates and eluted with ethanol and chloroform and gave, on evaporation of the eluant, 0.022 g of 2,5-dicyclohexyltriazolo[4,5-*d*]triazole (XIII, 15%), 0.044 g of 2-cyclohexyl-5-phenyltriazolo[4,5-*d*]-triazole (XII, 30%) and 0.036 g of the starting material, respectively.

2-Cyclohexyl-5-phenyltriazolo[4,5-*d*]triazole (Found: C, 62.94; H, 5.95; N, 28.77%. Calcd for $C_{14}H_{16}N_6$: C, 62.67; H, 6.01; N, 31.32%.), XII: mp 128.5—129.5°C (from ethanol); UV max. (ethanol) 304, 216 nm (log ε=4.52, 3.93, respectively); NMR ($CDCl_3$) τ 8.27 (m, 10H, cyclohexyl *H*), 5.22 (broad s, 1H, methine *H*),

2.55 (m, 3H, phenyl *H*), 1.74 (m, 2H, phenyl *H*).

2,5-Dicyclohexyltriazolo[4,5-*d*]triazole (Found: C, 61.07; H, 8.33; N, 30.33%. Calcd for $C_{14}H_{22}N_6$: C, 61.29; H, 8.08; N, 30.63%.), XIII: mp 171.0—171.2°C (from ethanol); UV max. (ethanol) 258 nm (log ε=4.43); NMR ($CDCl_3$) τ 8.2 (m, 10H, cyclohexyl *H*), 5.4 (broad s, 1H, methine *H*).