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Reaction cascades initiated by nucleophilic attack of heteropentalene mesomeric betaine and nitrogen-rich mesoionic tetrazolium-5-amides on electron-deficient unsaturated compounds. Synthesis of novel heterocyclic systems †

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The reactions of heteropentalene mesomeric betaine **1** and nitrogen-rich mesoionic tetrazolium-5-amides **4**, **11** and **16**–**18** with electron-deficient unsaturated compounds have been studied. Novel heterocyclic systems, tetrazolo[4,5-*a*][1,7]benzodiazonine inner salt **2** and 3-oxo-3,7-dihydro-2*H*-pyrazolo[3,4-*b*]pyridine **5**, have been synthesized by the reactions of dimethyl acetylenedicarboxylate with **1** and tetrazolium-5-anilide **4**, respectively, and fully characterized by X-ray crystallography. It has been found that the reactions of other tetrazolium-5-amides are also initiated by the nucleophilic addition of the electron-rich amide nitrogen to the electron-deficient unsaturated compounds.

Introduction

Heteropentalene mesomeric betaines are isoconjugate with the pentalenyl dianion which cannot be represented by covalent Kekulé structures.[1] Mesoionic compounds are five-membered heterocycles which cannot be represented satisfactorily by any one covalent or polar canonical structure.[2] Both types of heterocycle can only be represented by the hybrid of several dipolar structures and, owing to their interesting electronic structures, they have been extensively studied from theoretical, synthetic, and practical standpoints. As these compounds are highly polarized dipoles, among their chemical transformations, the reactions with electron-deficient unsaturated compounds are particularly intriguing and, indeed, several new heterocyclic systems with novel ring structures have hitherto been constructed *via* 1,3-dipolar cycloaddition reactions.[3]

In our continuing studies on tetrazole mesoionic systems, we recently synthesized heteropentalene mesomeric betaine **1** by the photolysis of a 5-azido-1,3-diphenyltetrazolium salt.[4] Here we disclose a series of addition reactions of **1**, as well as of related nitrogen-rich mesoionic heterocycles, to electron-deficient unsaturated compounds which give novel heterocyclic systems.

Results and discussion

(a) Reactions of 2-phenyl-1*H*-tetrazolo[1,5-*a*]benzimidazolium inner salt (1)

Heteropentalene mesomeric betaines are classified into four categories (types A–D) based on their electronic arrangements.[1] Most of the known heteropentalene mesomeric betaines are of types A and B; types C and D are rare. The compound **1** is a type C system. The reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) was examined first. When **1** was stirred with excess DMAD without solvent, the reaction proceeded smoothly and red crystals of **2** were obtained in 78% yield after recrystallization. Although the mass spectrum did not show the molecular ion peak, the nitrogen-lost fragment ion peak ($M^+ - N_2$) and the elemental analysis data indicate that this product is a 1 : 2 adduct of **1** and DMAD. The structure of **2** was unambiguously determined by X-ray crystallography, which reveals the unique tricyclic tetrazolo[1,5-*a*][1,7]benzodiazonine system (Fig. 1). The nine-membered ring is not planar but distorted in two different directions; hence two crystallographically independent molecules exist in the crystal. The compound **2** can be best expressed by the tetrazolium-methylide inner salt structure, in which the negative charge on C-4 is associated with the methoxycarbonyl group attached to this carbon. The high field chemical shift of C-4 (53.4 ppm) in the ^{13}C NMR spectrum supports this formulation.

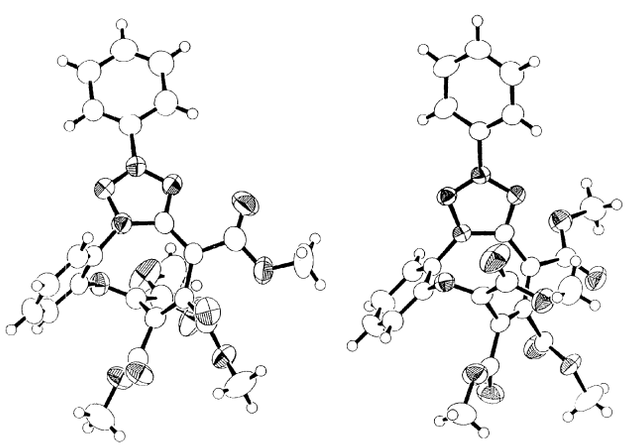

Fig. 1 X-ray crystal structure of compound **2**. The two crystallographically independent molecules are shown.

The reaction can be considered to proceed as depicted in Scheme 1. The electron-rich amide nitrogen reacts nucleophilically with two molecules of DMAD to give the tetracyclic intermediate, whose C-5–N_{exo} bond is cleaved to regenerate the stable 1,3-diaryl-5-substituted tetrazolium system. It is noted that no 1 : 1 adduct (seven-membered ring product) was found in the reaction mixture.

Compound **1** was next subjected to reaction with benzyne. Benzyne, generated *in situ* in refluxing dichloromethane, reacted readily to give a yellow solid. The characteristic absorption at 1688 cm^{-1} in the IR spectrum suggests that this product is a tetrazolium-5-olate derivative. The presence of an NH group is also indicated by the IR and ^1H NMR spectra. The structure

† Electronic supplementary information (ESI) available: synthesis of **4b**; reactions of **11** and **17** with electron-deficient unsaturated compounds; alternative synthesis of **19** from **20**. See http://www.rsc.org/suppdata/ob/b2/b211000h/

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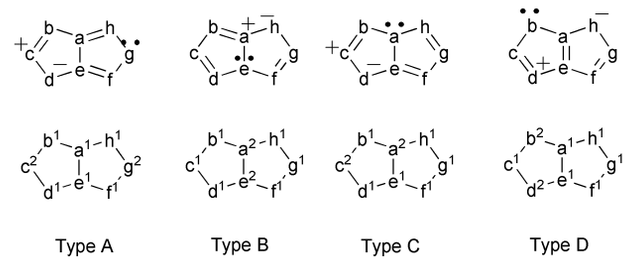
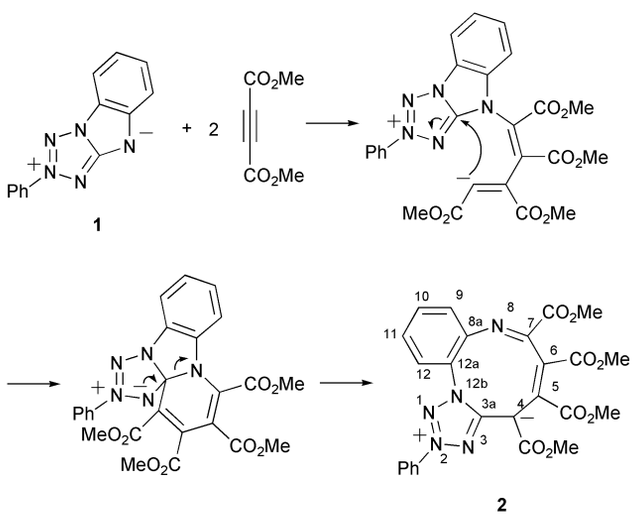
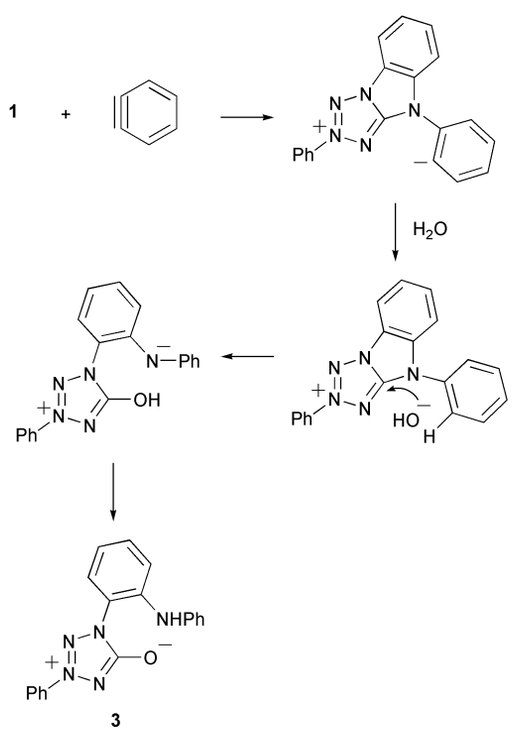


a - h represent suitably substituted carbon or heteroatoms and superscripts indicate the origin of the 10π-electrons



Scheme 1

was eventually deduced to be 1-(2-anilinophenyl)-3-phenyltetrazolium-5-olate (**3**) based on the elemental analysis and spectral data. A plausible mechanism for the formation of **3** is illustrated in Scheme 2. The electrophilic addition of benzyne to the electron-rich exocyclic nitrogen of **1** yields the *N*-phenylated tricyclic intermediate, which is nucleophilically attacked by hydroxide ion followed by a ring cleavage and prototropic



Scheme 2

rearrangement to furnish the product **3**. The reactions of **1** with other electrophiles such as tetracyanoethylene, ethyl propiolate, dimethyl [1,2,4,5]tetrazine-3,6-dicarboxylate, dibenzoylacetylene, and dimethyl azodicarboxylate were also examined; however, no addition products were obtained from these reactions.

(b) Reactions of 1,3-diphenyltetrazolium-5-anilide (4a)

The reaction of **4a** with DMAD in acetonitrile proceeded smoothly at room temperature. Column chromatographic separation of the reaction mixture gave the purple compound **5a** (12%) and olate **6a** (27%), together with a trace amount of naphthalenetetracarboxylate **7** (Scheme 3). The compound **5a** has a molecular formula ($C_{24}H_{19}N_3O_7$) which corresponds to a loss of PhN_2 and MeO groups from a 1 : 2 adduct of **4a** and DMAD. The structure was assigned as the pyrazolo[3,4-*b*]-pyridine derivative **5a**. In order to determine which phenyl groups of **4a** correspond to the two phenyl groups of **5a**, a labeling experiment was performed. The three phenyl groups of **4a** were labeled; *i.e.*, 3-phenyl-1-(4-tolyl)tetrazolium-5-(4-ethyl)anilide (**4b**) was synthesized and subjected to the same reaction. From this reaction, olate **6b** (43%) and pyrazolo-[3,4-*b*]pyridine **5b** (5%) were isolated. A naphthalene derivative corresponding to **7** was not obtained from this reaction; instead, maleate **8** was isolated in 2% yield. The formation of **7** and **8** could be attributed to phenyl (or 4-tolyl) radical derived from the aryldiazonium salts. The structure of **5b** was determined crystallographically. The crystals grown from dichloromethane–hexane contain four **5b** molecules and two CH_2Cl_2 molecules in the unit cell. These **5b** molecules are slightly different from each other in the tilting angle between the pyrazolopyridine ring plane and the substituent groups, though they have essentially identical geometries. One of these four molecules is depicted in Fig. 2. The phenyl ring at N-2 lies in almost the same plane as the pyrazolo[3,4-*b*]pyridine ring, whereas the 4-ethylphenyl group at N-7 is essentially perpendicular. It is evident that the tolyl group at the N-1 position of **4b** is not incorporated into **5b**. The most plausible reaction mechanism is shown in Scheme 4. Again, the reaction is initiated by nucleophilic attack of the exocyclic nitrogen of **4** on DMAD. In contrast to the case of **1**, the intermediate undergoes a cleavage and degradation of the tetrazolium ring to furnish the novel bicyclic system **5**. Only a few examples of this ring system have been previously prepared, *e.g.*, by the condensation of 5-amino-2,4-dihydro-3*H*-pyrazol-3-one with β-carbonyl compounds.[5]

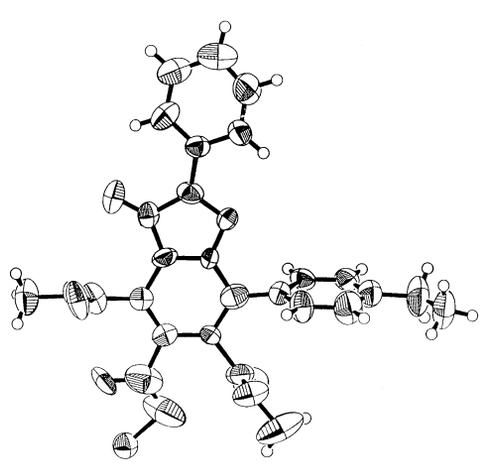
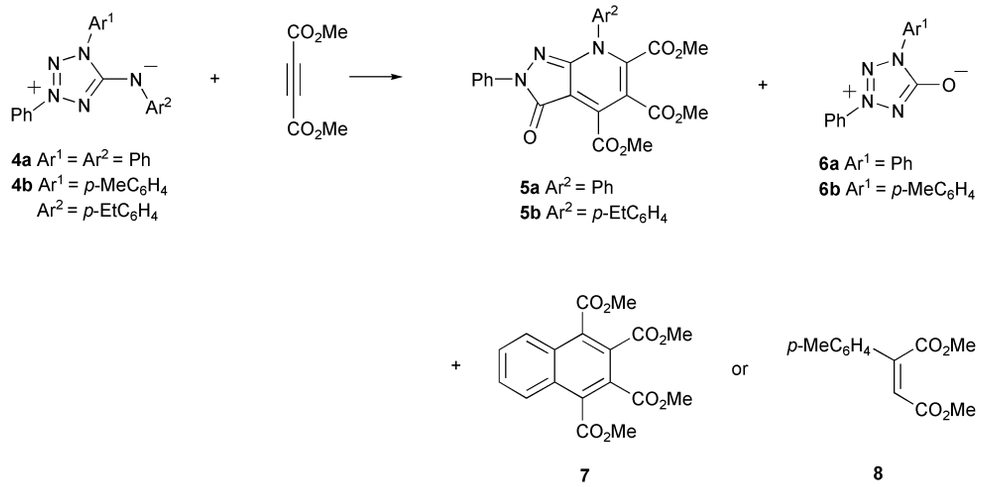
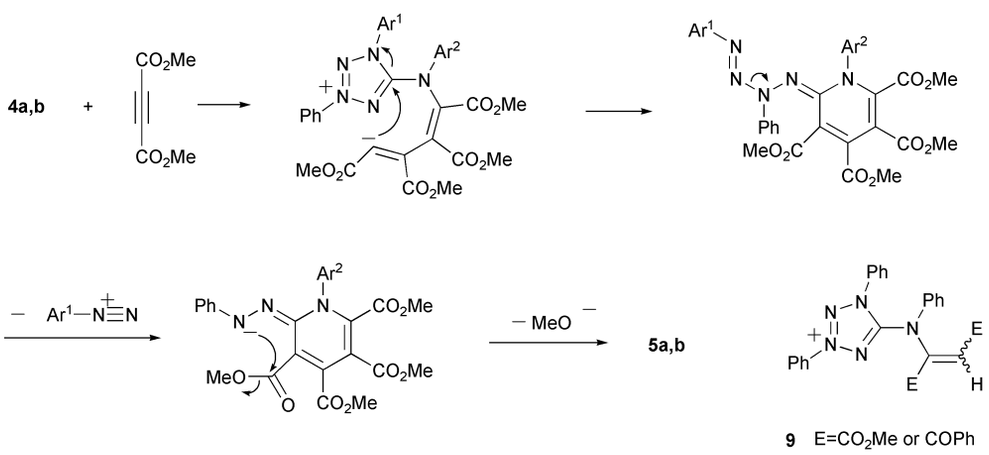


Fig. 2 X-ray crystal structure of compound **5b**.

The formation of olate **6** from **4** was unexpected. Similar reaction of **4a** with dibenzoylacetylene (4 equiv.) gave olate **6a** in 45% yield. When this reaction was carried out after the addition of a small amount of $H_2{}^{18}O$, the resulting olate **6a** contained 21% ^{18}O by mass spectroscopy. Therefore, the



Scheme 3



Scheme 4

formation of olate **6a** could be rationalized by the hydrolysis of the intermediate Michael adduct **9**, whose exocyclic amino group acts as a good leaving group.

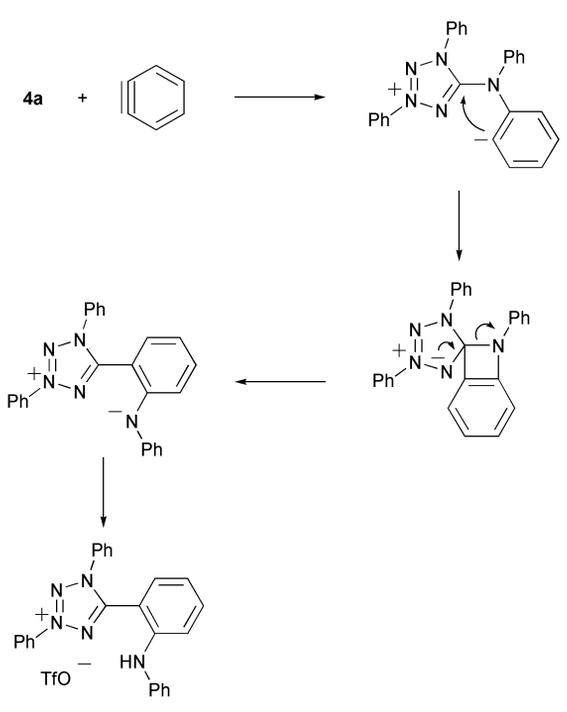
The reaction of **4a** with benzyne gave the 1,3-diphenyl-5-(2-anilinophenyl)tetrazolium salt **10**, where benzyne inserted into the exocyclic C–N bond of **4a**, probably *via* the course shown in Scheme 5. The attempted reactions of **4a** with dimethyl azodicarboxylate and tetracyanoethylene did not proceed.

(c) Reactions of 1,3-diphenyltetrazolium-5-amide (11)

The reaction of amide **11** with DMAD gave the Michael addition product **12** as a mixture of two geometrical isomers (Scheme 6). The isomers could be separated readily by column chromatography; however, the assignments could not be made. Benzyne inserted into the exocyclic N–H bond of **11** to give anilide **4a**. Tetracyanoethylene similarly reacted with **11** to give tricyanovinylamide **13**, *via* the Michael addition followed by the elimination of HCN. The reaction with tetrazine **14** proceeded smoothly to give the ring-opened product **15** as a mixture of geometrical isomers in the ratio of 59 : 29 : 12.

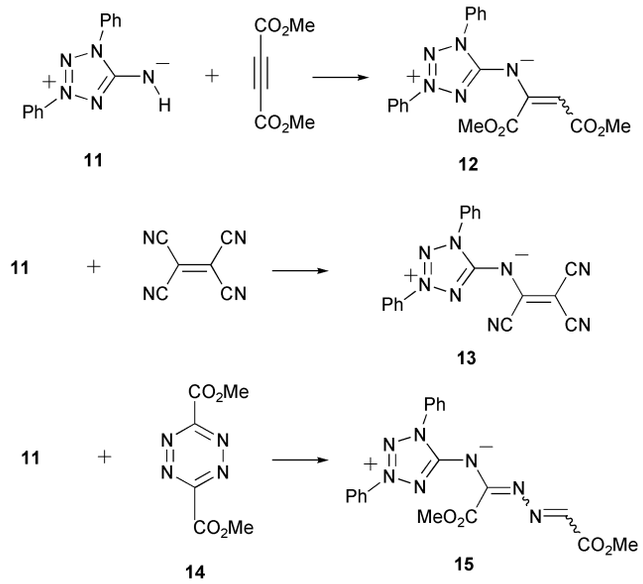
(d) Reactions of nitrogen-bridged tetrazolium mesoionic compounds 16–18

The nitrogen-bridged bis(tetrazolium) compounds **16**–**18** are another series of nitrogen-rich mesoionic heterocycles. The reactions of these compounds with electron-deficient alkenes and alkynes were also examined. The tripolar mesoionic compound **16** reacted neither with DMAD nor with tetracyanoethylene, probably owing to the steric crowding around the exocyclic active site. In contrast, compound **17** reacted smoothly with DMAD to give **19** (21%) and olate **6a** (21%)



Scheme 5

(Scheme 7). A small amount of **12** (2%) was also isolated. The compound **19** was alternatively prepared from **20** and DMAD in high yield (91%). Similarly, the reaction of **17** with dibenzoylacetylene gave **21** (19%) and olate **6a** (46%). Triazenide **18** did



Scheme 6

not react with DMAD, probably owing to the poor nucleophilicity, because the negative charge in **18** is delocalized over the three bridging nitrogen atoms.

Conclusion

The reactions of heteropentalene mesomeric betaine **1** and a variety of nitrogen-rich mesoionic tetrazolium-5-amides **4**, **11** and **16**–**18** with electron-deficient unsaturated compounds have been studied. The reactions are initiated by the nucleophilic attack of the electron-rich amide nitrogen. The resulting zwitterionic intermediates undergo further reactions to give a variety of products, depending on the substituent on the exocyclic nitrogen-atom and the electrophiles. The novel heterocyclic systems, tetrazolo[4,5-*a*][1,7]benzodiazonine inner salt **2** and pyrazolo[3,4-*b*]pyridine **5**, have been synthesized from **1** and **4**, respectively, and fully characterized by crystallography. The present work demonstrates that the tetrazole mesomeric compounds show unique reaction behavior towards electrophiles and have proved to be useful building blocks for the synthesis of new nitrogen heterocycles.

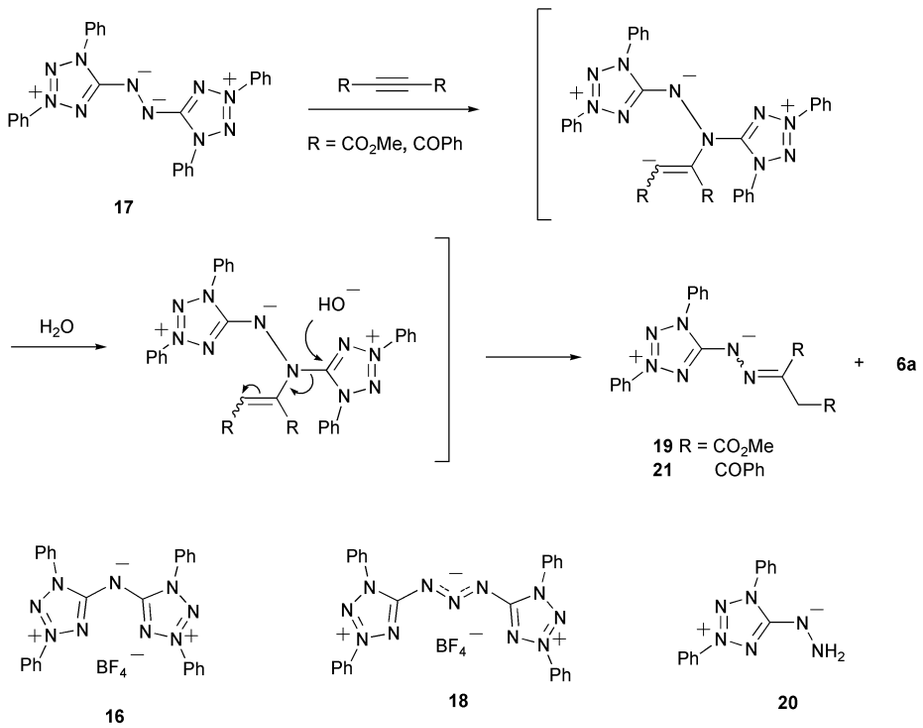
Experimental

General

Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were taken for potassium bromide discs with a JASCO A-102 instrument. ^{1}H and ^{13}C NMR spectra were run with a Varian Gemini 200 instrument (200 and 50 MHz, respectively) and referenced using either the residual non-deuterated solvent or tetramethylsilane. Electronic spectra were measured on a Hitachi U-3500 spectrophotometer. Mass spectra were measured with a Hitachi M-2000S spectrometer (EI, 70 eV). Elemental analyses were performed with a Perkin Elmer 2400 II CHNS/O or at the Elemental Analysis Centre of Kyoto University. Column chromatography was carried out on silica gel (Nacalai Tesque, silica gel 60 7734.5000) or on 3-aminopropylsilane-modified silica gel (Fuji Silysia Chemical, NH-DM 1020, 100–200 mesh). For TLC, Merck Silica gel 60 F254 Plate or Fuji Silysia Chemical NH was used. $H_2{}^{18}O$ (95–97%) was purchased from Cambridge Isotope Laboratories, Inc. CH_2Cl_2, toluene and MeCN were dried with CaH_2 and distilled before use.

Reaction of 2-phenyl-1*H*-tetrazolo[1,5-*a*]benzimidazolium inner salt (1) with DMAD

A mixture of **1**[3] (50 mg, 0.21 mmol) and DMAD (1.0 mL, 8.3 mmol) was stirred under argon for 5 h. The reaction mixture was subjected to column chromatographic purification (NH-DM 1020/CH_2Cl_2, $R_f = 0.50$) to give a red solid of 4,5,6,7-tetrakis(methoxycarbonyl)-2-phenyl-4*H*-tetrazolo[4,5-*a*][1,7]benzodiazonin-2-ium-4-ide (**2**) (85 mg, 78%). Analytical samples were obtained after recrystallization from ethanol: mp 144–146 °C; IR (KBr) cm^{-1} 1730, 1700, 1470, 1428, 1220, 1188, 764; ^{1}H NMR ($CDCl_3$) δ 3.55 (s, 3H), 3.66 (s, 3H), 3.73 (s, 3H), 3.88 (s, 3H), 7.00 (d, J = 8.8 Hz, 1H), 7.35–7.70 (m, 6H), 8.15 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 51.0 (Me), 51.7 (Me), 52.4 (Me), 53.4 (C^-), 53.6 (Me), 113.6, 120.7 (CH), 120.8 (*o*-C of



Scheme 7

Ph), 123.3, 126.9 (CH), 127.4 (CH), 129.9 (*m*-C of Ph), 132.6 (CH), 132.8 (CH), 135.1, 145.3, 147.8, 161.8, 162.5, 163.4, 166.1, 167.7, 168.3; MS *m*/*z* 492 (31%), 491 (100, $M^+ - N_2$), 460 (34), 400 (30), 338 (31), 324 (49); HRMS *m*/*z* ($M^+ - N_2$) calcd 491.1326, obsd 491.1320; UV/Vis (MeCN) λ_{max} (log ε)/nm 283.0 (4.27), 386.0 (4.08). Anal. Calcd for $C_{25}H_{21}N_5O_8 \cdot 1/2\ C_2H_5OH$ (542.6): C, 57.55; H, 4.47; N,12.91. Found: C, 57.49; H, 4.56; N, 12.88%.

Reaction of 1 with benzyne

A solution of tetra-*n*-butylammonium fluoride in THF (1.0 M, 1.0 mL, 1.0 mmol) was added over 5 min to a mixture of **1** (0.10 g, 0.42 mmol) and phenyl[2-(trimethylsilyl)phenyl]-iodonium triflate[6] (0.42 g, 0.84 mmol) in CH_2Cl_2 (5 mL) under reflux, and the mixture was further refluxed for 1 h. The solvent was removed and the residue was chromatographed on silica gel (CH_2Cl_2–MeCN gradient) to give a yellow solid of **3** (58 mg, 42%). Analytical samples were obtained after recrystallization from a CH_2Cl_2–hexane mixture: mp 108–110 °C; IR (KBr) cm^{-1} 3250, 1688, 1596, 1490, 1334, 1314, 1296, 750; ^{1}H NMR (DMSO-d_6) δ 6.91 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.67–7.72 (m, 3H), 7.96 (s, 1H), 8.03–8.04 (m, 2H); ^{13}C NMR (CD_3CN) δ 119.4 (*o*-C of Ph), 120.1 (CH), 121.1 (*o*-C of Ph), 122.1 (CH), 122.5 (CH), 124.2, 128.5 (CH), 130.4 (*m*-C of Ph), 130.9 (*m*-C of Ph), 132.1 (CH), 132.5 (CH), 137.8, 140.4, 143.5, 161.2; MS *m*/*z* 330 (22%), 329 (93, M^+), 168 (100), 167 (78), 77 (19). HRMS *m*/*z* (M^+) calcd 329.1275, obsd 329.1265; UV/Vis (MeCN) λ_{max} (log ε)/nm 280.0 (4.34), 316.0 (sh, 3.94), 370.5 (sh, 3.43). Anal. Calcd for $C_{19}H_{15}N_5O$: C, 69.29; H, 4.60; N, 21.25. Found: C, 69.44; H, 4.42; N, 21.12%.

Reaction of 4a and DMAD

DMAD (1.2 mL, 9.6 mmol) was added to a solution of **4a**[7] (0.30 g, 0.96 mmol) in acetonitrile (10 mL) and the mixture was stirred for 30 min. The solvent was removed and the residue was chromatographed on NH-SiO_2 to give the naphthalene derivative **7**[8] (8 mg, 1%), olate **6a** (61 mg, 27%), and the pyrazolo[3,4-*b*]pyridine derivative **5a** (55 mg, 12%). Analytical samples of **5a** were obtained after recrystallization from a CH_2Cl_2–hexane mixture.

Trimethyl 3-oxo-2,7-diphenyl-3,7-dihydro-2*H*-pyrazolo[3,4-*b*]-pyridine-4,5,6-tricarboxylate (5a)

Purple crystals, mp 210–214 °C; IR (KBr) cm^{-1} 1748, 1722, 1678, 1640, 1438, 1308, 1222; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 3H), 3.87 (s, 3H), 4.11 (s, 3H), 7.13 (t, 1H, J = 8.0 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.44–7.50 (m, 2H), 7.57–7.63 (m, 3H), 7.95 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 53.1 (Me), 53.5 (2 × Me), 119.5 (*o*-C of Ph), 125.3 (CH), 127.5 (*o*-C of Ph), 128.6 (*m*-C of Ph), 129.8 (*m*-C of Ph), 131.0 (CH), 134.6, 138.8, 142.7, 145.0, 148.6, 157.2, 160.8, 162.6, 163.9 (two quaternary carbons were not observed); MS *m*/*z* 462 (29%, M^+), 461 (100, M^+), 205 (56), 77 (46); HRMS *m*/*z* (M^+) calcd 461.1222, obsd 461.1253. UV/Vis (MeCN) λ_{max} (log ε)/nm 248.0 (4.22), 310.5 (4.29), 360.5 (sh, 3.59), 501.5 (3.07). Anal. Calcd for $C_{24}H_{19}N_3O_7 \cdot 1/2\ CH_2Cl_2$: C, 58.39; H, 4.01; N, 8.34. Found: C, 58.60; H, 4.08; N, 8.31%.

Reaction of 4b with DMAD

A solid of **4b** (0.30 g, 0.85 mmol) was placed in a flask and cooled to −30 °C. DMAD (1.0 mL, 8.6 mmol) was added slowly and the mixture was stirred at −1 °C for 14 h. The mixture was subjected to column chromatography (SiO_2 and then NH-DM 1020) to give **8**[9] (5 mg, 2%), olate **6b** (90 mg, 43%), and **5b** (21 mg, 5%). Analytical samples of **5b** were obtained after recrystallization from a CH_2Cl_2–hexane mixture.

Trimethyl 7-(4-ethylphenyl)-3-oxo-2-phenyl-3,7-dihydro-2*H*-pyrazolo[3,4-*b*]pyridine-4,5,6-tricarboxylate (5b)

Purple needles, mp 170–173 °C; IR (KBr) cm^{-1} 1750, 1722, 1678, 1640, 1434, 1306, 1220; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, J = 7.5 Hz, 3H), 2.78 (q, J = 7.5 Hz, 2H), 3.62 (s, 3H), 3.86 (s, 3H), 4.12 (s, 3H), 7.13 (t, J = 7.4 Hz, 1H), 7.28–7.43 (m, 6H), 7.96 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 15.0 (Me), 28.5 (CH_2), 53.1 (Me), 53.3 (2 × Me), 119.8 (*o*-C of Ar), 125.4 (CH), 127.4 (*o*-C of Ar), 128.8 (*m*-C of Ar), 129.3 (*m*-C of Ar), 132.5, 138.9, 145.0, 147.6, 148.9, 157.4, 161.1, 162.7, 163.9 (three quaternary carbons were not observed); MS *m*/*z* 491 (6%), 490 (30), 489 (100, M^+); UV/Vis (MeCN) λ_{max} (log ε)/nm 251.0 (4.42), 310.0 (4.50), 356.0 (sh, 3.54), 496.5 (3.39). Anal. Calcd for $C_{26}H_{23}N_3O_7 \cdot 1/2CH_2Cl_2$: C, 59.83; H, 4.55; N, 7.90. Found: C, 59.74; H, 4.42; N, 7.62%.

Reaction of 4a with benzyne

A solution of tetra-*n*-butylammonium fluoride in THF (1.0 M, 0.46 mL, 0.46 mmol) was added to a mixture of **4a** (0.10 g, 0.32 mmol) and phenyl[2-(trimethylsilyl)phenyl]iodonium triflate (0.19 g, 0.38 mmol) in CH_2Cl_2 (7.0 mL) under reflux, and the mixture was stirred at room temperature for 1 h. The solvent was removed and the residue was separated by column chromatography (silica gel/CH_2Cl_2, then NH-DM 1020/CH_2Cl_2 : hexane = 1 : 2) to give crude **10** (48 mg) and the starting compound **4a** (40 mg, 40% recovery). The crude **10** was recrystallized from ethanol to give pure compound (32 mg, 26%); yellow solid; mp 193–195 °C; IR (KBr) cm^{-1} 3320, 1596, 1496, 1284, 1254, 1158, 1032; ^{1}H NMR ($CDCl_3$) δ 6.73 (d, 2H, J = 7.5 Hz), 6.84 (t, 1H, J = 7.5 Hz), 6.99–7.10 (m, 3H), 7.34–7.51 (m, 4H), 7.56–7.73 (m, 7H), 8.33 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 119.5 (CH), 119.7 (*o*-C of Ph), 122.3 (CH), 122.5 (*o*-C of Ph), 123.3 (CH), 125.0 (*o*-C of Ph), 130.1 (*m*-C of Ph), 131.3 (*m*-C of Ph), 131.8 (*m*-C of Ph), 133.3 (CH), 133.7 (CH), 134.9 (CH), 135.9 (CH), 136.1, 141.9, 144.6, 159.6 (two quaternary carbons were not observed); MS *m*/*z* 391 (37%), 390 (100, M^+), 361 (52), 284 (29), 270 (41), 269 (67), 268 (22), 256 (17), 255 (16), 195 (31), 194 (23), 193 (18), 192 (17), 167 (16), 77 (85); UV/Vis (MeCN) λ_{max} (log ε)/nm 279.5 (4.36), 358.0 (sh, 3.65). Anal. Calcd for $C_{26}H_{20}F_3N_5O_3S$ (539.49): C, 57.88; H, 3.74; N, 12.98. Found: C, 57.75; H, 3.71; N, 12.74%.

Reactions of **11** and **17** with electron-deficient unsaturated compounds were carried out similarly. The details are given in the ESI. †

Crystal-structure determination of 2 and 5b ‡

Crystal data for $2_2 \cdot CH_3CH_2OH$. A crystal grown from ethanol was used for X-ray crystallography. $C_{52}H_{48}N_{10}O_{17}$, M = 1085.01, monoclinic, space group $P2_1/n$, a = 10.179(1), b = 24.478(2), c = 22.389(7) Å, β = 102.01(2)°, V = 5456(1) Å^3, Z = 4, D_c = 1.321 g cm^{-3}, $F(000)$ = 2264.00, μ = 1.01 cm^{-1}, radiation MoKα, T = 288 K, 2θ limit = 51.4°, 8096 reflections observed, 6464 reflections used ($I > 2.00\sigma(I)$), number of variables = 698, R = 0.092, R_w = 0.142.

Crystal data for $(5b)_4 \cdot (CH_2Cl_2)_2$. A crystal grown from CH_2Cl_2–hexane was used for X-ray crystallography. $C_{106}H_{96}Cl_4N_{12}O_{28}$, M = 2127.80, monoclinic, space group $P2_1/c$, a = 20.577(4), b = 23.749(4), c = 21.249(9) Å, β = 100.59(2)°, V = 10207.23 Å^3, Z = 4, D_c = 1.385 g cm^{-3}, $F(000)$ = 4432.00, μ = 2.01 cm^{-1}, radiation MoKα, T = 288 K, 2θ limit = 51.4°, 12240 reflections observed, 7212 reflections used ($I > 2.00\sigma(I)$), number of variables = 1350, R = 0.112, R_w = 0.174.

‡ CCDC reference numbers 197992 and 197993.

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