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Synthesis of 2-Amino-1,2,3-triazole Derivatives from Vicinal Diazides

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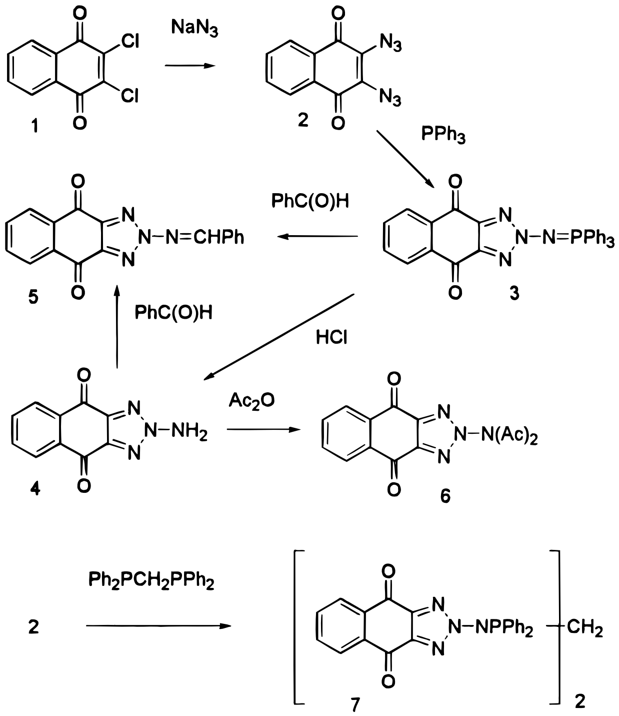
Triphenylphosphine reacts with naphthoquinone diazide to form almost quantitatively the phosphorane of a unique 2-amino-1,2,3-triazole derivative. This compound undergoes an aza-Wittig reaction with aldehydes and is readily hydrolyzed to the free 2-amino-1,2,3-triazole. The free amine reacts normally with acids and aldehydes. The 2-amino-1,2,3-triazole system is stable and high melting, and most derivatives give the parent ion as the largest peak in the mass spectrum. The compounds absorb at 300−350 nm with a strong emission in the range 500−700 nm, depending upon the substituents. Cyclic voltammetry shows one reversible, single-electron reduction wave.

During our investigation of the syntheses of dithiolene, 1,3-dithiole-2-thione, and tetrathiofulvalene derivatives of quinones, we prepared a unique 2-amino-1,2,3-triazole system, Scheme 1. Compound **3** was obtained in almost quantitative yield from dichloronaphthoquinone via formation of the diazide followed by reaction with triphenylphosphine. Although no mechanistic studies have been made, the triphenylphosphine probably adds to the end nitrogen of one azide via a Staudinger-like reaction.[1] The attack of the second nitrogen atom on the first nitrogen of the adjacent azide with displacement of N_2 is the easiest way to visualize product formation. The evolution of nitrogen gas is observed during the reaction. This reaction is similar to the thermal or photochemical intramolecular cyclizations of aryl azides with adjacent unsaturated substitutents.[2] Compound **3** is surprisingly stable. It has a sharp melting point (no decomposition), it does not decompose in air over a period of weeks, and the molecular ion (*m*/*z* 474, 100%) is the most abundant ion in the mass spectrum. The nitrogen bonded to the central nitrogen of the triazole eliminates most pathways for the ready evolution of N_2, which accounts for the stability of this system.

Scheme 1



An X-ray structure of **3** shows the entire molecule to be planar except for the triphenyl substituents, implying extensive electron delocalization in the system. Compound **3** hydrolyzes in dilute aqueous acid to produce the amine **4**, which is also stable to melting and moisture, and it gives a parent ion peak (*m*/*z* 294, 83%) in the mass spectrum. The five-membered ring in **4** exhibits an envelope conformation with the NH_2 group lying out of the molecular plane. Compound **3** undergoes an aza-Wittig reaction[3] with benzaldehyde, producing compound **5** which is obtained also by reaction of benzaldehyde with **4**. Compound **3** does not react readily with ketones presumably because of steric hindrance; however, **4** reacts normally. Compound **4** reacts with acetic acid to form the diamide **6**, but it could not be methylated with MeI. The diazide **2** reacts with a variety of phosphines; however, products using PHR_1R_2 types of phosphines could not be characterized. One reaction with $P(n\text{-Bu})_3$ led to the recovery of the free amine **4** in 38% yield, presumably due to traces of moisture. Compound **2** reacts readily with bis(diphenylphosphine)methane to form **7**.

Compound **3** is dark red in solution, garnet colored as a crystal, and has an absorption maximum at 322 nm. Excitation at 300 nm produces a strong emission at 620 nm. Compound **4** absorbs strongly at 302 and 330 nm with a broad emission centered at 530 nm. Compound **5** has an absorption maximum at 322 nm, but the emission resembles that of **4** with a broad band centered at 520 nm. Compound **7** absorbs at 309 nm. Excitation at 325 nm gives a broad, strong emission with a maximum at 586 nm and a 100 nm width at half-height. Preliminary investigations indicate that variation of the group which is double bonded to the amine nitrogen shifts the position of emission, opening up a number of areas

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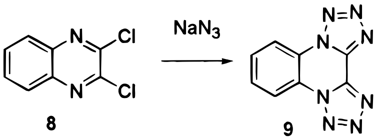
of possible application. Cyclic voltammetry measurements do not show the two peaks normally associated with the quinone → semiquinone → hydroquinone couples. Only one reversible reduction wave is observed for **3** and **4** at −0.93 and −0.89 V (vs NHE), respectively. All reductions are one-electron transfers, and they are scan rate independent. Compound **7** gives two reduction peaks at all scan rates (−0.98 and −1.16 V at peak maxima), but only one peak on the return sweep (−0.99 V). The addition of one electron to one triazole moiety influences the addition to the second.

Although we have not as yet investigated the generality of these reactions, all *cis*-ethylene diazide moieties do not close to form the 2-amino-1,2,3-triazole system. The diazide of the five-membered ring methylmaleimide gives only the Staudinger product when reacted with triphenylphosphine,[4] while other functionalities may provide alternate pathways for the reaction of the diazide. For example, the reaction of compound **8** with sodium azide immediately produces the ditetrazole **9** by a well-known reaction pathway.[5] Refluxing **9** with triphenylphosphine does not lead to the formation of the triazole. Irradiation of **9** at 324 nm gives an emission at 512 nm with decomposition or rearrangement. Cyclic voltammetry shows an irreversible peak around −0.89 V, which is scan rate dependent.



Experimental Section

NMR data were collected on a 300 MHz instrument, FT-IR spectra were collected on samples in KBr, and mass spectra were obtained by solid probe injection into a GC/MS. Cyclic voltammetry data for compounds **3**, **4**, **5**, and **10** were recorded with DMF as solvent TBAClO$_4$ as supporting electrolyte and ferrocene as internal standard[6] and with variable scan rates of 20−200 mV/s. All scans were reversible one-electron reductions except for compound **10**. All melting points are uncorrected. *CAUTION! Utmost care must be exercised when working with diazide derivatives.* Attempts to minimize the quantity of diazide by premixing the sodium azide and triphenylphosphine led to the isolation of only the mono Staudinger product (monoiminotriphenylphosphorane).

Compound 3. To 4.54 g (20 mmol) of dichloronaphthoquinone in 150 mL of methanol was added 2.6 g of sodium azide. The mixture was stirred for 2 h at rt with the yellow slurry turning orange. Triphenylphosphine (2.63 g, 10 mmol) was added slowly and was accompanied by the evolution of nitrogen. The solution which gradually turned red was stirred for 3 h. The solvent was removed on a rotavap and the solid washed three times with 100 mL portions of water; 4.71 g of compound **3** was recovered (>96% after recrystallization). Mp: 161−162 °C. Anal. Calcd for $C_{28}H_{19}N_4O_2P$: C, 70.89; H, 4.00. Found: C, 70.67; H, 4.21. MS: *m/z* 475 (32), 474 (M^+, 100), 304 (13), 277 (11), 276 (20), 263 (13), 262 (68). IR (cm^{-1}): 1678 (vs), 1508 (s), 1346 (vs), 1221 (s), 1111 (s), 953 (vs), 720 (s). UV−Vis: λ (nm) 316 (s), 424 (br). ^1H NMR($CDCl_3$): δ 8.12−8.15 (m, 2H), 7.86−7.93 (m, 6H), 7.62−7.68 (m, 2H), 7.46−7.89 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 176.47, 142.01, 133.75, 133.57, 133.44, 133.00, 128.99 and 128.82 (coupled to P), 126.93, 126.56 and 125.23 (coupled to P).

Compound 4. A suspension of 2.37 g (5 mmol) of **3** in 150 mL of 1 N HCl was refluxed for 4 h. After cooling, filtering, and washing three times with 50 mL portions of methanol, 460 mg of **4** (43% recovered yield; 100% of **3** hydrolyzed) was obtained. Mp: >260 °C. Anal. Calcd for $C_{10}H_6N_4O_2$: C, 56.07; H, 2.80. Found: C, 55.86; H, 2.68. MS *m/z* 215 (11), 214 (M^+, 83), 185 (14), 158 (14), 142 (19), 172 (10), 130 (14), 114 (100). IR (cm^{-1}): 3351, 3246, 1686 (vs), 1669 (vs), 1586 (s), 1223 (vs), 986 (m), 721 (m). UV−Vis: λ (nm) 274 (w, sh), 302 (s), 330 (s). ^1H NMR (DMSO-d_6): δ, 8.50 (br s, 2NH), 7.86−7.59 (dd, 2H), 7.62−7.65(dd, 2H). ^{13}C NMR (DMSO-d_6): δ 174.89, 141.15, 132.94, 131.93, 125.3.

Compound 5. (a) To 474 mg (1 mmol) of **3** in 20 mL of dichloromethane was added 10 drops of freshly distilled benzaldehyde. The solution stood overnight at rt. Removal of the solvent by slow evaporation and washing with 5 mL of methanol gave 110 mg of white crystalline **5** (yield 36%). (b) To 214 mg (1 mmol) of **4** in 20 mL of dichloromethane was added 10 drops of freshly distilled benzaldehyde and 1 g of molecular sieve, 4A (activated). The mixture was refluxed overnight and filtered. Removal of solvent gave 58 mg of white crystalline **5** (yield, 19%), mp 235−240 °C. No attempt has been made to optimize the yields. Anal. Calcd for $C_{17}H_{10}N_4O_2$: C, 67.58; H, 3.30. Found: C, 67.36; H, 3.00. MS: *m/z* 303 (19), 302 (M^+, 100), 219 (14), 142 (13), 114 (68), 104 (22). IR (cm^{-1}): 1698 (vs), 1595 (s), 1402 (s), 1227 (vs), 976 (s), 731. UV−Vis: λ (nm) 270 (w, sh), 322 (s). ^1H NMR ($CDCl_3$): δ 9.57 (s, =CHPh), 8.34−8.37 (m, 2H), 8.00−8.03 (m, 2H), 7.84−7.88 (m, 2H), 7.52−7.63 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 176.77, 160.18, 144.64, 134.76, 134.00, 133.90, 130.91, 130.16, 129.35, 127.86.

Compound 6. A mixture of 183 mg (0.386 mmol) of **4**, one drop of concentrated sulfuric acid in 2 mL acetic anhydride, and 2 mL of acetic acid was stirred at 50 °C for 10 min. The reaction mixture was cooled, and 20 mL of ice water was added. The precipitate was filtered and washed with 10 mL of methanol. Recrystallization of the precipitate from dichloromethane gave 60 mg of light yellow **6** (recovered yield 52%). Mp: 255−257 °C dec. Anal. Calcd for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.36. Found: C, 56.60; H, 3.48. IR (cm^{-1}): 1701 (vs), 1670 (vs), 1686 (s), 1229 (s). ^{13}C NMR ($CDCl_3$): δ 176.02, 168.30, 145.29, 135.13, 133.90, 128.10, 24.25.

Compound 7. To 2.27 g (10 mmol) of dichloronaphthoquinone in 100 mL of absolute ethanol was added 1.3 g of sodium azide. After 3 h of stirring, the mixture turned orange and 1.92 g (5 mmol) of bis(diphenyphosphino)methane in 20 mL of dichloromethane was added slowly, and the evolution of nitrogen was observed. The solution was stirred for 30 min and gradually turned red. The solid was filtered and washed three times with 30 mL of DMF. Slow evaporation of the combined filtrate and washing liquor gave 2.25 g of the DMF adduct of **7** (recovered yield 51%). Mp: >280 °C. Anal. Calcd for $C_{45}H_{30}N_8O_4P_2\cdot DMF$: C, 65.38; H, 4.23. Found: C, 65.12; H, 4.49. IR (cm^{-1}): 3420, 1682 (vs), 1663 (s). UV−Vis: λ (nm) 283 (s), 402 (br).

Compound 9. A mixture of 400 mg (2 mmol) of **8** with 260 mg (4 mmol) of sodium azide in 20 mL of ethanol was refluxed 2 h. Removal of solvent gave 343 mg of a white crystalline solid (yield, 65%). Mp: 213−215 °C. Anal. Calcd for $C_8H_4N_8$: C, 45.22; H, 1.90. Found: C, 43.35; H, 1.90. IR (cm^{-1}): 1584 (s), 1510 (s), 1483 (vs), 1460 (s), 1291 (s), 785 (vs). UV−Vis: λ (nm) 308 (s), 338 (w, sh). ^1H NMR (DMSO-d_6): δ 8.80−8.76 (m, 2H), 8.10−8.00 (m, 2H). ^{13}C NMR (DMSO-d_6) δ 140.36, 130.93, 122.67, 111.70.

Crystal structures for compounds **3**, **4**, **6**, **7**, and **9** and *ab initio* calculations on the 2-amino-1,2,3-triazole system will be reported elsewhere.

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Supporting Information Available: A complete listing of mass spectral data for compounds **3**, **4**, and **5** and infrared absorption bands for compounds **3**−**7** and **9** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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