The Synthesis and Cyclodehydration of 4-(3-Aryl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazoles. Novel Substituted Pyrrolo[1,2-*c*][1,2,3]triazoles

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The polyfunctionalized title triazolyl 1,3-diketones have been prepared by the addition-cyclization reaction of sodium azide to 1,5-diaryl-4-pentyne-1,3-diones, in the first instance, in good yields. These intermediate triazoles can readily be cyclodehydrated to the corresponding 3,6-diaryl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one derivatives. This cyclodehydration furnishes a new method of synthesis of a new class of pyrrolo[1,2-*c*]-[1,2,3]triazoles. The structures of the above compounds were confirmed from their spectral characteristics.

1,2,3-Triazoles and their derivatives have attracted considerable attention because of their wide spectrum of applications[1—3] and several methods have been adopted for the synthesis of 1,2,3-triazoles with a variety of substituents and functionalities and have been comprehensively reviewed.[1] The most important common and versatile route for the preparation of this class of heterocycle is the thermal 1,3-dipolar cycloaddition of azides to alkynes. However, addition of the azides to acetylenic 1,3-diketones was never reported. With the aim of repairing this gap, we studied, in the first time, the reaction of sodium azide with 1-aryl-5-phenyl-4-pentyne-1,3-diones[4] which are also attracted widespread interest in the synthesis of several useful heterocyclic systems.[5]

Treatment of the acetylenic 1,3-diketones **1a—c** with sodium azide in refluxing *N*,*N*-dimethylformamide (DMF) gave a new series of the corresponding 4-(3-aryl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazoles (**2a—c**) in good yields. It is worthy to mention that only one example, so far, of this class of triazoles is known. This triazole, 4-(1,3-dioxo-3-phenylpropyl)-1-phenyl-1*H*-1,2,3-triazole, has been prepared by indirect route involving the base catalyzed condensation of acetophenone with dimethyl 1-phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate.[6]

The reaction of acetylenic 1,3-diketones **1** with sodium azide was found to be completely regiospecific. Thin-layer chromatography using different solvent systems confirmed the presence of a sole product in this reaction. These products are believed to be triazoles **2** as depicted in Scheme 1. This belief is based on the assumption that the initial attack of the nucleophilic nitrogen of the azide on the electrophilic β-carbon (C-5) of the acetylenic linkage of **1** is electronically favored. Subsequent cyclization leads to the triazoles **2** (Scheme 1). It is worth mentioning here that a similar mechanism was suggested for the formation of 1,2,3-triazoles by the reaction of acetylenic carbonyl compounds with azides.[3,7,8] Thus, our thermal addition-cyclization reaction furnishes a new class of 1*H*-1,2,3-triazole ring carrying phenyl and 1,3-dioxo-3-(substituted phenyl)-propyl substituents at positions 4 and 5 which can be used as an appropriate starting material in the syntheses of different heterocycles. Also, the triazoles **2** form interesting class of compounds as they easily form green copper complexes and therefore they could be considered as organic ligands similar to those of acetylenic 1,3-diketones.[4]

Several tautomeric forms can be considered for the triazoles **2**. However, the spectral data of these compounds indicate that tautomers **2A**, **2B**, and **2C** are the most predominant forms (Chart 1). Their IR spectra have several characteristic features which aid in structure identification. Thus, a broad absorption in the regions 1588—1605 and 3391—3419 cm^{-1} for 1,3-diketone systems[4] and OH group, respectively. The appearance of a weak band at 1633—1640 cm^{-1} for the carbonyl group, a sharp absorption at 3062—3141 cm^{-1} for NH group and two strong bands in the regions 1400—1411 and 1448—1464 cm^{-1} for triazole ring is similar to that reported for 4-phenyl-1*H*-1,2,3-triazol-5-yl β-(α-aminostyryl) ketones.[8] The triazoles **2** gave a positive iron(III) chloride test and easily formed green copper complexes. Having this aspect in mind, the triazoles **2** in the solid state may be present in three tautomers **2A**, **2B**, and **2C** in which **2A** and **2B** may predominate due to the weakness of carbonyl absorption.[8]

The electronic spectra of the triazoles **2** (cf. Experimental), in methanol exhibited three main absorption maxima in the regions 226—253, 281—306, and 348—

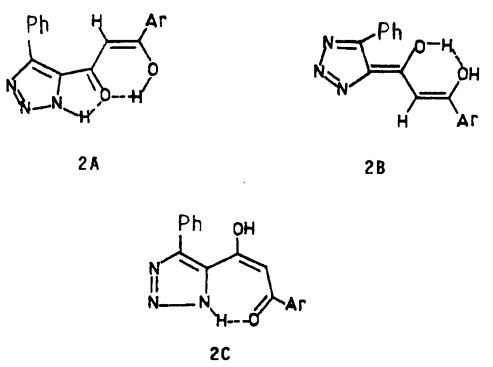
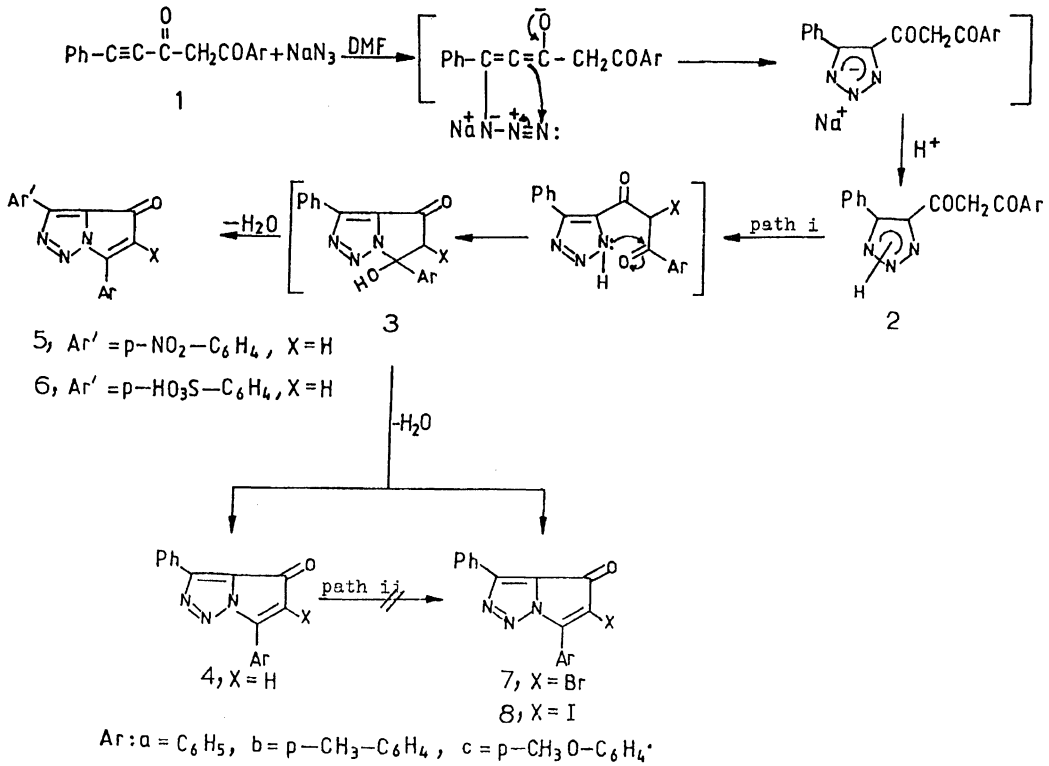


Chart 1.



Scheme 1.

364 nm. In the presence of 0.9 M sodium methoxide (1 M=1 mol dm^{-3}), a blue shift is observed for the wavelength maximum at 281 nm with disappearance of the maximum at 253 nm in the case of the spectrum of the compound **2a** which can be attributed to the dianionic species of these compounds.[4,8] However, in acidic solutions a different pattern was obtained. The intensity of the high wavelength band or shoulder gradually increased with increasing acidity. Meanwhile, the band at 281—306 nm disappeared and a red shift was observed for the maximum at 226—253 nm. This behavior is probably due to the formation of triazolium cation in acidic medium. The above data seem to be in accordance with any of the structures **2A**—**C**.

The ^{1}H NMR spectra of **2** (cf. Experimental), clearly indicate that they exist mainly in the diendiol form **2B** rather than the keto structures **2A** and **2C** since no separate signal could be detected for the NH triazole ring proton which was expected to appear in the range δ=10.92—15.90.[1,8] The ^{1}H NMR spectra showed a singlet at δ=6.76—6.93 and a broad exchangeable signal at δ=8.13—8.18 for the ethylenic and enolic OH protons, respectively.

E,E, *Z,Z*, and *E,Z*, isomerism is possible with diendiol triazole **2B**. The observation of a single chemical shift value for the ethylenic proton indicates the exclusive presence of only one form to which the *E,Z*-configuration is tentatively assigned to the diendiol **2B** since it is expected to be more favored due to the intramolecular hydrogen bonding[9—11] and the minimum steric repulsion between the phenyl and hydroxyl while it is greater in between the phenyl and hydrogen as present in *Z,Z* form (Chart 2).

Moreover, the mass spectrum of the triazole **2b** gave the molecular ion as the peak second in prominance to the base peak. The major fragmentation route involved explusion of hydrazoic acid molecule giving the base peak probably is due to acetylenic 1,3-diketone species **1b**. The latter gave rise to a series of fragments characteristic of acetylenic 1,3-diketone systems.[12] While the presence of the fragments $[M-N_2]^+$ and $[M-N_2-CO]^+$ which are characteristic of the triazolylcarbonyl compounds,[13] no $[M-OH]^+$ species was observed (cf. Experimental).

1-(1*H*-1,2,3-Triazol-4-yl)-1,3-diketones, with four reactive functional groups, appeared attractive starting materials for the synthesis of heterocyclic bicyclo compounds having a triazole ring which have a great vari-

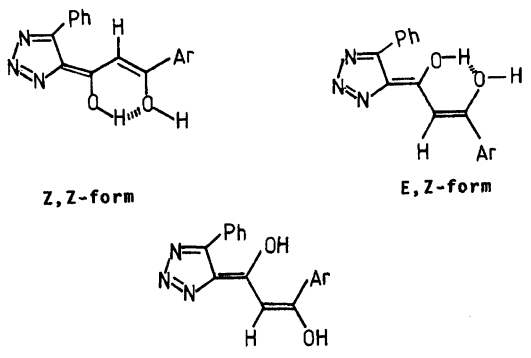


Chart 2.

ety of useful properties. However, the chemistry of this class of compounds has not been explored. Here we describe a new and apparently general method for the synthesis of a number of substituted 4*H*-pyrrolo[1,2-*c*]-[1,2,3]triazole derivatives by the cyclodehydration of the triazoles **2**. Thus, cyclodehydration of the above triazoles **2a**—**c** with sulfuric acid in refluxing ethanol gave the respective 6-aryl-3-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones **4a**—**c**. Moreover, cyclodehydration as well as electrophilic substitution in the phenyl residue occur on nitration of **2a**—**c** with nitric and sulfuric acids, and sulfonation with a mixture of 20% oleum and concentrated sulfuric acid. The nitro and sulfonic groups are most probably introduced into the *p*-position of the phenyl ring leading to the formation of the corresponding *p*-nitrophenyl compounds **5** (Ar=Ar′=*p*-nitrophenyl) and **5b**,**c**, and *p*-benzenesulfonic acid derivatives **6** (Ar=Ar′=*p*-benzenesulfonic acid) and **6b**,**c** derivatives. Such assignment is based on the fact that the C-triazolyl moiety activates the phenyl ring towards electrophilic substitution in the ortho–para positions.[14—16] The formation of 4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones **4**, **5**, and **6** probably proceeds through the formation of the intermediate **3** and subsequent dehydration (Scheme 1).

Bromination of **2a**—**c** with bromine or iodination with iodine monochloride in glacial acetic acid afforded the respective 5-bromo- (**7a**—**c**) or 5-iodo-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones (**8a**—**c**) in excellent yields. Since 1,3-diketones are easily halogenated at the methylene group,[5] the formation of 5-halopyrrolotriazoles may proceed either by initial halogenation of **2** and subsequent cyclodehydration (path-i) or by cyclodehydration followed by halogenation (path-ii) (Scheme 1). To differentiate between the two possible routes, halogenation of 6-aryl-3-phenyl-4*H*-pyrrolotriazol-4-ones (**4a**—**c**) was attempted. However, these were recovered unchanged under the halogenation conditions as used for triazoles **2**. These results exclude path-ii for the formation of 5-halopyrrolotriazoles.

The IR spectra of pyrrolo[1,2-*c*][1,2,3]triazole derivatives **4**—**8** exhibited characteristic triazole and pyrrole ring bands at 1445—1464 and 1578—1611 cm^{-1} as well as a carbonyl absorption at 1633—1695 cm^{-1} besides other characteristics (cf. Experimental). The ^1H NMR spectra of the compounds **4**—**6** gave a singlet at δ=6.56—6.84 for the H-5 proton almost in the same region reported for the 5-unsubstituted pyrrolo[1,2-*c*]-[1,2,3]triazoles,[17] while this signal was not observed in the case of pyrrolotriazoles **7** and **8**. The electronic spectra of the pyrrolotriazoles **4**—**8** in methanol exhibited two absorption maxima in the regions 222—268 and 280—354 nm. However, in acidic and basic media different patterns were observed which can be attributed to the anionic and cationic species of these compounds.[17]

Further support of the structure of the pyrrolotriazoles was obtained from their mass spectra. The pyrrolotriazoles **4b**, **5c**, and **7b** gave rise to a series of fragments characteristic of this bicyclic system (cf. Experimental).

The 4-(3-aryl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazoles (**2**) are therefore useful intermediates for the preparation of a number of a new class of pyrrolo[1,2-*c*]-[1,2,3]triazoles carrying aryl and carbonyl substituents which are not reported in the literature. Generally, this new pyrrolotriazole ring system is potentially bioactive heterocyclic compounds.[17] However, their synthesis has been recently achieved in only a very limited number of ways, involving thermal intramolecular cycloaddition of *trans-cis*-6-azido-2,4-hexadienoates[18] or 1-azido-2-penten-4-ynes[17] and by Wittig condensation of α-azido acid chlorides with phosphorus ylides.[19] The generality of these methods are impaired by the availability of the starting materials. Further reactions of these triazole 1,3-diketones and pyrrolotriazoles are under investigations.

Experimental

General Methods. IR spectra were measured with a Unicam SP 1025 spectrophotometer for potassium bromide pellets and electronic spectra were recorded with a Unicam SP 800 spectrophotometer. ^1H NMR spectra were determined on a Varian EM-390 90 MHz spectrometer and were recorded for $CDCl_3$ (or acetone-d_6) solutions containing Me_4Si as internal standard. Liquid secondary ion mass spectrometry (L.S.I.M.S) was performed on a Finnigan MAT TSQ-70 triple-stage quadrupole mass spectrometry equipped with an Antek Cesium gun. Glycerol was employed as the sample matrix. Melting points were determined on a Kofler Block and are uncorrected. Microanalyses were performed by the Microanalysis Unit, Cairo University, Cairo.

General Procedure for the Preparation of 4-(3-Aryl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazoles (2). A solution of 1-aryl-5-phenyl-4-pentyne-1,3-diones[4] (**1**) (4 mmol) in *N*,*N*-dimethylformamide (20 ml) was heated under reflux with sodium azide (4.6 mmol) for 3 h. The reaction mixture was then poured into cold water (200 ml), acidified with dilute sulfuric acid and the precipitated **2** was filtered, washed with water several times, dried and recrystallized from benzene–petroleum ether (bp 60—80 °C) as pale yellow needles.

4-(3-Phenyl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazole (2a). General procedure with **1a** gives **2a** (0.85 g) (72% yield): Mp 87 °C; IR (KBr) 3419, 3062, 1640, 1588, 1448, and 1405 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 253 (2.6), 281 (2.6), and 364_{sh} (0.5); in 0.9 M sulfuric acid/methanol 266 (1.4), and 341 (1.1); in 0.9 M sodium methoxide/methanol 276 (2.6), and 367_{sh} (0.6); ^1H NMR ($CDCl_3$) δ=6.76 (1H, s), 7.28—7.62 (10H, m of Ph and 1H, D_2O-exchangeable), and 8.13 (1H, s, D_2O-exchangeable). Anal. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.10; H, 4.47; N, 14.43%. Found: C, 70.22; H, 4.36; N, 14.50%.

5-Phenyl-4-(3-*p*-tolyl-1,3-dioxopropyl)-1*H*-1,2,3-triazole (2b). General procedure with **1b** gives **2b** (0.85 g) (72% yield): Mp 122 °C; IR (KBr) 3403, 3141, 1633, 1598, 1464, and 1411 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 260 (2.3), 306_{sh} (2.0), and 348 (1.8); ^1H NMR ($CDCl_3$) δ=

2.25 (3H, s), 6.93 (1H, s), 7.18—7.72 (9H, m of Ar-H and 1H, D_2O-exchangeable), and 8.16 (1H, s, D_2O-exchangeable); MS *m/z* 305 (M^+, 40), 277 (4), 262 (100), 261 (7), 250 (2), 235 (1), 223 (1), 172 (3), 161 (6), 145 (1), 133 (4), 119 (29), 105 (2), and 77 (5). Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.82; H, 4.92; N, 13.77%. Found: C, 70.70; H, 4.94; N, 13.92%.

4-(3-*p*-Methoxyphenyl-1,3-dioxopropyl)-5-phenyl-1*H*-1,2,3-triazole (2c). General procedure with **1c** gives **2c** (0.70 g) (60% yield): Mp 79 °C; IR (KBr) 3391, 3120, 1633, 1605, 1448, and 1405 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 226_{sh} (2.2), 248_{sh} (1.5), and 356 (2.5); ^1H NMR ($CDCl_3$) δ=3.76 (3H, s), 6.82 (1H, s), 7.42—7.82 (9H, m of Ar-H and 1H, D_2O-exchangeable), and 8.18 (1H, s, D_2O-exchangeable). Anal. Calcd for $C_{18}H_{15}N_3O_3$: C, 67.29; H, 4.67; N, 13.08%. Found: C, 67.32; H, 4.50; N, 12.92%.

General Procedure for 6-Aryl-3-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones (4). A solution of 1,3-diketone (**2**) (4 mmol) in ethanol (15 ml) was heated under reflux with concentrated sulfuric acid (1 ml) for 2 h. The reaction mixture was then concentrated to give **4** which crystallized from benzene–petroleum ether (bp 60—80 °C) as needles.

3,6-Diphenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (4a). General procedure with **2a** gives **4a** (0.2 g) (71% yield): Mp 88 °C; IR (KBr) 1638, 1584, and 1446 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 257 (1.0) and 282 (1.0); in 0.9 M sulfuric acid/methanol 266 (0.7) and 342 (0.5); in 0.9 M sodium methoxide/methanol 275 (2.5); ^1H NMR ($CDCl_3$) δ=6.72 (1H, s), and 7.46—7.88 (10H, m). Anal. Calcd for $C_{17}H_{11}N_3O$: C, 74.73; H, 4.03; N, 15.38%. Found: C, 74.62; H, 4.20; N, 15.29%.

3-Phenyl-6-*p*-tolyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (4b). General procedure with **2b** gives **4b** (0.2 g) (72% yield): Mp 68 °C; IR (KBr) 1658, 1597, and 1448 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 260 (2.3) and 293 (2.0); ^1H NMR ($CDCl_3$) δ=2.34 (3H, s), 6.82 (1H, s), and 7.44—8.20 (9H, m); MS *m/z* 287 (M^+, 24), 259 (16), 231 (22), 143 (9), 130 (12), 116 (30), 115 (29), 103 (10), 101 (8), 77 (100), and 91 (28). Anal. Calcd for $C_{18}H_{13}N_3O$: C, 75.26; H, 4.53; N, 14.63%. Found: C, 75.42; H, 4.26; N, 14.40%.

6-*p*-Methoxyphenyl-3-phenyl-4*H*-pyrrolo[1,2-*c*]-[1,2,3]triazol-4-one (4c). General procedure with **2c** gives **4c** (0.19 g) (64% yield): Mp 79 °C; IR (KBr) 1638, 1585, and 1447 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 268 (1.2), and 319 (1.0); ^1H NMR ($CDCl_3$) δ=3.72 (3H, s), 6.66 (1H, s), and 7.42—7.86 (9H, m). Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.29; H, 4.29; N, 13.86%. Found: C, 71.46; H, 4.40; N, 13.68%.

General Procedure for 3,6-Bis(*p*-nitrophenyl)- (5, Ar=*p*-NO_2–C_6H_4) and 6-Aryl-3-*p*-nitrophenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones (5b,c). A mixture of nitric (*d* 1.41, 0.5 ml) and sulfuric (*d* 1.84, 0.5 ml) acids in glacial acetic acid (7 ml) was gradually added to a solution of **2** (3 mmol) in glacial acetic acid (12 ml) with stirring for 4 h at room temperature and warmed for 15 min. The reaction mixture was then poured into cold water (200 ml) with stirring and the pale yellow precipitated nitro pyrrolotriazoles **5** was filtered, washed with water, dried and crystallized from benzene–petroleum ether (bp 60—80 °C) as yellow needles.

3,6-Bis(*p*-nitrophenyl)-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (5) (Ar=*p*-NO_2–C_6H_4). General procedure with **2a** gives **5a** (0.29 g) (78% yield): Mp 79 °C; IR (KBr) 1640, 1585, 1532, 1446, and 1365 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 254 (2.2) and 280 (1.1); in 0.9 M sulfuric acid/methanol 266 (1.4) and 341 (0.9); in 0.9 M sodium methoxide/methanol 276 (2.7); ^1H NMR ($CDCl_3$) δ=6.56 (1H, s) and 7.24—7.52 (8H, m). Anal. Calcd for $C_{17}H_9N_5O_5$: C, 56.20; H, 2.48; N, 19.28%. Found: C, 56.42; H, 2.64; N, 19.14%.

3-*p*-Nitrophenyl-6-*p*-tolyl-4*H*-pyrrolo[1,2-*c*][1,2,3]-triazol-4-one (5b). General procedure with **2b** gives **5b** (0.24 g) (74% yield): Mp 125 °C; IR (KBr) 1642, 1584, 1536, 1446, and 1372 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 259 (2.0) and 303 (1.8); ^1H NMR ($CDCl_3$) δ=2.26 (3H, s), 6.84 (1H, s), and 7.36—8.28 (8H, m). Anal. Calcd for $C_{18}H_{12}N_4O_3$: C, 65.06; H, 3.61; N, 14.46%. Found: C, 65.22; H, 3.64; N, 14.28%.

6-*p*-Methoxyphenyl-3-*p*-nitrophenyl-4*H*-pyrrolo-[1,2-*c*][1,2,3]triazol-4-one (5c). General procedure with **2c** gives **5c** (0.22 g) (68% yield): Mp 86 °C; IR (KBr) 1659, 1611, 1530, 1445, and 1347 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 258 (1.6) and 303_{sh} (1.1); ^1H NMR ($CDCl_3$) δ=3.82 (3H, s), 6.64 (1H, s), and 7.12—7.80 (8H, m); MS *m/z* 348 (M^+, 10), 320 (26), 292 (32), 188 (18), 160 (22), 148 (16), 147 (10), 146 (8), 131 (8), 122 (12), and 107 (100). Anal. Calcd for $C_{18}H_{12}N_4O_4$: C, 62.07; H, 3.45; N, 16.09%. Found: C, 62.18; H, 3.66; N, 16.18%.

General Procedure for 4-Oxo-4*H*-pyrrolo[1,2-*c*]-[1,2,3]triazole-3,6-bis[*p*-benzenesulfonic acid] (6) (Ar=*p*-$C_6H_4SO_3H$) and 6-Aryl-4-oxo-4*H*-pyrrolo-[1,2-*c*][1,2,3]triazole-3-[*p*-benzenesulfonic acid] (6b, c). A solution of **2** (1.3 mmol) in concentrated sulfuric acid (5 ml) was added dropwise at 0 °C in a period of 30 min to a stirred mixture of 20% oleum (0.2 ml) and concentrated sulfuric acid (0.4 ml). The reaction mixture was slowly allowed to warm to room temperature and stirred for 1 h. The acidic solution was then poured into crushed ice (3 g) with stirring and the precipitated sulfonic acid **6** was filtered, washed with water, dried and crystallized from benzene–petroleum ether (bp 60—80 °C) as needles.

4-Oxo-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole-3,6-bis[*p*-benzenesulfonic acid] (6) (Ar=*p*-$C_6H_4SO_3H$). General procedure with **2a** gives **6** (0.31 g) (70% yield): Mp 81 °C; IR (KBr) 1640, 1590, 1446, 1184, and 1077 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 254 (2.5) and 280 (2.5); in 0.9 M sulfuric acid/methanol 266 (1.4) and 341 (1.1); in 0.9 M sodium methoxide/methanol 276 (3.0) and 370 (0.6); ^1H NMR ($CDCl_3$) δ=6.66 (1H, s), 7.26—7.78 (8H, m), and 8.66 (2H, s, D_2O-exchangeable). Anal. Calcd for $C_{17}H_{11}N_3O_7S_2$: C, 47.11; H, 2.54; N, 9.70; S, 14.78%. Found: C, 47.28; H, 2.52; N, 9.66; S, 14.92%.

4-Oxo-6-*p*-tolyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazole-3-[*p*-benzenesulfonic acid] (6b). General procedure with **2b** gives **6b** (0.26 g) (72% yield): Mp 114 °C; IR (KBr) 1641, 1584, 1446, 1242, and 1101 cm^{-1}; UV λ_{max} nm ($\varepsilon\times10^{-4}$) in methanol 259 (3.3) and 348 (2.7); ^1H NMR ($CDCl_3$) δ=2.30 (3H, s), 6.72 (1H, s), 7.30—7.94 (8H, m), and 8.82 (1H, s, D_2O-exchangeable). Anal. Calcd for $C_{18}H_{13}N_3O_4S$: C, 58.86; H, 3.54; N, 11.44; S, 8.72%. Found: C, 58.62; H, 3.51; N, 11.34; S, 8.90%.

6-*p*-Methoxyphenyl-4-oxo-4*H*-pyrrolo[1,2-*c*][1,2,3]-triazole-3-[*p*-benzenesulfonic acid] (6c). General procedure with **2c** gives **6c** (0.27 g) (75% yield): Mp 80

°C; IR (KBr) 1658, 1599, 1464, 1257, and 1076 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 268 (1.6) and 354 (1.6); ^1H NMR ($CDCl_3$) δ=3.78 (3H, s), 6.68 (1H, s), 7.22—8.10 (8H, m), and 8.68 (1H, s, D_2O-exchangeable). Anal. Calcd for $C_{18}H_{13}N_3O_5S$: C, 56.40; H, 3.39; N, 10.97; S, 8.36%. Found: C, 56.42; H, 3.22; N, 10.79; S, 8.32%.

General Procedure for 6-Aryl-5-halo-3-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-ones (7) and (8). A solution of bromine (1.4 mmol) or iodine monochloride (1 mmol) in glacial acetic acid (3 ml) was gradually added to a solution of **2** (1 mmol) in glacial acetic acid (15 ml) with stirring for 2 h at room temperature. The reaction mixture was then poured into cold water (200 ml) and the precipitated 5-bromo compound **7** or 5-iodo compound **8** was filtered, washed with water, dried and recrystallized from benzene–petroleum ether (bp 60—80 °C) as needles.

5-Bromo-3,6-diphenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (7a). General procedure with **2a** gives **7a** (0.18 g) (75% yield): Mp 69 °C; IR (KBr) 1635, 1578, and 1447 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 257 (1.2) and 284 (1.3); in 0.9 M sulfuric acid/methanol 266 (0.9) and 340 (0.5); in 0.9 M sodium methoxide/methanol 275 (2.0); ^1H NMR (acetone-d_6) δ=7.44—7.88 (10H, m). Anal. Calcd for $C_{17}H_{10}BrN_3O$: C, 57.95; H, 2.84; Br, 22.73; N, 11.93%. Found: C, 57.98; H, 2.76; Br, 22.61; N, 11.92%.

5-Bromo-3-phenyl-6-*p*-tolyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (7b). General procedure with **2b** gives **7b** (0.31 g) (86% yield): Mp 128 °C; IR (KBr) 1638, 1605, and 1448 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 261 (2.9) and 284 (2.9); ^1H NMR (acetone-d_6) δ=2.32 (3H, s), and 7.52—8.12 (9H, m); MS m/z 286 (M^+−Br, 48), 258 (32), 230 (18), 143 (22), 129 (12), 115 (52), 103 (14), 101 (8), 91 (26), and 77 (100). Anal. Calcd for $C_{18}H_{12}BrN_3O$: C, 59.02; H, 3.28; Br, 21.86; N, 11.48%. Found: C, 58.94; H, 3.22; Br, 21.68; N, 11.36%.

5-Bromo-6-(*p*-methoxyphenyl)-3-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (7c). General procedure with **2c** gives **7c** (0.31 g) (87% yield): Mp 46 °C; IR (KBr) 1641, 1587, and 1463 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 261 (1.0) and 287 (0.8); ^1H NMR (acetone-d_6) δ=3.72 (3H, s), and 7.34—7.98 (9H, m). Anal. Calcd for $C_{18}H_{12}BrN_3O_2$: C, 56.54; H, 3.14; Br, 20.94; N, 10.99%. Found: C, 56.48; H, 3.32; Br, 21.08; N, 10.78%.

5-Iodo-3,6-diphenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (8a). General procedure with **2a** gives **8a** (0.32 g) (78% yield): Mp 86 °C; IR (KBr) 1635, 1590, and 1446 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 251 (1.6) and 284 (1.3); in 0.9 M sulfuric acid/methanol, 265 (0.9) and 342 (0.5); in 0.9 M sodium methoxide/methanol 272 (2.5) and 365_{sh} (0.6); ^1H NMR ($CDCl_3$) δ=6.92—7.78 (10H, m). Anal. Calcd for $C_{17}H_{10}IN_3O$: C, 51.13; H, 2.51; I, 31.83; N, 10.53%. Found: C, 51.20; H, 2.62; I, 31.94; N, 10.60%.

5-Iodo-3-phenyl-6-*p*-tolyl-4*H*-pyrrolo[1,2-*c*][1,2,3]-triazol-4-one (8b). General procedure with **2b** gives **8b** (0.33 g) (81% yield): Mp 59 °C; IR (KBr) 1634, 1581, and 1447 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 259 (3.1) and 284 (3.0); ^1H NMR ($CDCl_3$) δ=2.26 (3H, s) and 7.30—7.94 (9H, m). Anal. Calcd for $C_{18}H_{12}IN_3O$: C, 52.30; H, 2.91; I, 30.75; N, 10.17%. Found: C, 52.46; H, 2.78; I, 30.72; N, 10.30%.

5-Iodo-6-(*p*-methoxylphenyl)-3-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-one (8c). General procedure with **2c** gives **8c** (0.34 g) (85% yield): Mp 89 °C; IR (KBr) 1633, 1595, and 1449 cm^{-1}; UV λ_{max} nm ($\varepsilon \times 10^{-4}$) in methanol 222_{sh} (2.2) and 280 (1.7); ^1H NMR ($CDCl_3$) δ=3.82 (3H, s) and 7.18—7.74 (9H, m). Anal. Calcd for $C_{18}H_{12}IN_3O_2$: C, 50.35; H, 2.80; I, 29.60; N, 9.79%. Found: C, 50.54; H, 2.96; I, 29.81; N, 9.77%.

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