Cyclobutarenes. Part 2.[1] Azaquinomethanes as Reactive Intermediates: Synthesis of Cyclobuta[*b*]pyridine and Cyclobuta[*b*]pyrazine Derivatives

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Cyclisation of 2,3-bis(dibromomethyl)pyridine (**1**) and 2,3-bis(dibromomethyl)pyrazine (**3**) with sodium iodide gives the dibromodihydrocyclobutarenes (**10**) and (**13**). The intermediate quinomethanes (**6**) and (**7**), together with the pyrimidine and 1,2,4-triazine analogues (**8**) and (**9**), are readily trapped *via* cycloaddition reactions.

Cyclobutapyridines have been prepared from azocines,[2] and by thermolytic extrusion methods.[3-5] Cyclobutaquinolines[6,7] and quinoxalines[8] have also been reported. The Finkelstein cyclisation of *o*-bis(dibromomethyl)arenes provides a convenient route to carbocyclic cyclobutarenes,[1,9] and McOmie *et. al.* have used this method to prepare derivatives of cyclobuta[*c*]-thiophene.[10] Here, this reaction is extended to the synthesis of aza- and diaza-cyclobutarenes, and some cycloaddition reactions of the intermediate quinomethanes are described.

Results and Discussion

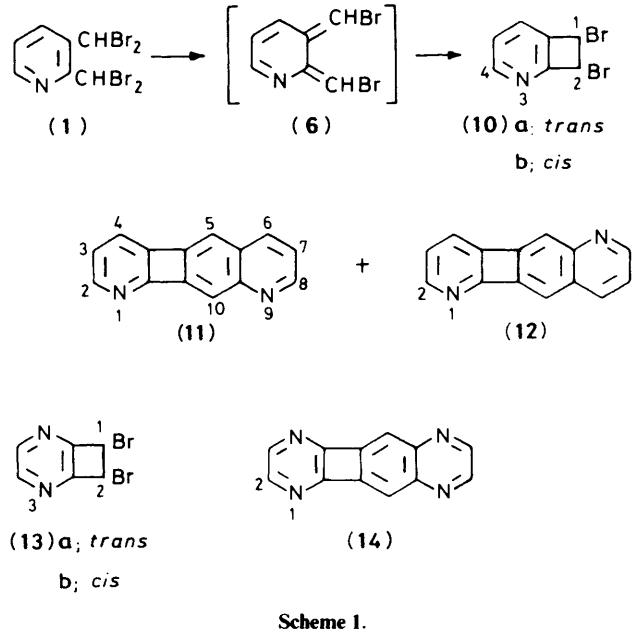
(1) – (5) (6) – (9)

(1),(6) A = N; B, C, D = CH
(2) B = N; A, C, D = CH
(3),(7) A, D = N; B, C = CH
(4),(8) A, C = N; B, D = CH
(5),(9) A, B, D = N; C = CH

Several examples of side-chain free-radical halogenation of π-deficient *N*-heterocycles have been reported in the literature,[11-14] but no bis(dibromomethyl) derivatives have been isolated.

In general, these tetrabromides can be easily prepared by photobromination of the appropriate dimethyl compound with *N*-bromosuccinimide in CCl_4. Thus a reaction of 2,3-dimethylpyridine, and the pyrazine, pyrimidine, and 1,2,4-triazine analogues gave the tetrabromides (**1**), (**3**)—(**5**) in yields ranging from 40—80%. The pyridine and pyrazine derivatives (**1**) and (**3**) can be stored indefinitely at room temperature. Formation of compounds (**4**) and (**5**) is accompanied by appreciable decomposition, probably due to intermolecular quaternisation of the intermediate monobromides,[11] but the recrystallised tetrabromides can be kept in the fridge for months without deterioration. In contrast, 3,4-bis(dibromomethyl)pyridine (**2**) could only be prepared under high-dilution conditions, and decomposed within hours at 0 °C. The relative stability of the isomer (**1**) is probably due to the blocking effect of the bulky, deactivating, 2-bis(dibromomethyl) group, which prevents polymerisation *via* electrophilic attack at the adjacent ring nitrogen.

Reaction of 2,3-bis(dibromomethyl)pyridine (**1**) with sodium iodide in DMF at 80 °C gave a 10:1 mixture of *trans*- and *cis*-1,2-dibromo-1,2-dihydrocyclobuta[*b*]pyridines (**10a,b**) in *ca.* 55% overall yield, cyclisation proceeding *via* the intermediate quinomethane (**6**) (Scheme 1). The cyclobutene protons in the *trans*-isomer (**10a**) resonate as singlets at δ 5.34 (1-H) and 5.52 (2-H), whereas the *cis*-isomer (**10b**) showed an AB system at lower field, δ 5.73 (1-H) and 5.91 (2-H), *J* 4.0 Hz. In addition to this low-field shift (**10b**) has a higher melting point, reflecting a trend shown by its carbocyclic analogues.[15] Low yields of the pale yellow 1,9- and 1,6-diazabenzo[*b*]biphenylenes (**11**) and (**12**)* were also formed in this reaction, possibly by a step-wise coupling of the tetrabromide (**1**). The mass spectrum of both (**11**) and (**12**) shows peaks at 204 (M^+, 100%) and 178 (M^+ – CN, 28%). N.m.r. data is listed in Table 1. The cyclobutapyridine protons show the expected high-field shift, and 5- and 10-H show a similar shift when compared with the corresponding protons in 6,7-dihydrocyclobuta[*g*]quinoline.[6] ^{13}C N.m.r. signals are assigned by comparison with data published for 1,6-diazabiphenylene[16] and pyrido[3,2-*g*]quinoline.[17] Both compounds are highly fluorescent in solution, an apparent characteristic of the benzo[*b*]biphenylenes. The precise mechanism of formation of these biproducts is unclear, and is currently under investigation.



Scheme 1.

Cyclisation of 2,3-bis(dibromomethyl)pyrazine (**3**) at 60 °C gave *trans*-1,2-dibromo-1,2-dihydrocyclobuta[*b*]pyrazine (**13a**) in 15% yield. This stereochemistry is assigned from the relatively high-field resonance of the cyclobutene ring protons 1,2-H at δ 5.46. The *cis*-isomer (**13b**) could not be detected. Traces of the

Table 1. ^1H and ^{13}C N.m.r. spectra of azabiphenylenes

Compd.	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H
(**11**)	8.04 (dd)	6.84 (dd)	7.15 (dd)	7.10 (s)	7.86 (dd)	7.29 (dd)	8.65 (dd)		7.55 (s)
(**12**)	8.04 (dd)	6.85 (dd)	7.21 (dd)	7.44 (s)		8.65 (dd)	7.28 (dd)	7.91 (dd)	7.22 (s)
(**14**)	7.93 (s)	7.93 (s)		7.74 (s)		8.70 (s)	8.70 (s)		7.74 (s)
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
(**11**)	148.7	124.4[a]	125.4[a]	116.8	136.6	121.9	149.2		118.5
(**12**)	149.3	124.3[a]	125.9[a]	118.6		151.3	121.5	137.2	116.5
(**14**)	143.8	143.8		121.6		144.7	144.7		121.6

[a] Signals may be interchanged.

Table 2. ^1H N.m.r. spectra of the adducts (**15**)—(**22**)

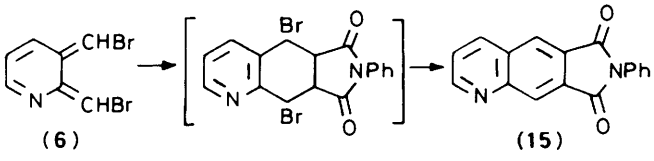
Compd.	2-H	3-H	4-H	5-H	7-H	8-H	9-H	10-H	7-Ph
(**15**)	9.14 (dd)	7.65 (dd)	8.43 (dd)	8.47 (s)			8.70 (s)		7.52 (5 H, s)
(**16**)	9.05 (s)	9.05 (s)		8.71 (s)			8.71 (s)		7.52 (5 H, s)
(**17**)	9.68 (s)		9.56 (s)	8.59 (s)			8.65 (s)		7.52 (5 H, s)
(**18**)		10.17 (s)		8.72 (s)			9.18 (s)		7.54 (5 H, s)
(**19**)	9.13 (dd)	7.61 (dd)	8.40 (dd)	8.63 (s)	7.12 (s)	7.12 (s)		8.84 (s)	
(**20**)	9.04 (s)	9.04 (s)		8.88 (s)	7.18 (s)	7.18 (s)		8.88 (s)	
(**21**)	9.67 (s)		9.53 (s)	8.77 (s)	7.19 (s)	7.19 (s)		8.77 (s)	
(**22**)		10.16 (s)		8.88 (s)	7.27 (s)	7.27 (s)		9.36 (s)	

fluorescent tetra-azabiphenylene (**14**)* were also formed, the mass spectrum showing peaks at 206 (M^+, 77%) and 180 (M^+ − CN, 100%).

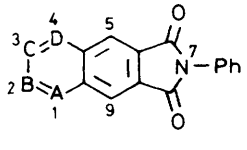
Attempts to cyclise the tetrabromides (**4**) and (**5**) were unsuccessful, no cyclobutarene or biphenylene derivatives could be detected.

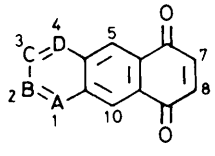
Cycloaddition Reactions of the Quinomethanes (**6**)—(**9**).—The use of carbocyclic quinomethanes as annelating agents is well established,[18,19] and increasing attention is now being directed towards the applications of heterocyclic analogues as synthetic intermediates.[20–22] Naiman and Vollhardt have described the trapping of a π-deficient azaquinomethane: thermolysis of 1,2,4,5-tetrahydrodicyclobuta[*b*,*e*]pyridine with bis(trimethylsilyl)acetylene gave a bis-adduct, which on aromatisation followed by desilylation gave acridine.[23]

Generation of the quinomethanes (**6**)—(**9**) in the presence of



(**6**) (**15**)





(**15**) − (**18**) (**19**) − (**22**)

(**15**),(**19**) A = N; B, C, D = CH
(**16**),(**20**) A, D = N; B, C = CH
(**17**),(**21**) A, C = N; B, D = CH
(**18**),(**22**) A, B, D = N; C = CH

Scheme 2.

* Systematic names: pyrido[3′,2′:3,4]cyclobuta[1,2-*g*]quinoline (**11**); pyrido[2′,3′:3,4]cyclobuta[1,2-*g*]quinoline (**12**); pyrazino[2′,3′:3,4]-cyclobuta[1,2-*g*]quinoxaline (**14**).

N-phenylmaleimide or cyclohexa-2,5-diene-1,4-dione gave the polycyclic derivatives (**15**)—(**22**) (*e.g.*, Scheme 2). The intermediate dibromo adducts aromatise with loss of HBr under the experimental conditions, and could not be isolated. ^1H N.m.r. data for these compounds is listed in Table 2. The quinones (**19**)—(**22**) are air-sensitive, and this may be a reason for the low yields obtained of the pyrimidine and triazine adducts (**21**) and (**22**). No bis-adducts formed in reactions at this temperature.

Experimental

Unless otherwise stated the following conditions apply: i.r. spectra were run as Nujol mulls. ^1H N.m.r. spectra were recorded on a JEOL JNM FX200 spectrometer, and ^{13}C n.m.r. spectra on a JEOL JNM FX90Q spectrometer, as solutions in deuteriochloroform containing 1% tetramethylsilane as an internal standard. Mass spectra were obtained on an AEI MS902 instrument. Flash chromatography[24] was performed on Merck Kieselgel 60, 230—400 mesh, and t.l.c. using Merck Kieselgel $HF_{254+354}$. 4,5-Dimethylpyrimidine[25] and 5,6-dimethyl-1,2,4-triazine[26] were prepared by literature methods.

2,3-*Bis*(*dibromomethyl*)*pyridine* (**1**).—A solution of 2,3-dimethylpyridine (1.0 g) and *N*-bromosuccinimide (6.60 g) in carbon tetrachloride (125 ml) was refluxed over a 200W light bulb for 7 h. The suspension was cooled, filtered, and the filtrate evaporated to give a brown solid (3.4 g). Recrystallisation from ethanol (30 ml) gave the *tetrabromide* (**1**) (3.1 g, 78%), m.p. 158—159 °C (Found: C, 19.9; H, 1.3; Br, 75.3; N, 3.0. $C_7H_5Br_4N$ requires C, 19.9; H, 1.2; Br, 75.6; N, 3.3%); δ_H 6.92 (s, 3α-H), 7.36 (s, 2α-H), 7.41 (dd, 5-H), 8.25 (dd, 4-H), and 8.49 (dd, 6-H); *m*/*z* 423 (M^+, 0.6%), 344, 342 (100), 263 (28), and 184, 182 (34). A reaction on a five-fold scale required a longer irradiation period (18 h) and gave a lower yield (55%). On this scale the succinimide turns black by the end of the reaction, and the solution should be washed with 10% aqueous sodium metabisulphite to remove bromine.

3,4-*Bis*(*dibromomethyl*)*pyridine* (**2**).—A solution of 3,4-dimethylpyridine (150 mg) and *N*-bromosuccinimide (1.10 g) in

carbon tetrachloride (500 ml) was refluxed over a 200W light bulb for 2 h. After the mixture had been cooled and the black residues filtered off the solution was evaporated under reduced pressure at room temperature. The solid residue was flash chromatographed on silica, using chloroform as the eluant, to give the *tetrabromide* (**2**) (55 mg, 9%) as a crystalline solid which decomposed rapidly without melting upon heating >30 °C (Found: C, 19.8; H, 1.4; N, 3.3. $C_7H_5Br_4N$ requires C, 19.9; H, 1.2; N, 3.3%); δ_H 6.97 (s, 3α-H), 7.22 (s, 4α-H), 7.72 (d, 5-H), 8.67 (d, 6-H), and 8.80 (s, 2-H); *m/z* 423 (M^+, 4%), 344, 342 (100), 263 (45), and 184, 182 (43).

2,3-*Bis*(*dibromomethyl*)*pyrazine* (**3**).—Photobromination of 2,3-dimethylpyrazine (2.0 g) with *N*-bromosuccinimide (14.0 g) in carbon tetrachloride (125 ml) for 14 h gave, after work-up as described for compound (**1**), the *tetrabromide* (**3**) (5.30 g, 67%), m.p. 168—170 °C (from $CHCl_3$–EtOH) (Found: C, 17.0; H, 0.9; Br, 75.5; N, 6.5. $C_6H_4Br_4N_2$ requires C, 17.0; H, 0.9; Br, 75.5; N, 6.6%); δ_H 7.05 (2 H, s, 2α-, 3α-H), and 8.51 (2 H, s, 5-, 6-H); *m/z* 424 (M^+, 1.7%), 345, 343 (100), 263 (25), and 185, 183 (23).

4,5-*Bis*(*dibromomethyl*)*pyrimidine* (**4**).—Photobromination of 4,5-dimethylpyrimidine (0.5 g) with *N*-bromosuccinimide (3.4 g) in carbon tetrachloride (125 ml) for 1 h gave, after work-up as described for compound (**1**), the *tetrabromide* (**4**) (1.3 g, 66%), m.p. *ca.* 160 °C (slow decomp. >140 °C) (from $CHCl_3$–EtOH) (Found: C, 17.1; H, 0.9; Br, 75.7; N, 6.4. $C_6H_4Br_4N_2$ requires C, 17.0; H, 0.9; Br, 75.5; N, 6.6%); δ_H 6.82 (s, 5α-H), 7.17 (s, 4α-H), 9.13 (s, 6-H), and 9.21 (s, 2-H); *m/z* 424 (M^+, 1.2%), 345, 343 (100), and 264 (18).

5,6-*Bis*(*dibromomethyl*)-1,2,4-*triazine* (**5**).—Photobromination of 5,6-dimethyl-1,2,4-triazine (0.5 g) with *N*-bromosuccinimide (3.3 g) and succinimide (1.0 g) in carbon tetrachloride (125 ml) for 24 h gave, after work-up as usual followed by flash chromatography on silica using 1:1 chloroform and light petroleum (b.p. 40—60 °C) as the eluant, the *tetrabromide* (**5**) (0.81 g, 42%), as bright yellow crystals, m.p. 120—121 °C (slow decomp.) (Found: C, 14.1; H, 0.8; Br, 75.5; N, 9.9. $C_5H_3Br_4N_3$ requires C, 14.1; H, 0.7; Br, 75.3; N, 9.9%); δ_H 7.15 (s, 6α-H), 7.20 (s, 5α-H), and 9.81 (s, 3-H); *m/z* 425 (M^+, 18%), 291, 289 (100), 210 (34), and 50 (49).

Reaction of 2,3-*Bis*(*dibromomethyl*)*pyridine* (**1**) *with Sodium Iodide*.—Sodium iodide (15 g) was added over a period of 5 min to a solution of the tetrabromide (**1**) (10 g) in dry DMF (100 ml) at 80 °C. The mixture was stirred for a further 3 h, cooled, extracted into ether, and washed with aqueous sodium thiosulphate followed by water (×5). The solution was dried and evaporated to give a brown oil (5 g), which was flash chromatographed on silica using 40% light petroleum (b.p. (40—60 °C) in chloroform as the eluant. This gave trans-1,2-*dibromo*-1,2-*dihydrocyclobuta*[b]*pyridine* (**10a**) (3.1 g, 50%), m.p. 43—44 °C (Found: C, 31.7; H, 1.6; Br, 61.0; N, 5.0. $C_7H_5Br_2N$ requires C, 31.9; H, 1.9; Br, 60.8; N, 5.3%); δ_H 5.34 (1 H, s, 1-H), 5.52 (1 H, s, 2-H), 7.33—7.61 (2 H, m, 5-, 6-H), and 8.66 (1 H, dd, 4-H); δ_C 46.5 (C-1), 52.1 (C-2), 126.8 (C-6), 131.4 (C-5), and 153.9 (C-4); *m/z* 263 (M^+, 57%), 184, 182 (100), 103 (70), and 102 (53), closely followed by the cis-*isomer* (**10b**) (290 mg, 5%), m.p. 117—118 °C (decomp.) (Found: C, 32.0; H, 2.0; Br, 60.9; N, 5.0%); δ_H 5.73 (1 H, d, *J* 4.0 Hz, 1-H), 5.91 (1 H, d, 2-H), 7.24—7.59 (2 H, m, 5-, 6-H), and 8.59 (1 H, dd, 4-H); δ_C 48.1 (C-1), 53.6 (C-2), 126.6 (C-6), 131.5 (C-5), and 159.0 (C-4); the mass spectrum was identical to that for the isomer (**10a**). Further elution gave the *biphenylene* (**11**) (55 mg, 2.2%), pale yellow crystals, m.p. 184—186 °C (sublimes >120 °C) (Found: C, 82.2; H, 3.6; N, 13.6. $C_{14}H_8N_2$ requires C, 82.4; H, 3.9; N, 13.7%); n.m.r. and mass spectra, see text, followed by the *isomer* (**12**) (38 mg, 1.6%), pale yellow crystals, m.p. 172—174 °C (decomp.) (Found: C, 82.4; H, 3.9; N, 13.6%); n.m.r. and mass spectra, see text. Traces of iodocyclobuta[*b*]pyridines were also formed in this reaction, but these were not isolated.

Reaction of 2,3-*Bis*(*dibromomethyl*)*pyrazine* (**3**) *with Sodium Iodide*.—Sodium iodide (17 g) was added over a period of 5 min to a solution of the tetrabromide (**3**) (10 g) in dry DMF (150 ml) at 60—65 °C, the mixture stirred for a further 1 h, and then worked up as described above. The black product (*ca.* 4 g) was chromatographed on silica, as above, giving a fore-run of unchanged (**3**), and then trans-1,2-*dibromo*-1,2-*dihydrocyclobuta*[b]*pyrazine* (**13a**) (0.93 g, 15%), m.p. 101—103 °C (decomp.) (Found: C, 27.2; H, 1.5; Br, 60.8; N, 10.4. $C_6H_4Br_2N_4$ requires C, 27.3; H, 1.5; Br, 60.6; N, 10.6%); δ_H 5.46 (2 H, s, 1-, 2-H) and 8.62 (2 H, s, 4-, 5-H); δ_C 49.1 (C-1, -2) and 149.6 (C-4, -5); *m/z* 264 (M^+, 40%), 185, 183 (100), and 104 (65). Further elution gave the *biphenylene* (**14**) (16 mg, 0.7%), air-sensitive yellow crystals which decomposed above 150 °C (sublimed >130 °C) (Found: C 69.8; H, 2.9; N, 27.2. $C_{12}H_6N_4$ requires C, 69.9; H, 2.9; N, 27.2%); n.m.r. and mass spectra, see text.

General Procedure for Adduct Formation between the Quinomethanes (**6**)—(**9**) *and* N-*Phenylmaleimide and Cyclohexa*-2,5-*diene*-1,4-*dione*.—Sodium iodide (1.0 g) was added in one portion to a stirred solution of the tetrabromide (1.0 g) and dienophile (0.5 g, excess) in DMF at 70—80 °C. The mixture was stirred for 2 h. [30 min is sufficient for adduct formation for (**8**) and (**9**)], cooled, and extracted into chloroform. The suspension was washed with aqueous sodium thiosulphate [adducts of (**8**) and (**9**) are decomposed by sodium metabisulphite], and then with water (×10). The solution was dried and evaporated to give the product:

7-*Phenyl*-6H-*pyrrolo*[3,4-g]*quinoline*-6,8(7H)-*dione* (**15**): 75%, (after sublimation at 270 °C at 0.1 Torr), m.p. 295—297 °C (decomp.) (Found: C, 74.2; H, 3.7; N, 10.3. $C_{17}H_{10}N_2O_2$ requires C, 74.4; H, 3.6; N, 10.2%); ^{1}H n.m.r. data for this and other adducts, see text; $\nu_{max.}$ 1 704, 1 110, and 753 cm^{-1}; *m/z* 274 (M^+, 100%), 230 (27), and 127 (19).

7-*Phenyl*-6H-*pyrrolo*[3,4-g]*quinoxaline*-6,8(7H)-*dione* (**16**): 78%, (sublimation at 250 °C, 0.1 Torr), m.p. 309—310 °C (Found: C, 69.5; H, 3.5; N, 15.2. $C_{16}H_9N_3O_2$ requires C, 69.8; H, 3.3; N, 15.3%); $\nu_{max.}$ 1 714, 1 199, 1 120, 941, and 746 cm^{-1}; *m/z* 275 (M^+, 100%) and 231 (26).

7-*Phenyl*-6H-*pyrrolo*[3,4-g]*quinazoline*-6,8(7H)-*dione* (**17**): 51% (sublimation at 210 °C, 0.1 Torr) pale yellow crystals, m.p. 289—291 °C (decomp.) (Found: C, 69.8; H, 3.3; N, 15.3. $C_{16}H_9N_3O_2$ requires C, 69.8; H, 3.3; N, 15.3%); $\nu_{max.}$ 1 715, 1 584, 1 130, and 752 cm^{-1}; *m/z* 275 (M^+, 100%) and 231 (22).

7-*Phenyl*-6H-*isoindolo*[5,6-e][1,2,4]*triazine*-6,8(7H)-*dione* (**18**): 46%, bright orange crystals, m.p. 240—242 °C (Found: C, 65.1; H, 3.1; N, 20.3. $C_{15}H_8N_4O_2$ requires C, 65.2; H, 2.9; N, 20.3%); $\nu_{max.}$ 1 725, 1 145, 1 018, and 760 cm^{-1}; *m/z* 276 (M^+, 60%), 248 (66), 221 (100), and 99 (60).

Benzo[g]*quinoline*-6,9-*dione* (**19**): 69%, yellow crystals ($CHCl_3$), decomp. >160 °C (Found: C, 74.6; H, 3.2; N, 6.7. $C_{13}H_7NO_2$ requires C, 74.6; H, 3.6; N, 6.7%); $\nu_{max.}$ 1 660, 1 595, 1 369, 1 287, and 848 cm^{-1}; *m/z* 209 (M^+, 100%), 153 (50), and 127(24).

Benzo[g]*quinoxaline*-6,9-*dione* (**20**): 48%, pale yellow crystals ($CHCl_3$), decomp. >200 °C (Found: C, 68.5; H, 2.7; N, 13.3. $C_{12}H_6N_2O_2$ requires C, 68.6; H, 2.9; N, 13.3%); $\nu_{max.}$ 1 164, 1 602, 1 329, 1 180, 1 006, and 853 cm^{-1}; *m/z* 210 (M^+, 100), 182 (22), 154 (34), and 128 (22).

Benzo[g]*quinazoline*-6,9-*dione* (**21**): 25%, yellow crystals ($CHCl_3$–EtOH), decomp. >160 °C (Found: C, 68.3; H, 3.1; N, 13.3. $C_{12}H_6N_2O_2$ requires C, 68.6; H, 2.9; N, 13.3%); $\nu_{max.}$ 1 163,

1 601, 1 286, and 842 cm^{-1}; *m/z* 210 (M^+, 100%), 182 (20), and 145 (39).

Naphtho[2,3-e][1,2,4]*triazine-6,9-dione* (**22**): 11%, (after preparative t.l.c. on silica with 1:1 $CHCl_3$–EtOAc) orange-red crystals, decomp. >130 °C (Found: C, 62.5; H, 2.5; N, 20.0. $C_{11}H_5N_3O_2$ requires C, 62.6; H, 2.4; N, 19.9%); $\nu_{max.}$(KCl disk) 1 659, 1 591, 1 302, 1 250, 1 042, and 845 cm^{-1}; *m/z* 211 (M^+, 11%), 197 (12), 183 (100), and 156 (21).

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