Preparations and Properties of 5-Phenyl-5*H*[1,2,3]-triazolo[4,5-*c*][1,2,5]-oxadiazole, -thiadiazole, and -selenadiazole

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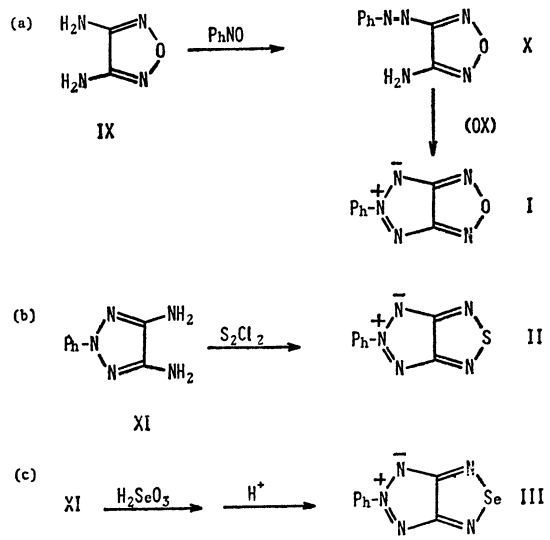
The title compounds have been synthesized, and their chemical reactivities and spectroscopic properties are discussed in comparison with those of 2,5-diphenyl-*v*-triazolo[4,5-*d*]-*v*-triazole.

The preparations and properties of some meso-ionic 1,2,4,5-tetra-aza- as well as 1,2,3,4,5,6-hexa-aza-pentalenes were described previously.[1,2] These investigations and a polarographic study of azapentalenes have shown that the major factor affecting the properties of the above polyazapentalenes is the number of nitrogen atoms in the azapentalene nucleus.[3] Thus, it seemed of interest to examine the physical and chemical consequences of replacing one of the nitrogen atoms in the polyazapentalene nucleus with another electronegative atom such as oxygen, sulphur, and selenium. This paper presents the syntheses and properties of a series of new heteropentalenes, 5-phenyl-5*H*[1,2,3]-triazolo[4,5-*c*][1,2,5]-oxadiazole (I), -thiadiazole (II), and -selenadiazole (III), in which a hetero atom at position 2 contributes two π-electrons to the π-electronic system of the nucleus.

The preparative routes to these compounds are summarized in Scheme 1. The details of the synthetic procedures are given in the Experimental Part.



Scheme 1. The Preparative Routes to Heteropentalenes.

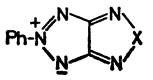
The behaviour of these heteropentalenes under oxidizing or reducing conditions is particularly interesting. Whereas 2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes are readily oxidized or reduced with ring-opening,[1,3] 2,5-diphenyl-hexa-azapentalene (V) is entirely resistant to oxidation and is catalytically hydrogenated to yield products with the azapentalene nucleus being left intact, *viz.*, 2,5-dicyclohexyl-(VIII) and 2-cyclohexyl-5-phenyl-hexa-azapentalene (VI).[2] These results caused us to examine the reactions of the triazolothiadiazole (II) under similar conditions. It was resistant to oxidation with *m*-chloroperoxybenzoic acid in chloroform or with hydrogen peroxide in acetic acid. Heated at 95 °C for 9 hr with potassium permanganate in a mixture of pyridine and water (10 : 1), however, it underwent extensive oxidation giving no isolable compounds. On the other hand, the triazolothiadiazole (II) was not hydrogenated at 1 atm of hydrogen with platinum catalyst under acidic conditions. Possible poisoning of the catalyst by the sulphur-containing substrate was suspected, but an excess of catalyst did not effect the reduction. However, reduction with lithium aluminium hydride in tetrahydrofuran occurred readily at room temperature, giving 4,5-diamino-2-phenyl-*v*-triazole (XI) in 90% yield.

The triazolooxadiazole (I) was resistant to attack by *m*-chloroperoxybenzoic acid, a result not unexpected in view of the stability of II described above.

The ultraviolet and NMR spectral characteristics and the half-wave reduction potentials of these heteropentalenes (I–III) as well as those of phenyl-substituted hexa-azapentalenes (IV–VII) are listed in Tables 1 and 2. All of these compounds exhibit two ultraviolet absorption maxima without vibrational structure. It is noteworthy that the absorption peaks of compounds I, II, and and III show an appreciable shift to longer wavelength regions according as the atom at position 2 varies from O to S to Se; this effect is particularly pronounced with the maxima of the longer wavelength. Obviously, electronic conjugation occurs between the nitrogen-containing system and the hetero atom at position 2.

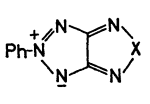
In view of the apparent similarity in reactivity observed between compounds II and V, the polarographic reduction of these compounds was examined. As shown in Table 2, the half-wave potentials of compounds II and III are strikingly higher than those of the hexa-azapentalenes, IV–VII. Apparently, the difference is attributable to the effect of a sulphur or selenium atom present in the nucleus in place of a nitrogen, although

TABLE 1. ABSORPTION MAXIMA OF PHENYL-SUBSTITUTED HETEROPENTALENES IN ETHANOL

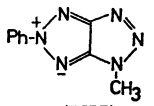

(I—V)

	X	λ_{max} in nm (log ε)
I	O	319(4.27), 234(3.59)
II	S	337(4.47), 235(3.61)
III	Se	365(4.52), 238(3.74)
IV	NCH_3	301(4.40), 226(3.79)
V	NPh	342(4.62), 231(4.11)

Table 2. Chemical shifts (τ) in $CDCl_3$ and polarographic half-wave reduction potentials (*vs.* Hg pool) for 5-phenyl-substituted heteropentalenes



(I–VI)



(VII)

		(*o*-H)	(*m*, *p*-H)	$-E_{1/2}$	(i_d/c)
I	O	1.51	2.32		
II	S	1.55	2.41	0.28	(3.1)
III	Se	1.44	2.37	0.21	(3.1)
IV	NCH_3	1.69	2.48	0.90	(3.4)
V	NPh	1.62	2.45	0.62	(3.2)
VI	NC_6H_{11}	1.74	2.55	0.94	(2.7)
VII		1.87	2.54	1.06	(4.3)

$E_{1/2}$: Half-wave reduction potential (V) for the first wave in dimethylformamide containing tetra-*n*-butylammonium iodide (0.155 M) as supporting electrolyte.
i_d: Diffusion current in μA.
c: Concentration (mmol/l).

nitrogen is more electronegative than sulphur.[4]

In these phenyl-substituted heteropentalenes, the phenyl group may be regarded as almost coplanar with the bicyclic nucleus, since large bathochromic shifts are observed in the ultraviolet absorption spectra of phenyl substituted hexa-azapentalenes when compared to those of the corresponding cyclohexyl derivatives.[2] This conclusion is further supported by the fact, shown in Table 2, that the NMR signals of the *ortho*-protons of the substituent phenyl group occur in lower field regions than those of the *meta*- and *para*-protons. Finar and Rackham attributed similar deshielding observed with 1-phenyl-substituted aza-aromatic compounds such as 1-phenylpyrazole to the interaction due to a large electric field associated with the lone pair of electrons of the nitrogen atom at position 2, this effect being operative only when both rings are coplanar.[5] Thus, the large difference in chemical shift (0.81—0.93 ppm) between the *o*-protons and the *m*- and *p*-protons in 5-phenyl heteropentalenes (I–VII, Table 2) can be attributed to the coplanarity of the phenyl-substituent and the presence of two lone pairs at 4- and 6-positions. Similar strong deshielding was observed with the NMR spectrum of 2-phenyl-*s*-triazolo[1,5-*a*]pyridine.[6]

Experimental

3-Amino-4-phenylazo-1,2,5-oxadiazole (X). 3,4-Diamino-1,2,5-oxadiazole (IX)[7] (2.9 g, 29 mmol) was suspended in a mixture of aqueous sodium hydroxide (50%, 60 ml) and benzene (2 ml). Nitrosobenzene (3.1 g, 29 mmol) was added in small portions to the stirred mixture kept at 60 °C over a period of 7 min, and the mixture was stirred for an additional 7 min. The solution was poured onto *ca.* 500 ml of ice-water, and the orange solid deposited was collected by filtration, washed with water, and recrystallized from benzene to give 1.5 g (27%) of X as orange crystals, mp 172.4—174.0 °C (Found: C, 50.61; H, 3.81; N, 37.07%. Calcd for $C_8H_7N_5O$: C, 50.79; H, 3.73; N, 37.02%), ν_{max} (Nujol) 3450, 3300, 1610, 1020, 770, 735, and 680 cm^{-1}, *m/e* 189 (M^+, 29%), 105(20), 91(3), 78(10), and 77(100).

5-Phenyl-5H[1,2,3]-triazolo[4,5-c][1,2,5]oxadiazole (I). 3-Amino-4-phenylazo-1,2,5-oxadiazole (X) (1.1 g, 58 mmol) was heated under reflux with 3.5 g of lead tetraacetate in 50 ml of benzene for 23 hr. After filtration of insoluble solid and evaporation of the solvent, the residue was eluted through a column of silica-gel (Wakogel C-200) with benzene. The solvent was evaporated from the eluate, and the residue recrystallized first from benzene and then from ethanol (with active charcoal) yielded 0.3 g (28%) of the triazolooxadiazole (I) as yellow crystals, mp 165.5—166.5 °C (Found: C, 51.59; H, 2.44; N, 37.59%. Calcd for $C_8H_5N_5O$: C, 51.34; H, 2.69; N, 37.42%), ν_{max} (Nujol) 1580, 1300, 1185, 1110, 1070, 930, 830, 800, 765, and 670 cm^{-1}, *m/e* 187 (M^+, 27%), 131(6), 105(13), 78(11), 77(100), and 51(33).

5-Phenyl-5H[1,2,3]-triazolo[4,5-c][1,2,5]thiadiazole (II). To a mixture of 0.57 g (3.3 mmol) of 4,5-diamino-2-phenyl-*v*-triazole[8] (XI) and 14 ml of benzene was slowly added 0.88 g (6.6 mmol) of sulphur monochloride to give a dark violet solution. The mixture was heated under reflux for 18 hr and the solvent was evaporated, yielding a brownish black solid mixture. Column chromatography on silica-gel (Wakogel C-200) in benzene gave a yellowish crystalline mixture containing sulphur. The mixture was freed from sulphur by percolating a dilute benzene solution of the mixture through a chromatographic tube packed with copper powder treated with 30% sulphuric acid at room temperature. Evaporation of the solution and recrystallization of the residue from benzene gave 0.26 g (38%) of the triazolothiadiazole (II) as yellow crystals, mp 181.0—182.5 °C (Found: C, 47.44; H, 2.21; N, 34.72%. Calcd for $C_8H_5N_5S$: C, 47.28; H, 2.48; N, 34.46%), ν_{max} (KBr) 1610, 1480, 1450, 1290, 1180, 1095, 1065, 915, 855, 800, 760, 680, and 660 cm^{-1}, *m/e* 203(M^+, 50%), 105(7), 78(5), and 77(100).

5-Phenyl-5H[1,2,3]-triazolo[4,5-c][1,2,5]selenadiazole (III). To a solution of 3.4 g (19 mmol) of 4,5-diamino-2-phenyl-*v*-triazole (XI) in 75 ml of ethanol was added 2.75 g (21 mmol) of selenous acid.[9] The solution was kept at 40 °C for 10 hr, giving black precipitate. The precipitate was collected by filtration, washed with water and then added to a mixture of 50 ml of benzene and 5 ml of concd hydrochloric acid in 100 ml of water. The mixture was heated under reflux for 4 hr, and the resulting yellow benzene layer was separated and replaced with 50 ml of fresh benzene. Heating and separation in the same way were repeated additional three times each with addition of 50 ml of benzene, and the combined benzene solutions (200 ml), on evaporation, gave 0.6 g of dark-red crystals. Recrystallization from benzene and column chromatography on silica-gel (Wakogel C-200) in benzene gave 0.35 g (7.2%) of the triazoloselenadiazole as yellow crystals, mp 203.8—204.5 °C (Found: C, 38.56; H, 2.01; N, 28.04%. Calcd for $C_8H_5N_5Se$: C, 38.42; H, 2.02; N, 28.00%), ν_{max} (Nujol) 1330, 1290, 1190, 1095, 1070, 925, 770, 750, 680, and 670 cm^{-1}, *m/e* 251 (M^+, 12%), 105(20), 78(13), 77(100), and isotopic peaks (due to the isotopes of selenium) at 253, 249, 248, and 247.

Oxidation of 5-Phenyl-5H[1,2,3]-triazolo[4,5-c][1,2,5]thiadiazole (II). *(a) With m-Chloroperoxybenzoic Acid*: Phenyltriazolothiadiazole (II) (0.102 g, 0.50 mmol) was refluxed with *m*-chloroperoxybenzoic acid (0.42 g, 2.44 mmol in 40 ml of of dichloromethane) for 18 hr. Acidic matter was removed with aqueous sodium carbonate solution and the residual solution was dried (Na_2SO_4). Removal of dichloromethane left 0.082 g (80%) of the starting material.

(b) With Hydrogen Peroxide: A mixture of 0.086 g (0.42 mmol) of II, 13 ml of hydrogen peroxide (30%), 1 ml of diluted sulphuric acid (1%), 30 ml of acetic acid, and 10 ml

of chloroform was heated at 60 °C for 20.5 hr. The mixture was neutralized with dilute sodium carbonate solution and the chloroform layer was separated, which, on evaporation, gave back 0.081 g of the starting material.

(c) With Potassium Permanganate: A mixture of 0.103 g (0.51 mmol) of II, 0.1 g of potassium permanganate and 0.50 ml of water in 5 ml of pyridine was stirred at 95 °C for 1.5 hr. Stirring was continued for a further 2 hr at 95 °C with an additional 0.1 g of potassium permanganate, but most of compound II remained unoxidized. The oxidation was complete after further heating for 5 hr with an additional 0.2 g of the oxidizing agent. The manganese dioxide was removed by filtration and the filtrate was concentrated to give only a trace amount of reddish black tarry matter.

*Reduction of 5-Phenyl-5*H[*1,2,3*]-*triazolo*[*4,5*-c][*1,2,5*]*thiadiazole (II). (a) Catalytic Hydrogenation*: The phenyltriazolothiadiazole (II) (0.506 g, 2.4 mmol) in 30 ml of dioxane was hydrogenated with 0.106 g of platinum oxide catalyst at 1 atm of hydrogen for 5 days. The starting material was recovered (91%) from the reaction mixture.

(b) With Lithium Aluminium Hydride (LAH): A mixture of 0.46 g (2.2 mmol) of II and 0.1 g of LAH in 30 ml of anhydrous tetrahydrofuran was stirred for 18 hr at room temperature, followed by heating under reflux for 4.3 hr with an additional 0.2 g of LAH. Water (2 ml) was added carefully to the mixture and the solvent was removed under reduced pressure. Organic products were extracted with ethanol and evaporation of the solvent from the extract gave 4,5-diamino-2-phenyl-*v*-triazole (XI) in 90% yield.

Polarographic Measurements. Polarographic measurements of the heteropentalenes (I, II, and III) were carried out in a similar manner to that described in the literature.[10] No distinct polarogram was obtained for compound I.

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