1,3-Dipolar Character of Six-membered Aromatic Rings. Part X.[1] Pyridazine and Benzopyridazine Betaines

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The betaines 3-methyl-1-oxidophthalazinium and 6-chloro-2-methyl-4-oxidocinnolinium react as 1,3-dipoles across the 2- and 4-positions with acetylenic dipolarophiles. Phthalazin-1(2*H*)-one and 6-chloro-4-cinnolone also possess 1,3-dipolar reactivity and react with benzyne. The preparations of 1-methyl-3-oxidopyridazinium and 1,6-dimethyl-3-oxidopyridazinium are described, and the tautomerism of the betaine monoprotonated cations is discussed.

MONOAZA-AROMATIC betaines such as 1-methyl-,[2,3] 1-phenyl-,[4] and 1-(2,4-dinitrophenyl)-3-oxidopyridinium[1] show 1,3-dipolar character across the 2- and 6-positions and give cycloadducts with electron-deficient olefins such as acrylonitrile and methyl acrylate. We now report on the 1,3-dipolar character of certain 1,2-diaza-aromatic betaines.

Pyridazine Betaines.—The methylation of pyridazin-3(2*H*)-one (1) under alkaline conditions with methyl iodide or dimethyl sulphate gives[5,6] 2-methylpyridazin-3(2*H*)-one (2). Under neutral conditions, pyridazin-3(2*H*)-one is reported as unreactive towards methyl iodide[7] or methyl toluene-*p*-sulphonate[7] but the 6-

[1] N. Dennis, B. Ibrahim, A. R. Katritzky, I. G. Taulov, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 1883.
[2] A. R. Katritzky and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4134.
[3] A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc.* (*C*), 1971, 874.
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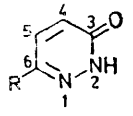
methyl derivative (4) reacts with diazomethane [8] to give a mixture of 2-methylpyridazin-3(2*H*)-one and 3-methoxypyridazine (3). We now find that pyridazin-3(2*H*)-one (1) and its 6-methyl homologue (4) are quaternised by methyl toluene-*p*-sulphonate in kerosene at 130 °C. The resulting tosylates [(5) and (6)] show no carbonyl stretching frequency in the i.r. spectra (Table 1) and so are assigned the lactim [(5a) and (6a)] rather than the tautomeric lactam structures [(5b) and (6b)]. The n.m.r. spectra (Table 2) provide evidence for quaternisation of pyridazin-3(2*H*)-one at N-1, since the H-6 signal is shifted from δ 7.80 to 9.00 on quaternisation, a deshielding explicable by a positive charge on an adjacent nitrogen. Similarly, the 6-methyl protons of (6a) are also deshielded on quaternisation.

1-Methyl- (5a) and 1,6-dimethyl-3-hydroxypyridazinium toluene-*p*-sulphonate (6a) with IRA 401 (OH^-) ion-exchange resin gave the corresponding betaines [(7) and (8)] in 70 and 80% yields, respectively. The i.r. spectra (Table 1) of the betaines [(7) and (8)] show strong bands at 1 550 cm^{-1}, which are characteristic for six-membered



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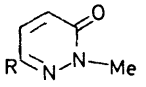
(4) R = Me



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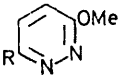
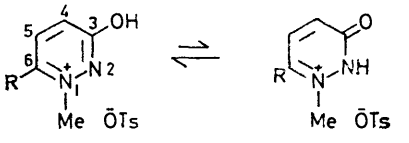


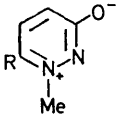
(3) R = H



(5a) R = H
(6a) R = Me

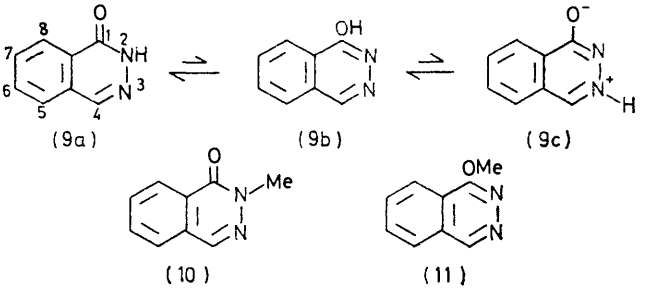
(5b) R = H
(6b) R = Me

heterocyclic betaines.[9] The n.m.r. spectra (in D_2O) are given in Table 2. These betaines are readily soluble in water but sparingly so in organic solvents, and are unreactive towards a variety of ethylenic and acetylenic dipolarophiles.



(7) R = H
(8) R = Me

Phthalazine Betaines.—Phthalazin-1(2*H*)-one (9)[10] was shown [11] by u.v. comparisons with model compounds to exist as the lactam (9a) rather than as the lactim (9b) or the betaine (9c). In agreement we find that the n.m.r. spectrum (Table 2) of phthalazin-1(2*H*)-one has the H-4 signal at δ 8.42, close to the position (δ 8.40) for 2-methylphthalazin-1-one (10) but not to that (δ 9.38) for 1-methoxyphthalazine (11). Further support for the lactam



(9a) (9b) (9c)

(10) (11)

structure is the strong i.r. carbonyl absorption at 1 650 cm^{-1}, characteristic of the lactam (*cf.* 1 645 cm^{-1} for 2-methylphthalazin-1-one). Although there is no direct physical evidence for the presence of the betaine tautomer (9c), its presence as a minor component explains the 1, 3-dipolar cycloadditions exhibited by (9) (see later).

Phthalazin-1(2*H*)-one (9a)[10] gave the tosylate (12), for which two tautomeric structures (12a and b) are possible. The absence of any carbonyl absorption in the i.r. spectrum (Table 1) favours the hydroxy-tautomer (12a). To confirm this conclusion two model compounds were prepared. 2-Methylphthalazin-1-one [12,13] (10) with methyl toluene-*p*-sulphonate at 160 °C gave 1,2-dihydro-2,3-dimethyl-1-oxophthalazinium toluene-*p*-sulphonate (13), m.p. 224—225°. 1-Methoxy-3-methylphthalazinium toluene-*p*-sulphonate (14) was prepared by treating 1-methoxyphthalazine (11) (from 1-chlorophthalazine with sodium methoxide) [14] with methyl toluene-*p*-sulphonate at 20 °C. The i.r. spectrum (Table 1) of the lactam tosylate (13) shows a characteristic strong $\nu_{C=O}$ band at 1 670 cm^{-1}, as does the parent lactam (10); the spectrum of the ether tosylate (14) shows no $\nu_{C=O}$ band at frequencies higher than the $\nu_{C=O}$ band at 1 605 cm^{-1}

The tosylate (12a) with alkali gave a 35% yield of the water-soluble betaine (15), m.p. 225°. Kost *et al.*[15] recently reported the preparation of the betaine (15) in low yield (13%). The n.m.r. spectra of phthalazin-1(2*H*)-one (9), 1-hydroxy-3-methylphthalazinium toluene-*p*-sulphonate (12), and 3-methyl-1-oxidophthalazinium (15) in $(CD_3)_2SO$ are given in Table 2. The 4-proton acts as a convenient probe of the electronic environment. Quaternisation of N-3 of 1-methoxyphthalazine (11) shifts the H-4 signal downfield by 0.86 p.p.m. in compound (14) relative to 1-methoxyphthalazine, owing in part to the deshielding effect of the positive charge at N-3. In 3-methyl-1-oxidophthalazinium (15), the H-4 signal suffers a substantial upfield shift of 1.46 p.p.m. relative to the tosylate (12a), supporting the betaine structure for compound (15) since the negative charge on the oxygen atom is delocalised.[3]

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[9] Unpublished results from this laboratory.
[10] S. Gabriel and A. Neumann, *Ber.*, 1893, **26**, 521.
[11] A. Albert and G. B. Barlin, *J. Chem. Soc.*, 1962, 3129.
[12] K. Fujii and S. Sato, *Ann. Reports G. Tanabe Co. Ltd.*, 1956, **1**, 1 (*Chem. Abs.*, 1957, **51**, 6650*c*).
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[14] E. Hayashi, T. Higashino, C. Iijima, Y. Kano, and T. Doihara, *Yakugaku Zasshi*, 1962, **82**, 584 (*Chem. Abs.*, 1963, **58**, 3425*c*.)
[15] A. N. Kost, K. V. Grabliauskas, V. G. Vinokurov, and A. M. Zjakun, *J. prakt. Chem.*, 1970, **312**, 542.

3-Methyl-1-oxidophthalazinium (15) with diphenylacetylene gave the adduct (16), m.p. 170°; the structure is demonstrated by $\nu_{C=O}$ (1 700 cm^{-1}), the mass spectrum (*m/e* 338), and the n.m.r. spectrum (Table 3) in which the

tions with dimethyl acetylenedicarboxylate (DMAD) and benzyne give resinous products.

Cinnoline Betaines.—6-Chlorocinnolin-4(1*H*)-one (17) can exist as the lactim (17a), as the lactam (17b), and as the betaine (17c). Studies of the ionization constants [16] and the u.v. spectra of cinnolin-4(1*H*)-one (18) show that the lactam (18b) form is the predominant tautomer. Again, although there is no direct physical evidence for

TABLE 1

I.r. stretching frequencies of bases, tosylates, and betaines

	Compound [a]													
ν/cm^{-1}	(5a)	(6a)	(7)	(8)	(9)	(10)	(11)	(12a)	(13)	(14)	(15)	(17)	(19)	(20)
O–H	3080 [b]	3060 [d]											3050 [d]	
C=O			1550	1550	1650 [b]	1645 [b]			1670 [b]		1550	1620		1560
C=C	1630 [b]	1630 [b]			1600 [b]	1590 [b]	1590 [c]	1605 [d]	1635 [c]	1605 [c]	1600		1570 [d]	1600
	1580 [c]	1500 [b]			1560 [c]		1550 [c]	1575 [c]	1605 [c]	1580 [b]				

[a] Nujol mull. [b] Strong. [c] Medium. [d] Weak.

TABLE 2

^{1}H N.m.r. spectra (δ values) of bases, tosylates, and betaines

(A) Pyridazinones [a,b]

Compound	H-4	H-5	H-6	*N*(1)-Me	C(6)-Me	H-1′	H-2′	*C*-Me
(1)	6.90 [c,d]	7.50 [c,d,f]	7.80 [c,f]					
(4)	6.89 [c,d]	7.43 [c,d]			2.30 [g]			
(5a)	7.70 [c,d]	8.15 [d–f]	9.00 [c,f]	4.34 [g]		7.35 [c,h]	7.60 [c,h]	2.31 [g]
(6a)	7.53 [c,d]	7.91 [c,d]		4.28 [g]	2.74 [g]	7.11 [c,h]	7.5 [c,h]	2.38 [g]
(7)	7.25 [c,d]	7.99 [d–f]	8.75 [c,f]	4.45 [g]				
(8)	7.14 [c,d]	7.50 [c,d]		4.12 [g]	2.61 [g]			

(B) Phthalazinones [i,j]

Compound	H-4	H-5 to -8	*N*(3)-Me	*C*-Me	NH	*N*(2)-Me	*O*-Me	H-1′	H-2′
(9)	8.42 [g]	7.97 [k]			14.55 [g]				
(10)	8.40 [g]					3.36 [g]			
(11)	9.38 [g]	8.04 [k]					3.36 [g]		
(12a)	9.85 [g]	7.32 [k]	4.38 [g]	2.25 [g]				7.10 [c,l]	7.35 [c,l]
(13)	9.76 [g]	8.30 [k]	4.45 [g]	2.23 [g]		3.89 [g]		7.76 [c,l]	7.06 [c,l]
(14)	10.24 [g]	8.27 [k]	4.44 [g]	2.24 [g]			4.22 [g]	7.46 [c,l]	7.04 [c,l]
(15)	8.39 [g]	7.39 [k]	4.34 [g]						

(C) Cinnolinones [i,j]

Compound	H-3	H-5	H-7, -8	*N*(2)-Me	*C*-Me	H-1′	H-2′
(17)	7.76 [g]	7.96 [e,m,n]	7.70 [k,l,o,p]				
(19)	8.32 [g]	8.04 [e,m,n]	7.84 [k,l,o,p]	4.30 [g]	2.26 [g]	7.48 [c,q]	7.10 [c,q]
(20)	8.22 [g]	7.98 [e,m,n]	7.76 [k,l,o,p]	4.28 [g]			

[a] Relative to sodium 3-(trimethylsilyl)propanesulphonate as internal standard. [b] In D_2O. [c] Doublet. [d] $J_{4,5}$ 10 Hz. [e] Quartet. [f] $J_{5,6}$ 5 Hz. [g] Singlet. [h] $J_{1',2'}$ 9.5 Hz. [i] Relative to Me_4Si as internal standard. [j] $(CD_3)_2SO$. [k] Multiplet. [l] $J_{1',2'}$ 8.0 Hz. [m] $J_{5,7}$ 2 Hz. [n] $J_{5,8}$ 0.5 Hz. [o] $J_{5,8}$ 1 Hz. [p] $J_{7,8}$ 8.5 Hz. [q] $J_{1',2'}$ 10 Hz.

TABLE 3

^{1}H N.m.r. spectra (δ values) of cycloadducts [a,b]

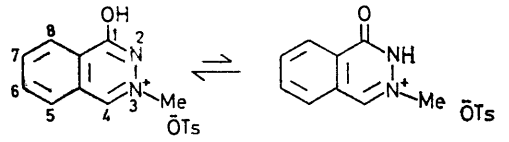
Compound	H-3	H-4	H-5	H-7	H-8	H-10	H-2′	Aromatic	*N*-Me	CO_2Me
(16)		4.94 [c]						7.47 [d]	3.35 [c]	
(22)	4.38 [c]		7.92 [e]	7.44 [f]	7.2 [f]			7.51 [d]	2.74 [c]	3.80 [c]
										3.80 [c]
(24)	4.34 [c]		7.98 [e]	6.7—8.6 [f]	6.7—8.6 [f]			6.7—8.6 [f]	2.84 [c]	
(26)	4.12 [c,g]		7.90 [f]	7.08 [f]	7.2 [f]	6.05 [c,g]		7.70—7.34 [f]	2.70 [c]	
(30)		[5.53 [c] (H-11)]						7.27 [d]		
										3.78 [c]
(31)		5.69 [c]					6.00 [c]	7.80 [d]		3.85 [c]
										3.86 [c]
										3.96 [c]
(33)	[4.42 [c] (H-11)]		[7.87 [f] (H-9)]	6.2—6.8 [f]	[6.2—6.8 [f] (H-6)]			6.2—6.8 [f]		

[a] Relative to Me_4Si as internal standard. [b] In $CDCl_3$. [c] Singlet. [d] Centre of broad band. [e] Doublet. [f] Multiplet. [g] *J* 3 Hz.

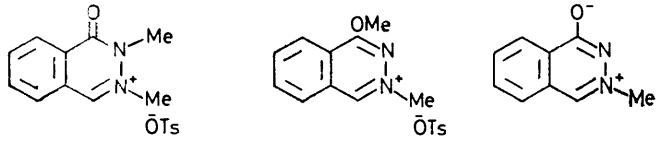
N-Me band (δ 3.35) is upfield from that of the anhydrobase (N-Me δ 4.34). The 4-proton signal at δ 8.39 in (15) moves upfield to δ 4.94 in (16). The betaine (15) is unreactive towards phenylacetylene, acrylonitrile, *N*-phenylmaleimide, and tetracyanoethylene, whereas reac-

[16] G. B. Barlin, *J. Chem. Soc.*, 1965, 2260.

the presence of the betaine tautomer (17c), its presence as a minor tautomer best explains the 1,3-dipolar

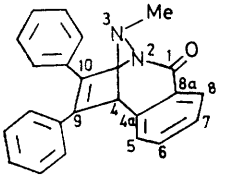


(12a) (12b)



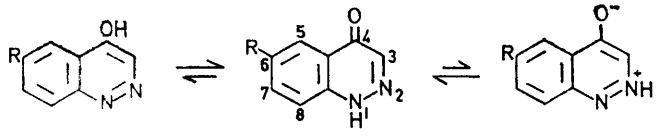
(13) (14) (15)

cycloadditions exhibited by (17). 6-Chlorocinnolin-4(1*H*)-one (17) was readily quaternised with methyl tosylate. The quaternary salt could exist in two possible tautomeric structures (19a and b), but the absence

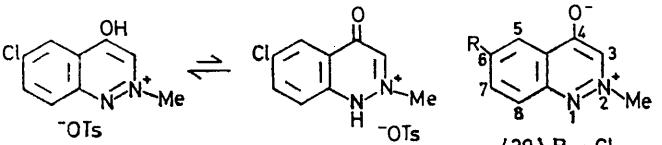


(16)

of any $\nu_{C=O}$ band in the i.r. spectrum (Table 1) indicates that the hydroxy-tautomer (19a) predominates. Previous work from this laboratory [17] had already shown that protonated cinnolin-4(1*H*)-one exists predominantly in the enol form. The tosylate (19) with alkali gave the water-soluble betaine (20), m.p. 218°. Barber and Lunt,[18] and also Ames and Novitt [19] have previously described the preparation of the corresponding parent betaine (21) from cinnolin-4(1*H*)-one (18). The n.m.r.



(17a) R = Cl (17b) R = Cl (17c) R = Cl
(18a) R = H (18b) R = H (18c) R = H

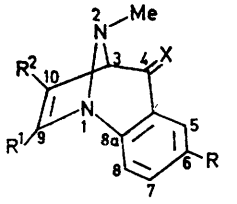


(19a) (19b) (20) R = Cl (21) R = H

spectra of 6-chlorocinnolin-4(1*H*)-one (17), 6-chloro-4-hydroxy-2-methylcinnolinium toluene-*p*-sulphonate (19a), and 6-chloro-2-methyl-4-oxidocinnolinium (20) in [$^2H_6$]dimethyl sulphoxide are given in Table 2. The signal for H-3 in compound (17) is shifted downfield by 0.52 p.p.m. on quaternisation, owing in part to the deshielding effect of the positive charge at N-2. In 6-chloro-2-methyl-4-oxidocinnolinium, the signal for H-3 is found upfield of that displayed by the tosylate (19).

6-Chloro-2-methyl-4-oxidocinnolinium (20) with DMAD gives a crystalline cycloadduct (22), m.p. 89°. Ames and Novitt [19] described the analogous reaction between DMAD and 2-methyl-4-oxidocinnolinium (21) to give cycloadduct (23). The chloro-betaine (20) with diphenylacetylene in refluxing *o*-dichlorobenzene gave the expected cycloadduct (24), m.p. 64—68°. The i.r. spectrum shows a $\nu_{C=O}$ band at 1 715 cm^{-1}, and the mass spectrum has *m/e* 372. The n.m.r. spectrum (Table 3) shows a singlet at δ 4.14 for the single bridgehead proton (H-3) and a singlet at δ 2.84 for the *N*-methyl group.

A single cycloadduct, m.p. 149—150° (*m/e* 296), was isolated from the betaine (20) and phenylacetylene in boiling xylene. The presence of the carbonyl group ($\nu_{C=O}$ 1 700 cm^{-1}) was confirmed by conversion into the exocyclic methylene compound (25) by a Wittig reaction. Two possible regioisomeric structures (26) and (28) were considered for the phenylacetylene cycloadduct, m.p. 149—150°. The n.m.r. spectrum (Table 3) shows a one-proton doublet (*J* 3 Hz) at δ 4.12 assignable to the bridgehead proton, H-3, and a second one-proton doublet (*J* 3 Hz) at δ 6.05 assignable to the olefinic proton, H-10.



	R	R^1	R^2	X
(22)	Cl	CO_2Me	CO_2Me	O
(23)	H	CO_2Me	CO_2Me	O
(24)	Cl	Ph	Ph	O
(25)	Cl	Ph	H	CH_2
(26)	Cl	Ph	H	O
(27)	H	Ph	H	O
(28)	Cl	H	Ph	O
(29)	H	H	Ph	O

Since H-3 and H-10 are coupled to each other (as demonstrated by double irradiation), the cycloadduct was assigned structure (26). Lunt and Threlfall [20] reported the formation of a single cycloadduct from the reaction of phenylacetylene and 2-methyl-4-oxidocinnolinium. By analogy to the present work, this cycloadduct can be assigned the structure (27) rather than the alternative regioisomeric structure (29). The betaine (20) is unreactive towards olefinic dipolarophiles including acrylonitrile, methyl acrylate, and *N*-phenylmaleimide: reactions with benzyne and tetracyanoethylene give resinous products.

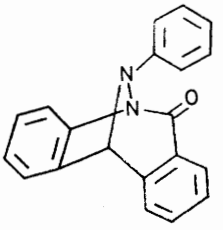
[17] A. R. Katritzky, E. Lunt, B. Ternai, and G. J. T. Tiddy, *J. Chem. Soc.* (*B*), 1967, 1243.

[18] H. J. Barber and E. Lunt, *J. Chem. Soc.*, 1965, 1468.

[19] D. E. Ames and B. Novitt, *J. Chem. Soc.* (*C*), 1969, 2355.

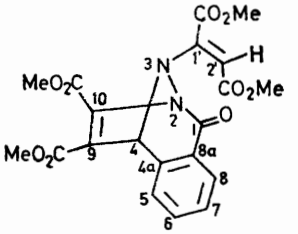
[20] E. Lunt and T. L. Threlfall, *Chem. and Ind.*, 1964, 1805.

Betaine Reactivity of Phthalazinone and Cinnolinone.—We have previously shown [21] that 3-hydroxypyridine, 3-hydroxy-6-methylpyridine, and 4-hydroxyisoquinoline themselves possess 1,3-dipolar character and react with numerous dipolarophiles to form cycloadducts. We now find that phthalazin-1(2*H*)-one (9) possesses similar reactivity: 2 mol. equiv. of benzyne [22,23] produced the cycloadduct (30), m.p. 196—197°, the structure of which was supported by the i.r. spectrum ($\nu_{C=O}$ 1 720 cm^{-1}), the mass spectrum (*m/e* 298), and the n.m.r. singlet at δ 5.53 (Table 3) for the bridgehead proton H-4.

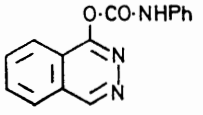


(30)

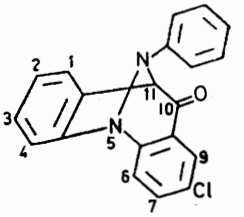
Two moles of DMAD converted phthalazin-1(2*H*)-one at 140 °C into the cycloadduct (31), m.p. 140—141°. The i.r. spectrum included ester and ring $\nu_{C=O}$ bands and the mass spectrum had *m/e* 430. The n.m.r. (Table 3) signal for the bridgehead proton H-4 appears as a singlet at δ 4.94 and all four CO_2Me signals appear as singlets, at δ 3.78, 3.85, 3.86, and 3.96. The treatment of phthalazin-1(2*H*)-one (9) with phenyl isocyanate yielded the urethane (32). No cycloadducts were isolated from (9) with diphenylacetylene, phenylacetylene, acrylonitrile, *N*-phenylmaleimide, or tetracyanoethylene.



(31)



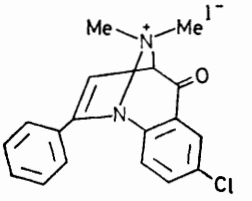
(32)



(33)

6-Chlorocinnolin-4(1*H*)-one possesses similar 1,3-dipolar reactivity. Two mol. equiv. of benzyne react with the base (17) to produce the cycloadduct (33). The structure (33) was supported by the i.r. spectrum ($\nu_{C=O}$ 1 710 cm^{-1}) and the mass spectrum (*m/e* 332). The n.m.r. spectrum (Table 3) shows a singlet at δ 4.42 for the bridgehead proton, H-3. The ketone (33) formed a dinitrophenylhydrazone. No cycloadducts were isolated from the reaction of (17) with diphenylacetylene, phenylacetylene, DMAD, or tetracyanoethylene under various conditions. The mechanism for cycloadduct formation appears to involve an initial cycloaddition reaction between the dipolarophile and the betaine form [(9c) and (17c)] of the base, followed by the addition of a second molecule of the dipolarophile at the bridge nitrogen as is discussed in the next section.

The cycloadducts (16), (22), (24), (26), (30), (31), and (33) were resistant to catalytic hydrogenation (Pd–C),[24] di-imide reduction,[25] and sodium borohydride reduction.[26] Treatment with Zn–AcOH [27] or Zn–Hg amalgam and acid [28] gave complex mixtures of products. Quaternisation of the cycloadduct (26) with methyl iodide in $[CH_2]_4O$ gave the salt (34).



(34)

Mechanism of the Reaction of Dipolarophiles with Phthalazin-1(2H)-one.—The reaction of phthalazin-1(2*H*)-one with benzyne parallels the reaction of 3-hydroxypyridine and 4-hydroxyisoquinoline with benzyne to give 1 : 2 adducts (*i.e.* 1 mol of base with 2 mol of dipolarophile). Two possible mechanisms could explain this benzyne addition.

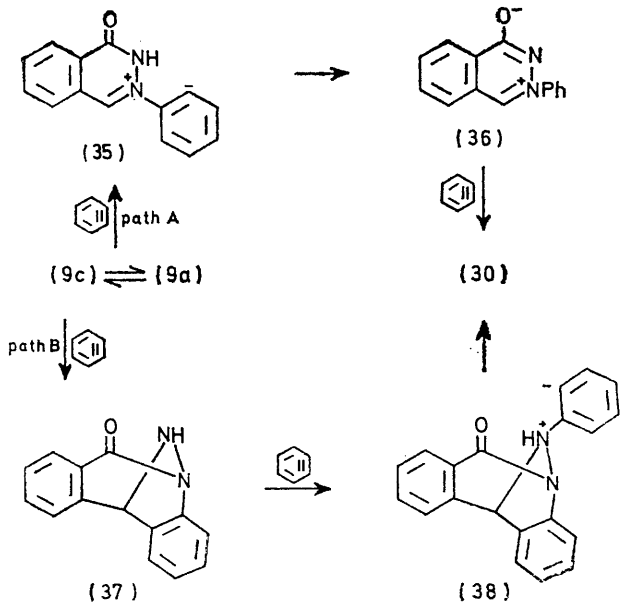
(*a*) Initial nucleophilic attack of the N-3 lone pair of (9a) on benzyne to give a zwitterion (35); this tautomerises to the betaine (36), which reacts with a second molecule of benzyne across the 2- and 4-positions to yield the 1 : 2 cycloadduct (30) (Scheme, path A).

(*b*) The dipolar tautomer (9c) reacts with benzyne across the 2- and 4-positions to give the 1 : 1 cycloadduct (37). The N-H lone pair of (37) then attacks a second molecule of benzyne to produce the zwitterion (38), which tautomerises to (30) (Scheme, path B).

None of the intermediates of the Scheme could be isolated. The stable *N*-phenylphthalazinium betaine (36), prepared by an unambiguous route,[29] did not give the cycloadduct (30) under the conditions for the preparation of (30) from phthalazin-1(2*H*)-one (9) and benzyne.

[21] N. Dennis, A. R. Katritzky, and S. K. Parton, in preparation.
[22] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.
[23] D. C. Dittmer and E. S. Whitman, *J. Org. Chem.*, 1969, **34**, 2004.
[24] M. Smith in 'Catalytic Hydrogenation. Techniques and Applications in Organic Synthesis,' ed. R. L. Augustine, Arnold, London, 1965, p. 1.
[25] J. M. Hoffman, jun., and R. H. Schlessinger, *Chem. Comm.*, 1971, 1245.
[26] N. G. Gaylord, 'Reduction with Complex Metal Hydrides,' Interscience, New York, 1956.
[27] J. H. Brewster and M. W. Kline, *J. Amer. Chem. Soc.*, 1952, **74**, 5179.
[28] R. L. Augustine, 'Reduction. Techniques and Applications in Organic Synthesis,' Arnold, London, 1968, p. 138.
[29] N. Dennis, A. R. Katritzky, and M. Ramaiah, in preparation for *J.C.S. Perkin I*.

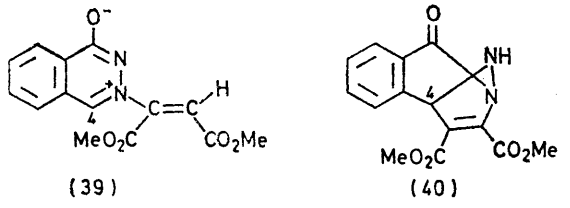
(However, *N*-phenyl-3-oxidopyridinium betaine does give the corresponding cycloadduct with benzyne.[9]) Reaction of 1 mol. equiv. of benzyne with phthalazin-1(2*H*)-one (9) gave (30) in poor yield.



SCHEME

Of the two possible mechanisms, path B of the Scheme is preferred on mechanistic grounds and was proved for the closely related dimethyl acetylenedicarboxylate (DMAD) reaction, chosen because of the experimental convenience and spectral simplicity. We believe that under similar conditions other dipolarophiles react analogously to DMAD.

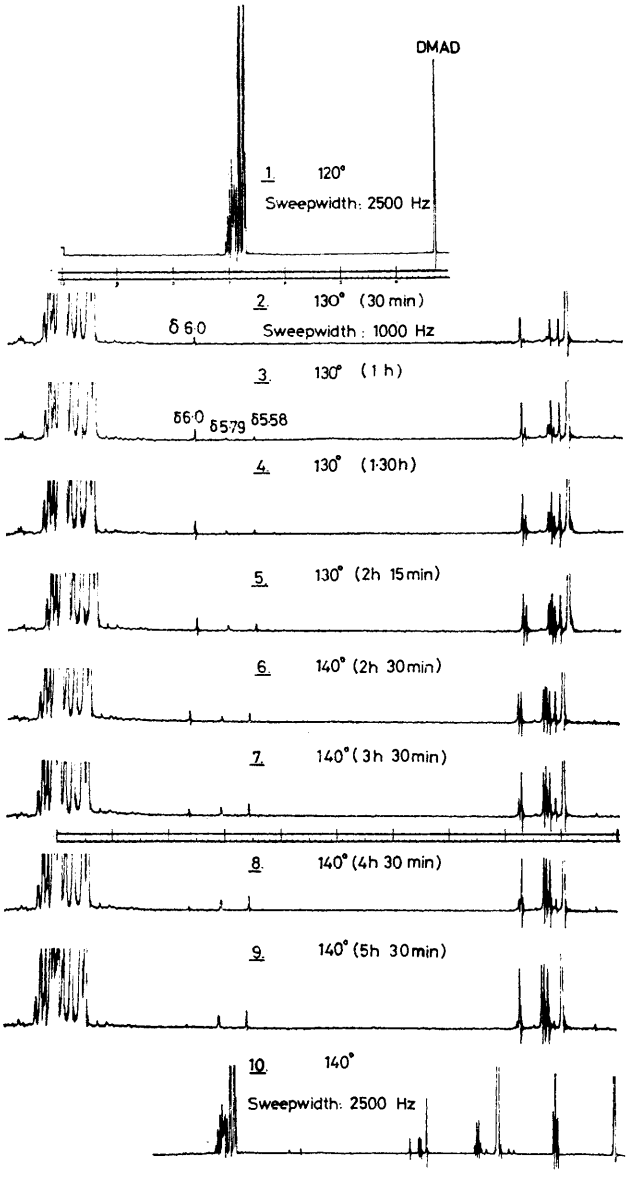
The diazinium betaine reactions with dipolarophiles are rather slow (usually 12—24 h). The chemical shifts of the 4-proton of the diazinium betaines usually lie at δ 8.50—8.80 and those of the bridgehead (H-4) proton of the cycloadducts at δ 5.5—6.50, depending to some extent on the N-3 substituent. The signal for the *peri*-proton of the cycloadduct is seen in the region δ 7.2—7.8 as either a doublet or a multiplet.



According to the two possible reaction paths (Scheme) in the reaction of DMAD with the betaine (9), species (39) and (40) are the two possible monoadduct intermediates in the formation of 1 : 2 cycloadduct (31). The 4-proton of (39), (40), and (31) is a convenient probe for the identification of the reaction path. This proton should be clearly observable as for compound (15) H-4 absorbs at δ 8.4, clear of the other aromatic protons.

(i) A signal for the bridgehead proton (H-4) for the 1 : 1 cycloadduct (40) should be observed during the reaction if it proceeds by path B. As (40) reacts with the second molecule of DMAD, two further signals corresponding to the bridgehead proton and the olefinic proton of (31) should be seen.

(ii) If the reaction involves the betaine intermediate (39) (path A), transient signals for the 4-proton downfield and for an olefinic proton at higher field should be observed.



Reaction of phthalazin-1(2*H*)-one and DMAD in xylene at various temperatures

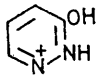
(iii) If the reaction proceeds through both the A and B pathways transient signals for both (39) and (40) are expected.

(iv) If the addition of the second molecule of DMAD is much faster than the first, signals corresponding to (9) and (31) alone should be observed.

DMAD (2 mol. equiv.) and phthalazin-1(2*H*)-one were heated in xylene in the n.m.r. probe. Spectra recorded at *ca.* 0.5 h intervals with a gradual increase of temperature (Figure) show unambiguously that (40) is the intermediate (*cf.* path B of Scheme). No reaction was observed until the probe reached the temperature 130 °C. At this temperature (0.5 h) a singlet at δ 6.0 appeared (Figure) assigned to H-4 of (40). After another 0.5 h at the same temperature two additional signals for H-4 and the olefinic proton of the cycloadduct (31) appeared at δ 5.58 and 5.79, respectively, along with H-4 of (40) (Figure). As the reaction proceeded the peak at δ 6.0 started decreasing while two peaks at δ 5.58 and 5.79 continued to grow. At the end of 6 h there appeared only the protons corresponding to (31) (Figure). At no stage were any signals corresponding to the betaine intermediate (39) observed.

Conclusions regarding the Tautomeric Structure of Azinone Monocations.—We have shown that the hydroxy-forms (5a), (6a), (12a), and (19a) predominate over the corresponding oxo-forms in the pyridazine, phthalazine, and cinnoline series.

An adjacent positive charge clearly reduces the basicity of a nitrogen atom so that the equilibrium is swung over: the situation recalls that found for α-chloro-substitution (see discussion in ref. 30). Little previous work has been done on the structure of such cations: Cookson and Cheeseman [31] suggested structure (41) but apparently did not consider a structure analogous to (5a), which is more probable.



(41)

Conclusions regarding 1,3-*Dipolar Reactivity of Azinium Betaines.*—The 1,3-dipolar character of monocyclic pyridazine betaines is low, and no successful additions were achieved with the *N*-methyl derivatives here studied. Benzo-annulation considerably increases the reactivity, and both phthalazinium and cinnolinium betaines reacted with acetylenic and some olefinic dipolarophiles. In these two benzo-series, the demethyl compounds also show 1,3-dipolar reactivity. However, the introduction of a second nitrogen atom into an α-position of 3-hydroxypyridinium appears to cause a marked reduction in the reactivity towards 1,3-dipolarophiles.

EXPERIMENTAL

M.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, a Unicam SP 800A spectrophotometer, and a Varian HA-100 n.m.r. spectrometer. Compounds were purified until they were observed as single spots on t.l.c. [silica gel (PF 254); chloroform as eluant].

3-Hydroxy-1-methylpyridazinium Toluene-p-sulphonate (5a).—Pyridazin-3(2*H*)-one (0.96 g, 0.01 mol) and methyl toluene-*p*-sulphonate (1.86 g, 0.01 mol) were suspended in kerosene and stirred for 0.5 h. The temperature was gradually raised to 130 °C and kept at 130 °C for 12 h. The cooled mixture was dissolved in abs. EtOH (5 ml) and acetonitrile (20 ml) was added. The precipitate was collected and crystallised from acetonitrile to give *3-hydroxy-1-methylpyridazinium toluene-p-sulphonate* (5a) (1.35 g, 45%) as needles, m.p. 155—157° (Found: C, 51.1; H, 5.0; N, 9.9. $C_{12}H_{14}N_2O_4S$ requires C, 50.7; H, 4.9; N, 9.9%); $\nu_{max.}$ (Nujol) 3 080 (NH), 1 630, 1 580, 1 250, 1 150, 1 120, 1 020, 1 000, 820, and 680 cm^{-1}.

3-Hydroxy-1,6-dimethylpyridazinium Toluene-p-sulphonate (6a).—6-Methylpyridazin-3(2*H*)-one (1.10 g, 0.01 mol) and methyl toluene-*p*-sulphonate (1.86 g, 0.01 mol) were treated as (5a) above to give *3-hydroxy-1,6-dimethylpyridazinium toluene-p-sulphonate* (6a) (0.98 g, 33%) as needles, m.p. 169—170° (Found: C, 52.2; H, 5.4; N, 9.5. $C_{13}H_{16}N_2O_4S$ requires C, 52.0; H, 5.3; N, 9.3%); $\nu_{max.}$ (Nujol) 3 060 (NH), 1 630, 1 500, 1 240, 1 150, 1 030, 1 000, 850, 820, and 675 cm^{-1}.

1-Methyl-3-oxidopyridazinium (7).—3-Hydroxy-1-methylpyridazinium toluene-*p*-sulphonate (5a) (2.82 g, 0.01 mol) in water (10 ml) was chromatographed on a column of pretreated [32] Amberlite IRA-401 (OH^-) ion-exchange resin (75 g). The column was eluted with distilled water and the first 100 ml collected. Evaporation of the water *in vacuo* (25°; 30 mmHg) gave a red-brown residue which was crystallised from chloroform–light petroleum (b.p. 60—80°) (1 : 5) to give *1-methyl-3-oxidopyridazinium* (7) (1.82 g, 70%) as buff-coloured needles, m.p. 137—138° (Found: C, 50.5; H, 5.9; N, 23.0. $C_5H_6N_2O,H_2O$ requires C, 50.4; H, 5.9; N, 23.5%); $\nu_{max.}$ (Nujol) 3 320 (OH), 1 610, 1 550, 1 520, 1 250, 1 200 930, and 815 cm^{-1}; *m/e* 110 (M^+), 82, 81, and 39.

1,6-Dimethyl-3-oxidopyridazinium (8).— 3-Hydroxy-1,6-dimethylpyridazinium toluene-*p*-sulphonate (6a) (3.0 g, 0.01 mol) in water (10 ml) was treated as for (5a) above to give *1,6-dimethyl-3-oxidopyridazinium* (8) (0.6 g, 50%) as buff-coloured needles, m.p. 171—172° (Found: C, 50.4; H, 5.0; N, 19.5. $C_6H_8N_2O,H_2O$ requires C, 50.7; H, 7.0; N, 19.7%); $\nu_{max.}$ (Nujol) 3 300 (OH), 1 610, 1 550, 1 510, 1 260, 1 190, 1 040, 940, 850, and 730 cm^{-1}; *m/e* 124 (M^+), 96, 95, 53, and 43.

3-Methyl-1-oxidophthalazinium (15).—NaOH (2N; 10 ml) was added to 1-hydroxy-3-methylphthalazinium toluene-*p*-sulphonate (3.36 g, 0.01 mol) in water (2 ml) until pH 6 and the solution continuously extracted with chloroform. The dry (Na_2SO_4) extract was evaporated *in vacuo* (25° at 18 mmHg) to give 3-methyl-1-oxidophthalazinium (15) (0.73 g, 35%) as needles from ethanol–ether, m.p. 235° (decomp.) (lit.,[15] 238°) (Found: C, 67.4; H, 5.1; N, 17.5. Calc. for $C_9H_8N_2O$; C, 67.5; H, 5.0; N, 17.5%); $\nu_{max.}$ (Nujol) 1 665 and 1 560 cm^{-1}; *m/e* 160.

Phthalazin-1(2H)-one (9).—Hydrazine hydrate (98%; 15 ml) was added slowly, with stirring, to *o*-carboxybenzaldehyde (15 g, 0.1 mol) in water (50 ml). The solution was kept at 20 °C for 12 h. Phthalazin-1(2*H*)-one (8 g, 70%), separated from EtOH as buff-coloured needles, m.p. 186° (lit.,[10] 182°); $\nu_{max.}$ (Nujol) 1 650 cm^{-1} (C=O); *m/e* 146.

2-Methylphthalazin-1-one (10).—This was prepared from phthalazin-1(2*H*)-one by the method of ref. 12; m.p. 105—

[30] J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, 'The Tautomerism of Heterocycles,' Academic Press, New York, in the press.

[31] R. F. Cookson and G. W. H. Cheeseman, *J.C.S. Perkin II*, 1972, 392.

[32] The British Drug Houses Ltd., B.D.H. Laboratory Chemicals Division, 'Ion Exchange Resins,' Poole, 1965, 5th edn., p. 20.

108° (lit.,[33] 111—112°) (Found: C, 67.5; H, 4.6; N, 17.3. Calc. for $C_9H_8N_2O$: C, 67.5; H, 5.0; N, 17.5%); $\nu_{max.}$ (Nujol) 1 640 cm^{-1}; *m/e* 160.

1-*Methoxyphthalazine* (11).—This was prepared from 1-chlorophthalazine [10] by the method of ref. 14; m.p. 59° (lit.,[10] 60—61°) (Found: C, 67.4; H, 17.4; N, 5.0. Calc. for $C_9H_8N_2O$: C, 67.5; H, 17.5; N, 5.0%); $\nu_{max.}$ (Nujol) 1 590 and 1 550 cm^{-1}; *m/e* 160.

1-*Hydroxy*-3-*methylphthalazinium Toluene*-p-*sulphonate* (12a).—Phthalazin-1(2*H*)-one (1.46 g, 0.01 mol), methyl toluene-*p*-sulphonate (1.86 g, 0.01 mol), and kerosene (8 ml) were stirred at 20 °C for 1.5 h. The temperature was gradually raised to 140 °C and maintained for 6 h. The solution was cooled, the kerosene decanted, and the residue dissolved in EtOH (10 ml), and added to light petroleum (b.p. 40—60°; 30 ml). The precipitated *tosylate* (12a) crystallised from EtOH as needles (3.2 g, 98%), m.p. 196° (Found: C, 57.6; H, 4.9; N, 8.5. $C_{16}H_{16}N_2O_4S$ requires C, 57.8; H, 4.8; N, 8.4%); $\nu_{max.}$ (Nujol) 1 605 and 1 575 cm^{-1}.

1,2-*Dihydro*-2,3-*dimethyl*-1-*oxophthalazinium Toluene*-p-*sulphonate* (13).—2-Methylphthalazin-1-one (10) (0.160 g, 0.001 mol) and methyl toluene-*p*-sulphonate (0.186 g, 0.001 mol) were stirred at 160 °C for 2 h. Acetonitrile (10 ml) was then added and the mixture heated under reflux for 10 min and cooled; the *product* (13) separated as needles (0.300 g, 90%), m.p. 224—225° (Found: C, 58.3; H, 5.2; N, 8.3. $C_{17}H_{18}N_2O_4S$ requires C, 58.9; H, 4.9; N, 8.1%); $\nu_{max.}$ (Nujol) 1 670 cm^{-1}.

1-*Methoxy*-3-*methylphthalazinium Toluene*-p-*sulphonate* (14).—1-Methoxyphthalazine (11) (0.160 g, 0.001 mol) and methyl toluene-*p*-sulphonate (0.186 g, 0.001 mol) were kept with occasional agitation at 20 °C for 2 h; the mixture liquefied and then solidified. The solid was triturated with acetonitrile (10 ml); the precipitate crystallised from acetonitrile–ether (50 : 50) to give the *product* (14) as needles (0.345 g, 100%), m.p. 155° (Found: C, 58.9; H, 5.3; N, 8.2. $C_{17}H_{18}N_2O_4S$ requires C, 58.9; H, 4.9; N, 8.1%); $\nu_{max.}$ (Nujol) 1 580 cm^{-1}.

Thermal Conversion of (14) *into* (13).—1-Methoxy-3-methylphthalazinium toluene-*p*-sulphonate (14) (0.080 g, 0.000 1 mol) was heated to 160 °C for 2.5 h with occasional stirring. The product crystallised from acetonitrile to give 1,2-dihydro-2,3-dimethyl-1-oxophthalazinium toluene-*p*-sulphonate (13) (0.075 g, 94.0%), m.p. 224—225° (mixed m.p. 224°).

Reaction of 3-*Methyl*-1-*oxidophthalazinium* (15) *with Diphenylacetylene*.—3-Methyl-1-oxidophthalazinium (1.6 g, 0.01 mol) and diphenylacetylene (3.56 g, 0.02 mol) in *o*-dichlorobenzene (10 ml) were heated under reflux for 24 h. The solvent was removed *in vacuo* (50° at 18 mmHg) and the residue was stirred with light petroleum (b.p. 40—60°; 3 × 10 ml). Filtration and crystallisation gave 3,4-*dihydro*-3-*methyl*-9,10-*diphenyl*-2,4-*ethenophthalazin*-1(2H)-*one* (16) (2.7 g, 80%) as yellow needles (from EtOH), m.p. 170° (Found: C, 79.5; H, 5.3; N, 7.7. $C_{23}H_{18}N_2O,0.5H_2O$ requires C, 79.5; H, 5.5; N, 8.0%); $\nu_{max.}$ (Nujol) 1 700 (C=O) and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ ($CHCl_3$) 256 (log ε 6.30) and 295 nm (6.98); *m/e* 338.

6-*Chloro*-4-*hydroxy*-2-*methylcinnolinium Toluene*-p-*sulphonate* (19a).—6-Chlorocinnolin-4(1*H*)-one (17) (0.180 g, 0.001 mol), methyl tosylate (0.186 g, 0.001 mol), and kerosene (10 ml) were stirred at 165—175 °C for 4 h and cooled. The kerosene was decanted and the solid washed with light petroleum (b.p. 40—60°; 3 × 15 ml). The residue was dissolved in hot EtOH (8 ml) and a large excess of light petroleum (b.p. 40—60°) added to give the *tosylate* (19a) (0.284 g, 80%) as green-blue needles, m.p. 165° (Found: C, 52.3; H, 4.3; N, 7.8. $C_{16}H_{15}ClN_2O_4S$ requires C, 52.4; H, 4.2; N, 7.7%); $\nu_{max.}$ (Nujol) 1 570, 1 240m, 1 150br, 1 100m, 1 010m, 1 000br, and 840w cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 328 (log ε 3.69), 313 (3.86), 285 (s) (4.18), and 274 nm (4.26).

6-*Chloro*-2-*methyl*-4-*oxidocinnolinium* (20).—NaOH solution (2N) was added to 6-chloro-4-hydroxy-2-methylcinnolinium toluene-*p*-sulphonate (19a) (0.354 g, 0.001 mol) in water (5 ml) until pH 8 and the solution was extracted with chloroform (10 × 25 ml). The filtered chloroform solution was heated under reflux with animal charcoal (3 g) for 5 min and filtered. The chloroform extract was dried (Na_2SO_4) and the solvent removed *in vacuo* (25° at 18 mmHg) to give 6-chloro-2-methyl-4-oxidocinnolinium (20) (0.078 g, 40%) as needles from benzene, m.p. 218° (lit.,[18] 221—223°) (Found: C, 54.7; H, 3.7; N, 14.6. Calc. for $C_9H_7ClN_2O$: C, 55.7; H, 3.6; N, 14.4%); $\nu_{max.}$ (Nujol) 1 560 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 365 (log ε 3.92), 356 (3.83), 262 (3.90), and 245 nm (3.76); *m/e* 194.

Reactions of 6-*Chloro*-2-*methyl*-4-*oxidocinnolinium*. (20)—(i) *With dimethyl acetylenedicarboxylate*. 6-Chloro-2-methyl-4-oxidocinnolinium (0.194 g, 0.001 mol), DMAD (0.212 g, 0.001 5 mol), and benzene (10 ml) were heated (80 °C) under reflux (water-bath) for 12 h. The solvent was removed *in vacuo* (20° at 30 mmHg) and the residue purified by preparative t.l.c. on silica gel PF 254. Elution with chloroform gave *dimethyl* 6-*chloro*-1,3-*etheno*-1,2,3,4-*tetrahydro*-2-*methyl*-4-*oxocinnoline*-9,10-*dicarboxylate* (22) (0.225 g, 66%) as needles from EtOH, m.p. 89° (Found: C, 53.2; H, 4.1; N, 7.9. $C_{15}H_{13}ClN_2O_5$ requires C, 53.5; H, 3.9; N, 8.3%); $\nu_{max.}$ (Nujol) 1 730 br (C=O) and 1 600 (C=C) cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 248 (log ε 4.04) nm; *m/e* 336.

(ii) *With diphenylacetylene*. 6-Chloro-2-methyl-4-oxidocinnolinium (0.194 g, 0.001 mol) and diphenylacetylene (0.235 g, 0.002 mol) in *o*-dichlorobenzene (10 ml) were heated under reflux (180°) for 36 h. The solvent was removed *in vacuo* (50° at 18 mmHg) and the residue was purified by preparative t.l.c. on silica gel PF 254. Elution with chloroform and crystallisation from EtOH gave 6-*chloro*-1,2,3,4-*tetrahydro*-2-*methyl*-4-*oxo*-9,10-*diphenyl*-1,3-*ethenocinnoline* (24) (0.125 g, 30%) as yellow needles, m.p. 64—68° (Found: C, 73.6; H, 4.8; N, 7.4. $C_{23}H_{17}ClN_2O$ requires C, 74.2; H, 4.6; N, 7.5%); $\nu_{max.}$ (Nujol) 1 715 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 300 (log ε 3.95) and 248 nm (4.26); *m/e* 372.

(iii) *With phenylacetylene*. 6-Chloro-2-methyl-4-oxidocinnolinium (0.194 g, 0.001 mol), phenylacetylene (0.172 g, 0.001 5 mol), and xylene (5 ml) were heated under reflux (140 °C) for 24 h. The solvent was removed *in vacuo* (20° at 30 mmHg) and the residue triturated with light petroleum (b.p. 40—60°; 10 ml). Filtration and crystallisation gave 6-*chloro*-1,2,3,4-*tetrahydro*-2-*methyl*-4-*oxo*-9-*phenyl*-1,3-*ethenocinnoline* (26) (0.17 g, 60%) as needles (from EtOH), m.p. 149—150° (Found: C, 68.3; H, 4.5; N, 9.5. $C_{17}H_{13}ClN_2O$ requires C, 68.9; H, 4.4; N, 9.5%); $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 300 (log ε 3.78) and 247 nm (4.18); *m/e* 296.

Reactions of the Phthalazin-1(2H)-*one* (9).—(i) *With benzyne*. Benzenediazonium-2-carboxylate hydrochloride [23] (3.7 g, 0.02 mol), phthalazin-1(2*H*)-one (1.4 g, 0.01 mol), and propylene oxide (2 ml, 5.5 mol) in 1,2-dichloroethane (20 ml) were heated under reflux (water-bath). After 2 h, the solvent was removed *in vacuo* (50°; 18 mmHg) and EtOH (15

[33] S. Gabriel and A. Neumann, *Ber.*, 1893, **26**, 705.

ml) was added. The precipitated solid (2.2 g, 75%) was removed by filtration and crystallised from EtOH to give 12-*phenyl*-5,11-*imino*-5H-*dibenz*[b,e]*azepin*-6(11H)-*one* (30) as plates, m.p. 196—197° (Found: C, 80.9; H, 4.8; N, 9.5. $C_{20}H_{14}N_2O$ requires C, 80.6; H, 4.7; N, 9.4%); $\nu_{max.}$ (Nujol) 1 720 (C=O) and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ ($CHCl_3$) 252 (log ε 4.49) and 292 nm (5.98); *m/e* 298.

(ii) *With dimethyl acetylenedicarboxylate.* Phthalazin-1(2*H*)-one (1.46 g, 0.01 mol) and DMAD (2.84 g, 0.02 mol) were heated (140 °C) for 6 h. The cooled melt was dissolved in benzene (10 ml) and chromatographed on alumina (B.D.H. neutral; 50 g). Elution with benzene gave *dimethyl* 3-(trans-1,2-*bismethoxycarboxylvinyl*)-1,2,3,4-*tetrahydro*-1-*oxo*-2,4-*ethenophthalazine*-9,10-*dicarboxylate* (31) (1.1 g, 58%), which crystallised from benzene–ether as needles, m.p. 140—141° (Found: C, 55.4; H, 4.4; N, 6.4. $C_{20}H_{18}N_2O_9$ requires C, 55.8; H, 4.2; N, 6.5%); $\nu_{max.}$ (Nujol) 1 760 (ester, C=O), 1 710 (ring, C=O), 1 615 (C=C), and 1 552 cm^{-1} $\lambda_{max.}$ ($CHCl_3$) 253 (log ε 4.57), 285 (4.12), and 328 nm (4.41); *m/e* 430.

(iii) *With phenyl isocyanate.* Phthalazin-1(2*H*)-one(0.16 g, 0.001 mol) and an excess of phenyl isocyanate were heated (100 °C) on a steam-bath for 3 h. A white crystalline solid separated from the cooled solution. Recrystallisation from ether gave *phthalazin*-1-*yl phenylcarbamate* (32) (0.2 g, 75%) as white plates, m.p. 115° (Found: C, 67.7; H, 4.1; N, 15.7. $C_{15}H_{11}N_3O_2$ requires C, 67.9; H, 4.2; N, 15.8%); $\nu_{max.}$ (Nujol) 3 025 (NH) and 1 730 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 251 (log ε 4.88) and 312 nm (4.88); *m/e* 146.

8-*Chloro*-12-*phenyl*-5,11-*imino*-5H-*dibenz*[b,f,]*azepin*-10(11H)-*one* (33).—Benzenediazonium-2-carboxylate hydrochloride [23] (0.37 g, 0.002 mol), 6-chlorocinnolin-4(1*H*)-one (0.180 g, 0.001 mol), and propylene oxide (1 ml) in 1,2-dichloroethane (50 ml) were heated under reflux (water-bath). After 12 h, the solvent was removed *in vacuo* (50° at 18 mmHg). The residue in chloroform was chromatographed on a silica gel column (12 × 1 in) and eluted with chloroform. The first 50 ml of eluate was collected and evaporated in *vacuo* to give a resinous oil. Preparative t.l.c. (silica gel PF 254; chloroform) gave the *adduct* (33) as a red viscous gum, $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (C=O); δ ($CDCl_3$) 7.87 (1H, m), 6.8—6.2 (11H, m) and 5.58 (1H, s); *m/e* 332.

2,4-*Dinitrophenylhydrazone.* A solution of (33) (0.125 g) in EtOH (10 ml) was heated under reflux (95 °C) for 4 h with a solution of 2,4-dinitrophenylhydrazine [prepared by dissolving 2,4-dinitrophenylhydrazine (0.110 g) in conc. H_2SO_4 (2 ml) followed by dilution to 10 ml with EtOH (95%)]. The mixture was concentrated to 10 ml and cooled. The precipitate was collected and crystallised from EtOH to give the 2,4-*dinitrophenylhydrazone* as orange needles, m.p. 219° (decomp.); (Found: C, 61.0; H, 2.4; N, 16.3. $C_{20}H_{22}ClN_6O_4$ requires C, 61.5; H, 2.4; N, 16.6%).

6-*Chloro*-1,2,3,4-*tetrahydro*-2-*methyl*-4-*methylene*-9-*phenyl*-1,3-*ethenocinnoline* (25).—Triphenylmethylphosphonium bromide [34] (0.357 g, 0.001 mol) was added during 5 min to a solution of n-butyl-lithium (0.064 g, 0.43 ml of 15% solution in hexane) in abs. ether (10 ml). A solution of the cycloadduct (26) (0.237 g, 0.1 × 10^{-4} mol) in ether (10 ml) was added dropwise and then the mixture was heated (40 °C) under reflux overnight. The mixture was filtered and washed with ether (5 ml). The ether was removed and the residue purified by preparative t.l.c. (silica gel; chloroform) to give the *product* (25) as an oil (0.82 g, 35%) (Found: C, 72.9; H, 4.9; N, 9.3. $C_{18}H_{15}ClN_2$ requires C, 73.2; H, 5.1; N, 9.5%); δ ($CDCl_3$) 7.7—7.0 (8H, m, aromatic), 5.85 (1H, d, H-10), 5.48 (1H, s, C=CH_2), 4.80 (1H, s, C=CH_2), 4.08 (1H, d, H-3), and 2.57 (3H, s, N-Me); *m/e* 282.

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[34] G. Wittig and U. Schoellkopf, *Org. Synth.*, 1960, **40**, 66.