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Synthesis of New Dipyridotetraazapentalenes

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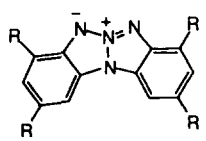
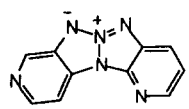
Abstract: The new heteroaromatic compounds, dipyridotetraazapentalenes **3**–**5**, were synthesized in two steps from readily available triazolopyridines **6** and **10**. *N*-Arylation of **6** and **10** followed by subsequent reductive cyclization of the *N*-(nitropyridyl)-triazolopyridines with triethylphosphite in toluene afforded **3**, **4** and **5**, respectively, in good yields. Nitration of **3** afforded the new energetic tetranitrotetraazapentalene derivative **15** in 58% yield. © 1997 Elsevier Science Ltd.

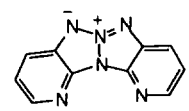
The design and synthesis of new insensitive energetic compounds with high density and improved energetic properties have been the focus of recent studies in our laboratories.[1-4] Because of the inherent thermal stability of the tetranitrodibenzotetraazapentalene (**1**, Y-Tacot, mp 400 °C)[5], the dibenzotetraazapentalene ring system **2** was initially identified as an attractive precursor for the development of new classes of high density insensitive energetic materials. To this end several energetic nitrated dibenzotetraazapentalenes were synthesized.[2-4] However, these compounds were found to be relatively sensitive to impact and were chemically unstable to moisture and air.[3] To avoid the problems of sensitivity and chemical instability associated with highly nitrated species of **2**,[2-4] several dipyridotetraazapentalenes (**3**–**5**) have been envisaged as attractive alternatives. Preliminary computational studies revealed that replacement of a CH moiety in the benzo ring of **1** by a nitrogen atom had the effect of increasing the density of the compound while potentially decreasing the sensitivity by eliminating the need for the additional nitro groups.[1] Herein we wish to describe an expedient synthesis of three isomeric forms of the dipyridotetraazapentalene ring system.



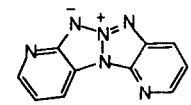
1 R = NO_2
2 R = H



3



4

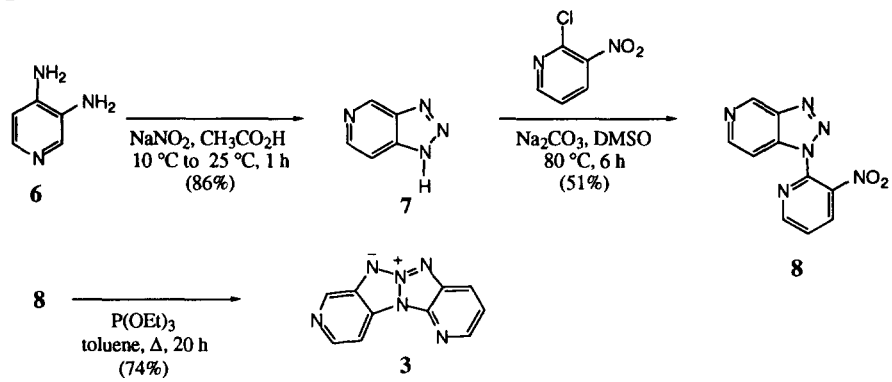


5

The syntheses of the aza-analogs of **2** were envisaged to proceed in similar fashion to that previously described for **2**.[5] As illustrated in Scheme 1, the 1,2,3-triazolo[4,5-c]pyridine (**7**) was readily prepared from

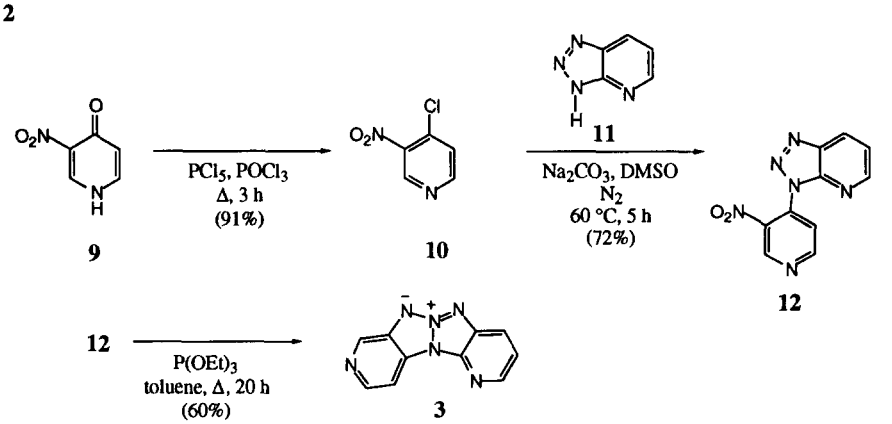
3,4-diaminopyridine (**6**).[6] *N*-Arylation of **7** with 2-chloro-3-nitropyridine in DMF at 150 °C afforded a low yield of three isomeric *N*-arylated products. However, when DMSO was employed as the solvent at a lower reaction temperature (80 °C) *N*-arylation of **7** in the presence of anhydrous Na_2CO_3 gave 1-(3-nitro-2-pyridyl)-1,2,3-triazolo[4,5-*c*]pyridine (**8**) as the only product in 51% yield.[7-9] Reductive cyclization of **8** with triethyl phosphite in toluene at reflux for 20 h then furnished **3** in 74% yield.

Scheme 1



In order to unequivocally establish the structure of **3** an alternative synthesis was executed. As illustrated in Scheme 2, **3** was prepared from the commercially available 1,2,3-triazolo[4,5-*b*]pyridine (**11**). Treatment of 3-nitro-4-pyridone (**9**) with phosphorous pentachloride/phosphorous oxychloride gave 4-chloro-3-nitropyridine (**10**) in 91% yield.[10] *N*-Arylation of triazole **11** with **10** in DMSO/Na_2CO_3 at 60 °C furnished 3-(3-nitro-4-pyridyl)-1,2,3-triazolo[4,5-*b*]pyridine (**12**) in 72% yield. Subsequent reductive cyclization of **12** then afforded **3** in 60% yield.

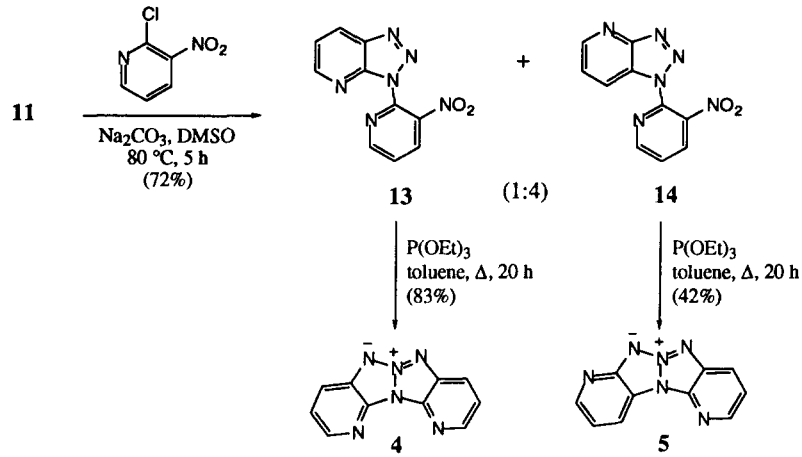
Scheme 2



Extension of this chemistry for preparation of the dipyridotetraazapentalenes **4** and **5** was also investigated. *N*-Arylation of **11** with 2-chloro-3-nitropyridine afforded a mixture of the regioisomers 3-(3-nitro-2-pyridyl)-1,2,3-triazolo[4,5-*b*]pyridine (**13**) and 1-(3-nitro-2-pyridyl)-1,2,3-triazolo[4,5-*b*]pyridine (**14**)

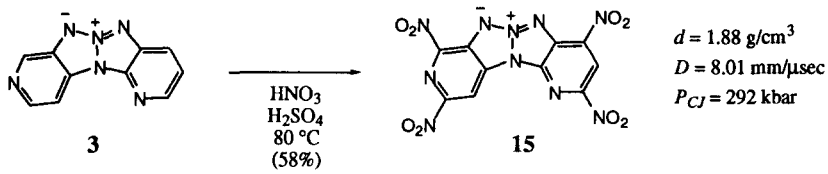
in a ratio of 1:4 (**13**:**14**) and in 72% yield (Scheme 3). The two regioisomers **13** and **14** were easily separated by column chromatography (SiO_2, $CHCl_3$). The structures of isomers **13** and **14** were established by independent reductive cyclization to the corresponding dipyridotetraazapentalenes **4** and **5**, respectively. The structures of **4** and **5** were easily differentiated by NMR spectroscopy due to the C_2-symmetry of **4** (Scheme 3).[11]

Scheme 3



Similar to the dibenzotetraazapentalene **2**[5] the dipyridotetraazapentalene **3** could be readily nitrated in HNO_3/H_2SO_4 at 80 °C Under these conditions the tetranitrodipyridotetraazapentalene **15** was obtained in 58% yield (Scheme 4). The aza-Tacot derivative **15** was found to exhibit excellent thermal stability which decomposed without explosion at 340-342 °C. In addition, **15** was found to be insensitive to impact in a hammer/anvil test. Moreover, based on calculated values, the density and the energetics properties, detonation velocity (D)and detonation pressure (P_{CJ}), of **15** are significantly enhanced over those measured for Y-Tacot (**1**).[12]

Scheme 4



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References and Notes

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11. Spectral data for selected compounds. Pyrido[3",4":4',5'][1,2,3]triazolo[2',1':2,3][1,2,3]triazolo[4,5-*b*]pyridin-6-ium inner salt (**3**): mp 226–228 °C; IR (KBr) 1613, 1589, 1506, 1441, 1391, 1389, 1275, 1171, 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.70 (d, 1H, J = 5.49 Hz), 8.56 (d, 1H, J = 4.4 Hz), 8.21 (m, 2H), 7.6 (dd, 1H, J = 8.5, 4.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz), δ 143.7, 142.0, 140.5, 140.0, 137.7, 136.1, 125.3, 124.3, 122.6, 105.0. Pyrido[2",3":4',5'][1,2,3]triazolo[2',3':2,3]-[1,2,3]triazolo[4,5-*b*]pyridin-6-ium inner salt (**4**): mp 274–276 °C; IR (KBr) 1598, 1538, 1503, 1458, 1309, 1229, 1135 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, 2H, J = 4.6 Hz), 8.22 (d, 2H, J = 8.3 Hz), 7.6 (dd, 2H, J = 8.5, 4.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.3, 137.2, 136.2, 124.2, 122.5. Pyrido[2",3":5',4'][1,2,3]triazolo[2',3':2,3][1,2,3]triazolo-[4,5-*b*]pyridin-6-ium inner salt (**5**): mp 216–218 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (dd, 1H, J = 4.75, 1.4 Hz), 8.61 (m, 2H), 8.3 (dd, 1H, J = 8.4, 1.2 Hz), 7.63 (dd, 1H, J = 8.4, 4.7 Hz), 7.49 (dd, 1H, J = 8.2, 4.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.4, 144.0, 136.6, 136.2, 124.7, 122.4, 118.5, 118.5, 117.8, 115.4. 2,4,8,10-Tetranitropyrido-[3",4":4',5'][1,2,3]triazolo[2',1':2,3][1,2,3]triazolo[4,5-*b*]pyridin-6-ium inner salt (**15**): mp 340–342 °C; IR (KBr) 1705, 1555, 1464, 1406, 1325, 1244, 1187, 1133, 1104 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 9.31 (s, 1H).
12. The density (*d*), detonation velocity (*D*) and detonation pressure (P_{CJ}) were computed with a program (Dickerson Method) obtained from the Naval Weapons Center, China Lake, CA. See ref. 4 for the calculated properties of **1**.

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