Addition Reactions of Heterocyclic Compounds. Part L.[1] Reactions of 1-Alkylbenzotriazoles and Benzo[*c*]cinnolines with Dimethyl Acetylenedicarboxylate

By **P. J. Abbott, R. M. Acheson,* M. W. Foxton, N. R. Raulins,** and **G. E. Robinson,** Department of Biochemistry, South Parks Road, Oxford OX1 3QU

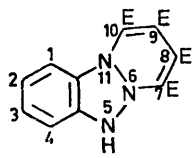
1-Alkylbenzotriazoles add 2 molecular proportions of dimethyl acetylenedicarboxylate, forming pyridazino[1,2-*a*]-benzotriazoles, which with acid undergo ring scission and an alternative cyclisation to form pyridazino[2,3-*a*]-quinoxalinones. Benzo[*c*]cinnolines add 2 molecular proportions of the dimethyl ester across the 5,6-double bond, but reaction with the diethyl ester in ethanol gives products involving this solvent. The n.m.r. spectra of benzo[*c*]cinnoline and some pyridazinobenzotriazoles have been computer-simulated.

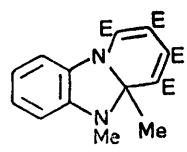
MANY heterocycles possessing pyridine-type –N=CR– systems in an aromatic ring combine readily with 2 mol. equiv. of dimethyl acetylenedicarboxylate to give quinolizine tetraesters and other products. There is considerable evidence [2] that the quinolizines are formed by nucleophilic attack from the nitrogen atom to give a 1 : 1 molar zwitterionic intermediate which can undergo a one- or two-stage cycloaddition with a second mol. equiv. of the acetylene. In the cases of pyridazine and its 3-methyl derivative [3] cyclisation could conceivably occur at the second nitrogen atom, but in fact cyclisation at the alternative carbon atom gave the only products isolated. No such alternative exists for 1-alkylbenzotriazoles and benzo[*c*]cinnoline [4] where two molecules of of the acetylenic ester could build on six-membered rings across the azo-linkage; these types of reaction have now been investigated. Benzotriazole itself with the ester gives dimethyl αβ-bis(benzotriazol-3-yl)succinate by Michael type additions.[5]

[1] Part XLIX, R. M. Acheson and M. S. Verlander, *J.C.S. Perkin I*, 1972, 1577.
[2] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.
[3] R. M. Acheson and M. W. Foxton, *J. Chem. Soc.*, 1966, 2218.
[4] A. N. Hughes and T. Monkoltananont, *Chem. and Ind.*, 1967, 662.
[5] R. M. Acheson and M. W. Foxton, *J. Chem. Soc.* (*C*), 1968, 389.

Dimethyl acetylenedicarboxylate reacted with 1-methyl-, 1-ethyl-, and 1-benzyl-benzotriazole in tetrahydrofuran to give a mixture of two 2 : 1 molar adducts

(1) 5-Me
(2) 5-Et
(3) 5-$PhCH_2$
E = CO_2Me





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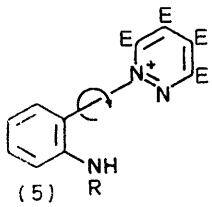

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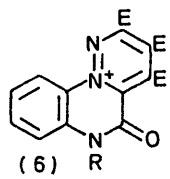

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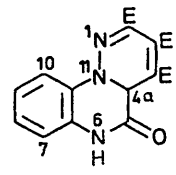
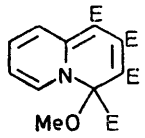


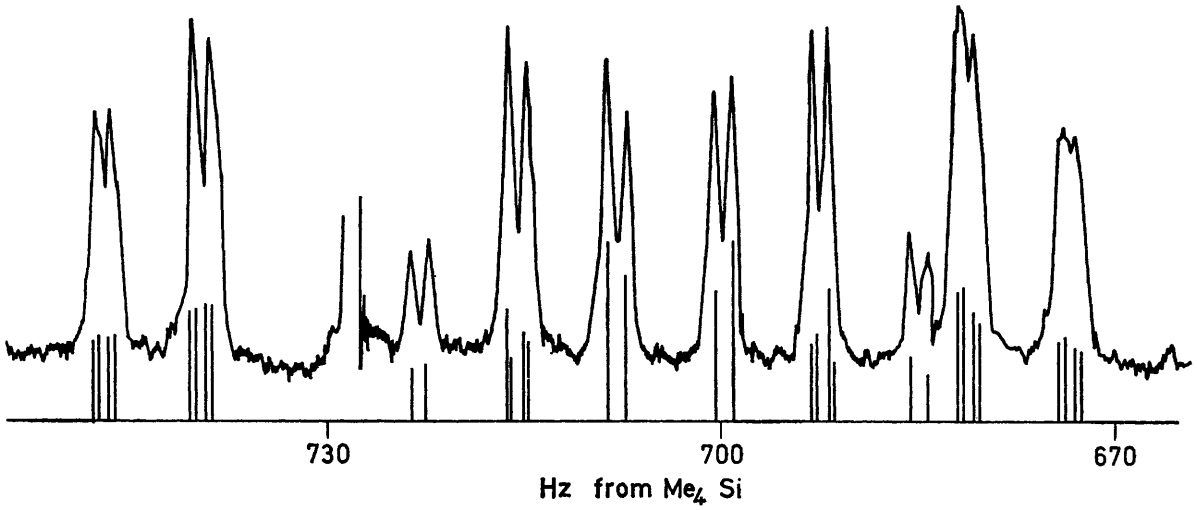
(7) 4a-MeO-6-Me
(8) 4a-MeO-6-Et
(9) 6-$PhCH_2$-4a-MeO
(10) 4a-HO-6-Me
(11) 6-$PhCH_2$-4a-HO
(12) 3,4-H_2-4a-MeO-6-Me
(13) 3,4-H_2-6-$PhCH_2$



(14)

in each case. The red adducts (1)—(3) were difficult to separate from their yellow isomers (7)—(9), and were proton is assigned to position 1, as the 11- (but not the 5-) nitrogen atom can lose electron density through resonance interactions with two of the ester groups. Large *peri*-deshielding of the 1-proton by the 10-ester group would not be expected unless the molecule is essentially planar. The aromatic proton spectra for both the adducts (1) and (2) have been accurately simulated by use of our seven-spin program [7] (Figure and Table 2). For the adduct (1) almost as good a fit with the experimental spectrum was obtained when the assignments for the 2- and 3-protons were reversed and the parameters readjusted. However, the present assignments reflect the downfield and upfield shifts expected at the *ortho*- and *para*-positions to the more and less electron deficient nitrogen atoms, respectively.

The corresponding red (1)—(3) and yellow (7)—(9) isomers gave identical n.m.r. spectra in trifluoroacetic acid, and in the case of the ethyl derivative (2) quenching the solution with methanol gave a solution from which the yellow isomer (8) was isolated. Although the u.v. spectra of solutions of the red compounds (1)—(3) did not change immediately after the addition of a drop of acid, the methyl derivative (1) dissolved in methanol–perchloric acid gave a spectrum, presumably due to the cation (6; R = Me), identical with that obtained from the yellow adduct (7) under the same conditions (Table 3). Examination of the n.m.r. spectra of solutions of the



The observed and calculated n.m.r. spectra for the pyridazinobenzotriazole (1)

minor products. Only the yellow isomers could be isolated when ether or acetonitrile was the reaction solvent. The u.v. spectra of the pyridazinobenzotriazoles (1)—(3) generally resemble that [6] of the benzimidazole derivative (4) except that the absorption bands are moved towards the visible range. All the corresponding proton resonances for compounds (1)—(4) are similar except for those of the adduct (3), in which case one ester methyl signal has moved upfield, presumably owing to shielding by the phenyl group. The lowest field aromatic adducts (8) and (9) in trifluoroacetic acid immediately after dissolution showed five resonances in the methyl region, three corresponding to three protons each and the other two together corresponding to three protons. After a few minutes one of the smaller peaks (τ *ca.* 6·32) had disappeared and the other had increased to the equivalent of three protons at τ 5·91. As the resonance (τ 6·32) due to methanol dissolved in trifluoroacetic acid was similarly replaced by that of methyl trifluoroacetate (τ 5·91) our observations suggest that the yellow adducts

[6] R. M. Acheson, M. W. Foxton, P. J. Abbott, and K. R. Mills, *J. Chem. Soc.* (*C*), 1967, 882.

[7] C. C. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.*, 1966, 835; P. C. Bell, Part II Thesis, Oxford, 1967.

TABLE 1

N.m.r. spectra (τ values; J in Hz; tetramethylsilane as internal reference)

Compound	Frequency (MHz)	Solvent	Proton resonances	Ester Me
(1)	60 and 100	$CDCl_3$	Ar-H_4, see Table 2; 5-Me, 6·84	6·12, 6·12, 6·18, 6·32
(2)	100	$CDCl_3$	Ar-H_4, and 5-Et, see Table 2	6·13, 6·13, 6·18, 6·33
(3)	100	$CDCl_3$	5-*Ph*CH_2, 2·71; [a] 5-PhC*H*$_2$, 4·89d, 5·63d, J 16·5; Ar-H_4,[b] 2·55m (1H), 3·07m (2H), 3·63m (1H)	6·10, 6·11, 6·29, 6·61
(4) *	60	$CDCl_3$	Ar-H_4, 2·9—3·45m; 5-Me, 6·91; 5a-Me, 8·56	5·96, 6·19, 6·23, 6·26
(7)	100	$CDCl_3$	4a-OMe, 6·96; 6-Me, 6·53; 10-H 2·05m; 7,8,9-H_3, 2·6—2·9m	6·10, 6·10, 6·10
	60	C_5H_5N	4a-OMe, 6·94; 6-Me, 6·66	6·00, 6·09, 6·09
	100	$CF_3{\cdot}CO_2H$	6-Me, 5·91; [c] 7,8,9-H_3, 1·66—2·21m; 10-H, 0·91d, J *ca.* 8	5·69 5·73, 5·80, 6·31 [d]
(8)	100	$CDCl_3$	4a-OMe, 6·96; 6-*Me*CH_2, 8·84t; 6-MeC*H*$_2$, 5·91q, J 7; 7,8,9-H_3, 2·55—2·90m; 10-H, 2·02*q*	6·09, 6·09, 6·09
	100	$CF_3{\cdot}CO_2H$	6-*Me*CH_2, 8·41t; 6-MeC*H*$_2$, 5·30q, J 7; 7,8,9-H_3, 1·72t, J 7, 1·85—2·20m; 10-H, 0·85d, J *ca.* 8	5·93,[c] 6·32 [d]
(9)	60 and 100	$CDCl_3$	4a-OMe, 6·91; 6-*Ph*CH_2, 2·73; [a] 6-PhC*H*$_2$, 4·49d, 5·02d, J 16; 7,8,9-H_3, 2·6—3·05m; 10-H, 2·03m [f]	6·07, 6·07, 6·10
	60 and 100	$CF_3{\cdot}CO_2H$	6*Ph*CH_2, 2·66; [a] 6-PhC*H*$_2$, 4·17; [a] 7,8,9-H_3, 1·8—2·2m; 10-H, 0·90d, J 8	5·68, 5·75, 5·80, 5·91,[c] 6·31 [d]
	60	C_5H_5N	4a-OMe, 6·89; 6-PhC*H*$_2$, 4·24d, 5·01d, J 16	6·00, 6·10, 6·10
	100	$PhNO_2$	4a-OMe, 6·82; 6-PhC*H*$_2$, 4·18d, 4·92d, J 16·5	5·89, 5·95, 6·00
(10)	60	$CDCl_3$	4a-OH, 5·30; [g] 6-Me, 6·45; 7,8,9-H_3, 2·59—2·91m; 10-H, 1·94m	6·05, 6·11, 6·11
(11)	100	$CDCl_3$	4a-OH, 5·29; [g] 6-*Ph*CH_2, 2·72; [a] 6-PhC*H*$_2$, 4·55d, 4·77d, J 16; 7,8,9-H_3, 2·55—3·0m; 10-H, 1·95q, J 8 and *ca.* 2	6·06, 6·11, 6·11
	100	$CF_3{\cdot}CO_2H$	6-*Ph*CH_2, 2·62; [a] 6-PhC*H*$_2$, 4·16; 7,8,9-H_3, 1·7—2·2m; 10-H, 0·86d, J 8·5	5·68, 5·73 5·78
(12)	60	$CDCl_3$	3-H, 5·74d; 4-H, 6·73d; $J_{3,4}$ 13·3; 4a-OMe, 6·91; 6-Me, 6·44; 7,8,9-H_3, 2·5—2·85m; 10-H, 2·00q, J 8 [h]	6·06, 6·15, 6·32
(13)	60	$CDCl_3$	3-H, 4a-H, 5·35—5·65m; 4-H, 5·80q, J 4 and 2; 6-*Ph*CH_2, 2·70; [a] 6-PhC*H*$_2$, 4·55d, 4·85d, J *ca.* 16; 7,8,9-H_3, 2·8—3·2m; 10-H, 2·20q, J 8 and 2	6·11, 6·20, 6·34
(18)	60	$CDCl_3$	5-Me, 6·43; 6,7,8,9-H_4, 2·3—2·8m	5·95, 6·02, 6·18
(19)	60	$CDCl_3$	3-H, 5·08; 6-Me, 6·50; 7,8,9-H_3, 2·68—2·93m; 10-H, 2·18m	6·05, 6·08, 6·25
(21)	100	$CDCl_3$	1,10-H_2, 1·74d; 2,9-H_2, 2·41q; 3,8-Me_2, 7·40; 4,7-H_2, 1·61; [f] $J_{1,2}$ 8·2; $J_{1,4}$ 1·8	
(22)	100	$(CD_3)_2SO$	1,14-H_2, 2·07m; 2,3,12,13-H_4, 2·4—2·65m; 4,11-H_2, 3·03m	6·30, 6·30, 6·43, 6·43
(23)	60 and 100	$(CD_3)_2SO$	1,14-H_2, 2·28d, J 8; 2,13-H_2, 2·88d,[h] J 8; 4,11-H_2 3·26; [h] 3,12-Me_2, 7·67	6·29, 6·29, 6·42, 6·42
(26)	100	$CDCl_3$	1-H, 2·45d; [i] 2-H, 3·04d; [h,i] 3-Me, 7·69; 4-H, 3·33; [h,i] 6-H, 4·79; [a,j] 9-H, 5·58; [a,j] 11-H, 3·36; [h,i] 12-Me, 7·74; 13-H, 3·14d; [h,i] 14-H, 2·54d; [h,i] $J_{1,2}$, $J_{13,14}$ 8	6·25, 6·25, 6·25, 6·73
(27)	100	$CDCl_3$	ArH_2, 2·4—2·6m; Ar-H_4, 2·8—3·25m; 6-H, 4·88; 6-$CH_3{\cdot}CH_2{\cdot}O$, 8·94t; 6-$CH_3{\cdot}CH_2{\cdot}O$, 6·26q, J 7	5·6—6·1m,[k] 8·5—8·85m [k]
(28)	100	$CDCl_3$	1-H, 2·63d; [i] 2-H, 3·14d; [h,i] 3,12-Me_2, 7·79; 4-H, 2·98; [h,i] 6-H, 4·88; 6-$CH_3{\cdot}CH_2{\cdot}O$, 8·93t; 6-$CH_3{\cdot}CH_2{\cdot}O$, 6·23q, J 7; 11-H, 3·32; [h,i] 13-H, 3·35d; [h,i] 14-H, 2·71d; [i] $J_{1,2}$, $J_{13,14}$ 8	5·45—6·0m,[k] 8·5—8·85m [d]
(29)	60	$CDCl_3$	1-*Ph*CH_2, 2·72; [a] 1-PhC*H*$_2$ 4·21; 4-H, 1·95m; 5,6,7-H_3, 2·6—2·8m	
1-$PhCH_2$	100	$CF_3{\cdot}CO_2H$	1-*Ph*CH_2, 2·48; [a] 1-PhC*H*$_2$, 3·78; [a] Ar-H_4, 1·7—2·1m	
(29) 1-Et	100	$CDCl_3$	1-*Me*CH_2, 8·39t; 1-MeC*H*$_2$, 5·33q, J 7; 4-H, 1·92d,[h] J 7; 5,6,7-H_3, 2·35—2·75m	
	100	$CF_3{\cdot}CO_2H$	1-*Me*CH_2, 8·09t; 1-MeC*H*$_2$, 4·84q, J, 7·5; 4,5,6,7-H_4, 1·65—2·0m [l]	
(29)	100	$CDCl_3$	1-Me, 5·76; 4-H, 1·98q, J *ca.* 7 and 2; 5,6,7-H_3, 2·5—2·8m	
1-Me	100	$CF_3{\cdot}CO_2H$	1-Me, 5·29; 4,5,6,7-H_4, 1·75—2·1m [m]	
(29) 1-$PhCH_2$-3-Me, Br^-	100	$(CD_3)_2SO$	1-*Ph*CH_2, 2·45—2·65m; 1-PhC*H*$_2$, 3·56; [a] 3-Me, 5·31; 4, 7-H_2, 1·40m; [n] 5,6-H_2, 1·95m [n]	
		$CF_3{\cdot}CO_2H$	1-*Ph*CH_2, 2·35—2·65m; 1-PhC*H*$_2$, 3·83; [a] 3-Me, 5·30; 4,5,6,7-H_4, 1·75—2·15m	
(29) 1-Et-3-Me, I^-	100	$CF_3{\cdot}CO_2H$	1-*Me*CH_2, 8·18t; 1-MeC*H*$_2$, 5·00q, J 7; 3-Me, 5·38; 4,5,6,7-H_4, 1·80—2·1m [o]	
	100	$(CD_3)_2SO$	1-*Me*CH_2, 8·32t; 1-MeC*H*$_2$, 4·90q, J 7; 3-Me, 5·33; 4,5,6,7-H_4, 1·4—1·75m,[p] 1·8—2·05m [p]	
(29)	100	$(CD_3)_2SO$	1,3-Me_2, 5·33; 4,7-H_2, 1·58; [n] 5,6-H_2, 1·93 [a]	
1,3-Me_2, I^-	100	$CF_3{\cdot}CO_2H$	1,3-Me_2, 5·31; 4,5,6,7-H_4, 1·90 [a]	
(30) 2-Et	100	$CDCl_3$	2-*Me*CH_2, 8·28t; 2-MeC*H*$_2$, 5·18q, J 7·5; Ar-H_4,[p] 2·0—2·2m, 2·5—2·7m	
	100	$CF_3{\cdot}CO_2H$	2-*Me*CH_2, 8·15t; 2-MeC*H*$_2$, 4·90q, J 7·5; Ar-H_4,[p] 1·7—1·95m, 2·05—2·3m	

TABLE 1 (*Continued*)

Compound	Frequency (MHz)	Solvent	Proton resonances	Ester Me
(30)	100	$CDCl_3$	2-Me, 5·48; Ar-H_4, 2·0—2·2m,[p,q] 2·5—2·7m [p,q]	
2-Me	100	$CF_3{\cdot}CO_2H$	2-Me, 5·22; Ar-H_4, 1·8—2·05m,[p,q] 2·15—2·4m [p,q]	
(30) † 1,2-Me_2, BF_4^-	100	$(CD_3)_2SO$	1-Me, 5·19; 2-Me, 5·39; 4-H, 1·68d; [r] 5-H, 1·91t; [h,j] 6-H, 2·03t; [h,j] 7-H, 1·61d; [r] J_{ortho} 7 and 9 and 8·3, J_{meta} 1·2	

* From ref. 6. † From ref. 10.

[a] Apparent singlet. [b] Almost an AM_2X system. [c] Increases to 6 protons as $CF_3{\cdot}CO_2Me$ forms. [d] MeOH, disappears as $CF_3{\cdot}CO_2Me$ forms. [e] $CF_3{\cdot}CO_2Me$ resonance. [f] Coupling could not be resolved. [g] Exchanges with D_2O. [h] Further coupled by 1—2 Hz. [i] The protons of one of these 3-spin systems cannot be differentiated from the corresponding protons of the other 3-spin system. [j] These assignments could be reversed. [k] Et groups. [l] Almost an A_2B_2 system centered on 1·85. [m] Large peak at 1·95. [n] 7 lines resolved; close to an A_2B_2 system. [o] Almost an A_2B_2 system centered on 1·96. [p] A_2B_2 system. [q] 8 lines resolved. [r] Partially superimposed.

TABLE 2

Computed [7] n.m.r. spectra for 100 MHz. The intensities of lines closer than 0·1 Hz have been summed

Compound	Proton assignments, chemical shifts in Hz from tetramethylsilane, and J in Hz	No lines observed	Worst agreement on any line
(1)	4-H, 677·7; 3-H, 714·4; 2-H, 693·2; 1-H, 743·0; $J_{3,4}$ 7·9; $J_{2,4}$ 1·0; $J_{1,4}$ 0·3; $J_{2,3}$ 7·4; $J_{1,3}$ 1·0; $J_{1,2}$ 7·6	32	±0·3
(2)	4-H, 677·8; 3-H, 709·9; 2-H, 688·3; 1-H, 740·3; $J_{3,4}$ 7·9; $J_{2,4}$ 1·0; $J_{1,4}$ 0·3; $J_{2,3}$ 7·4; $J_{1,3}$ 1·0; $J_{1,2}$ 7·6	31	±0·4
(2)	5-$CH_3{\cdot}CH_2$ (ABX_3), H_A 348·4; H_B 381·0; H_X 76·3; J_{AB} 13·8; J_{AX} 6·9; J_{BX} 6·9	13 [a]	±0·4
(20)	1-H, 843·50; 2-H, 780·65; 3-H, 781·65; 4-H, 867·05; $J_{1,2}$ 8·2; $J_{1,3}$ 1·6; $J_{1,4}$ 0·4; $J_{2,3}$ 7·5; $J_{2,4}$ 1·8; $J_{3,4}$ 8·0	27	±0·4

[a] Some computed lines obscured by OMe resonances.

TABLE 3

U.v. absorption data

	Solvent *	$\lambda_{max.}$/nm (10^{-4} ε)
(1)	MeOH [a]	214 (1·60), 280 (0·93), 499 (1·07)
(2)	MeOH [a]	211 (2·49), 288infl (2·20), 282 (1·15), 495 (0·67)
(3)	MeOH [a]	209 (3·82), 231infl (2·32), 280 (1·29), 488 (0·86)
(4) †	MeOH	220 (2·05), 256 (1·51), 315 (0·76), 441 (0·91)
(7)	MeOH	221 (1·99), 247infl (1·21), 276 (0·93), 396 (0·66)
	P	237 (2·52), 273infl (0·95), 358 (1·19), 475 (0·97)
(8)	MeOH	214 (3·13), 254infl (1·62), 277 (1·41), 392 (0·88)
	MeOH [b]	208 (3·13), 238 (2·53), 355 (1·09), 472 (0·67)
(9)	MeOH	209 (3·62), 251infl (1·64), 277 (1·28), 390 (0·82)
	MeOH [b]	208 (3·79), 236 (2·33), 276infl (0·73), 355 (0·91), 466 (0·55)
	MeCN	234 (2·16), 250infl (1·67), 280 (1·25), 328br (0·53), 389 (0·89)
	MeCN [b]	242 (2·87), 356 (1·24), 472 (0·85)
(10)	MeOH	218 (3·69), 275 (1·36), 318 (1·14), 332 (0·98), 385 (0·65)
	P	236 (2·71), 355 (1·14), 472 (0·60)
(11)	MeOH	214 (3·30), 268 (0·78), 277 (0·84), 319 (1·33), 333 (1·10), 380 (0·42)
	MeOH [b]	209 (2·72), 236 (1·62), 279infl (0·49), 321infl (0·55), 337infl (0·62), 349 (0·62), 466 (0·39)
	MeCN	231 (0·91), 241 (1·01), 268 (0·85), 276 (0·85), 306infl (1·17), 320 (1·68), 334 (1·33), 382 (0·48)
	MeCN [b]	242 (2·00), 354 (0·99), 473 0·72)
(12)	MeOH	225 (1·41 [c]), 267 (0·4 [c]), 342 (0·74 [c])
(13)	MeOH	223infl (1·93), 267 (0·57), 340 (1·14), 345 (1·18)
(18)	MeOH [a]	243 (3·71), 316 (0·91), 326infl (0·84)
(19)	MeOH	219 (2·74), 270 (0·81), 322 (1·38), 333infl (1·14), 402 (0·42)
(20) ‡	EtOH	252 (5·0), 308 (0·95), 355 (0·19), 373 (0·15)
(22)	$CHCl_3$	256 (2·53), 278infl (1·40), 317 (1·25), 478 (0·12)
(23)	$CHCl_3$	260 (2·77), 324 (1·48), 480 (0·12)
(26)	MeOH	212 (2·74), 244infl (2·46), 261·5 (3·03), 291infl (1·37), 345 (1·09)
(27)	MeOH	210 (2·32), 260 (2·97), 298infl (0·76), 406 (1·07)
(28)	MeOH	210 (2·82), 261 (3·47), 300infl (0·82), 407 (1·15)

* P = Methanol–72% perchloric acid (2 : 1 v/v). † From ref. 6. ‡ From ref. 12.

No immediate change after addition of 3 drops of 72% $HClO_4$. [b] Acidified with 3 drops of 72% $HClO_4$. Optical densities.

are not directly transesterified by the trifluoroacetic acid, but first form free methanol. Both the red (1) and yellow (7) adducts from 1-methylbenzotriazole behaved similarly, but there was the complication that the *N*-methyl resonance in trifluoroacetic acid coincided with that due to the methyl trifluoroacetate. The yellow adducts in deuteriochloroform all showed a high field *O*-methyl resonance (τ 6·91—6·96) similar to that (6·85) of the quinolizine (14).[8] The pyridazinoquinoxalinone (7) with hydrochloric and perchloric acids

[8] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1629.

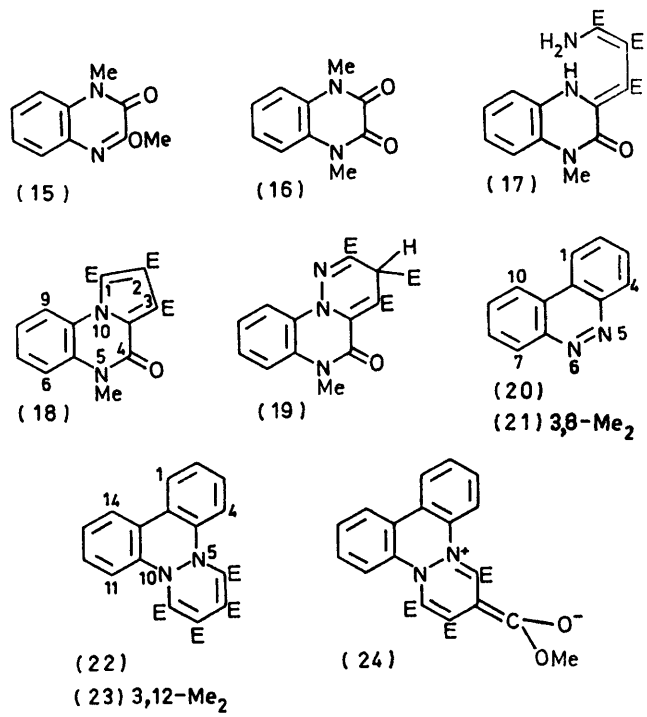
gave crystalline salts, presumably derived from the cation (6; R = Me), but attempted recrystallisation was unsatisfactory and good analytical data could not be obtained. The simplest way of accommodating the foregoing information is on the basis of structures (1)—(3) and (7)—(9) for the red and yellow compounds, respectively. Protonation and N–N bond scission in the red adducts, as for aromatic diazoamino-compounds, would lead to species (5) with a new aromatic ring. Rotation about the bond joining the rings, and cyclo-amide formation with the appropriate ester group, would yield the cation (6), which could accept a meth-oxide ion at position 3 or 4a. Position 4a is thought to be the more likely as it gives the more conjugated system in the product. In the absence of acids, heterolysis of the 5,6-bond in the red adducts (1)—(3) could lead to a similar result.

The hydroxypyridazinoquinoxalinone (10) was a minor product formed from dimethyl acetylenedicarb-oxylate and 1-methylbenzotriazole in ether; both com-pounds (10) and (11) were obtained from their methoxy-analogues (7) and (9) by treatment with trifluoroacetic acid, evaporating the methyl trifluoroacetate formed, and working up with water. The spectra of the hydroxy- and the methoxy-compounds were similar except that the hydroxy-compounds showed strong OH absorption in their i.r. and n.m.r. spectra and their n.m.r. spectra contained no high field methoxy-signals. Recrystallisation of compound (11) from methanol regenerated compound (9). The i.r. spectra of com-pounds (7)—(11) all showed intense absorption close to 1675 and 1677 cm^{-1}, where the quinoxalinones (15) and (16) possess strong absorption bands.[9]

All the pyridazinoquinoxalinones (7)—(13) and (19) in deuteriochloroform showed a signal for one low-field aromatic proton at τ *ca.* 2, the other three aromatic protons appearing as a complex multiplet at *ca.* 2·5—3·0 and the general pattern being very similar to that of the parent benzotriazoles. However on protonation in trifluoroacetic acid the pictures are different, thereby excluding a benzotriazole-type structure for the yellow adducts. The spectra of the pyridazinoquinoxalinones (7)—(9) and (11) show a one-proton multiplet at τ *ca.* 0·9 and a three-proton multiplet in the 1·7—2·2 region, whereas the 1-alkylbenzotriazoles show essentially A_2B_2-type spectra spanning the 1·7—2·1 region. The aromatic protons of 2-ethyl- and 2-methyl-benzotriazole in deuteriochloroform appear as A_2B_2 systems. In trifluoroacetic acid the spectra still show A_2B_2 systems, a marked downfield shift having taken place. 1,2-Di-methylbenzotriazolium tetrafluoroborate[10] similarly possesses two low-field protons, indicating that this type of structure is not acceptable for the cations of the yellow adducts.

The methylene resonances of the benzyl derivatives (3), (9), (11), and (13) in deuteriochloroform show as clearly defined AB systems. The adduct (2) from 1-ethylbenzotriazole in a similar way show the ethyl group as an ABX_3 system, which was computer-simulated (Table 2), but for the isomer (8) the methylene protons were apparently equivalent. These observations must reflect the asymmetry of the respective molecules, for when the effectively planar cations (6; R = $PhCH_2$ or Et) are formed in trifluoroacetic acid the methylene protons become equivalent.

The anhydrous tin(II) chloride–hydrochloric acid reduction of the pyridazinoquinoxalinone (7), which probably occurs by breaking of the N–N bond, may have proceeded *via* structure (17); cycloelimination of



ammonia would then give the product (18). Catalytic hydrogenation of the pyridazinoquinoxalinone (7) gave the dihydro-derivative (12) and compound (19) formed by subsequent elimination of methanol. The benzyl analogue (9) under the same conditions was reduced even further, to give compound (13). The spectral data for compounds (12), (13), (18), and (19) are consistent with the proposed structures.

The n.m.r. spectra of benzo[*c*]cinnoline (20) and its 3,8-dimethyl derivative have been measured and unam-biguous assignments have been made for the latter. On the assumptions for benzo[*c*]cinnoline that (i) the corresponding coupling constants are the same as those observed for the 3,8-dimethyl derivative, and that (ii) the lowest field multiplet is due to the 4- and 7-protons (this is anticipated as the methyl groups of the dimethyl derivative would be expected to shield the 4- and 7-protons more than the 1- and 10-positions) it has been

[9] G. W. H. Cheeseman, A. R. Katritzky, and S. Oksne, *J. Chem. Soc.*, 1961, 3983.

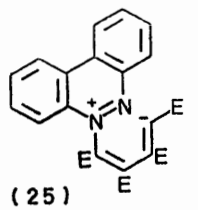
[10] R. M. Acheson and D. R. Harrison, *J. Chem. Soc.* (*C*), 1970, 1764.

possible to simulate accurately the observed spectrum (Table 2).

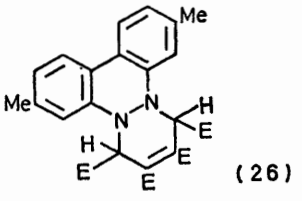
A 2 : 1 molar adduct (22) was first obtained from dimethyl acetylenedicarboxylate and benzo[*c*]cinnoline in methanol,[11] but better yields are reported [4] obtainable in the absence of solvent. A similar adduct (23) has been prepared from 3,8-dimethylbenzo[*c*]cinnoline, but the solubilities of the adducts made it impossible to obtain spectra of sufficient quality to attempt computer simulation. However the data for the dimethyl compound show that the highest field aromatic protons are at positions 4 and 11, and the lowest at 1 and 14. They resonate at much higher field than the corresponding protons of the parent heterocycles, and the two methyl groups also show a marked (τ 0·27) upfield shift. This is consistent with the change in hybridisation of the nitrogen atoms, but the 4- and 11-proton and the 3- and 12-methyl signals are at lower field (τ 0·37 and 0·23, respectively) than those of the 2-proton and the methyl group of *m*-toluidine, also measured in [$^2H_6$]dimethyl sulphoxide. These data suggest that appreciable positive charge is developed on the nitrogen atoms. This is much more likely to involve ester groups, as shown in structure (24), which may be compared with similar formulations put forward [12] for 9a*H*-quinolizine-1,2,3,4-tetraesters, rather than the 'no-bond' resonance contributors (25) which have been suggested.[4] The long-wavelength absorption bands of the adduct (22) are solvent dependent [4] and very broad, suggesting a charge-transfer type of spectrum, and they are similar to the long-wavelength bands of the red benzotriazole adducts (1)—(3).

Hydrogenation of the adduct (23) gave a dihydro-derivative, the u.v. spectrum of which showed no long-wavelength band and a chromophore generally resembling the original benzocinnoline (21) chromophore.[13] The n.m.r. spectrum showed that the carbocyclic rings had not been reduced, that the molecule had been reduced asymmetrically, and that the added hydrogen atoms were present in different environments on saturated carbon atoms and did not couple. No N–H absorption was detected in the i.r. The structure which fits this information best is (26). If the ring junction is *cis* or *trans* and the 6- and 9-hydrogen atoms *trans* or *cis*, respectively, then these atoms will be in different environments. Also one of the ester methyl groups, at position 6 or 9, will be above one of the carbocyclic rings, thereby accounting for its high field resonance.

Attempts to prepare the adducts corresponding to (22) and (23) from diethyl acetylenedicarboxylate failed completely, possibly for steric reasons, but in ethanol as reaction medium adducts involving 1 molecule of the solvent and 2 of the acetylenic ester were formed. The methyl esters (22) and (23) did not form corresponding compounds in refluxing ethanol. The adducts, provisionally considered to have structures (27) and (28), had u.v. spectra showing conjugation intermediate between that of the adduct (23) and that of its dihydro-derivative



(25)



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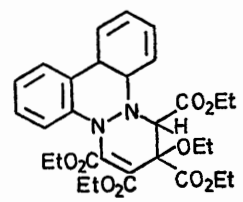
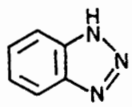
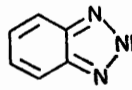


(27)

(28) 3,12-Me_2



(29)



(30)

(26). The n.m.r. spectra showed one-proton singlets at the same position as one of the singlets for the dihydro-compound (26), complex absorption due to the ethyl groups with one of these groups appearing at higher field than the others, and aromatic resonances showing that the environments of the carbocyclic rings are a little different. The adducts (22) and (23) could be formed *via* cyclisation of an intermediate such as (25). If the much more bulky ethyl groups inhibit this cyclisation then addition of a proton, from ethanol, at the negative centre, addition of ethoxide ion at the adjacent unsaturated carbon atom, and cyclisation of the new less sterically restricted carbanion could account for the formation of (27) and (28).

EXPERIMENTAL

The instruments and general procedures have been described previously.[1]

Methylbenzotriazoles.—Benzotriazole with methyl sulphate and sodium hydroxide [14] gave 2-methylbenzotriazole (23·5%), b.p. 108—112° at 22 mmHg (lit.,[14] 103·5—104° at 15 mmHg) and 1-methylbenzotriazole (41%), b.p. 154—155° at 17 mmHg, m.p. 62—64° (lit.,[14] b.p. 150—152° at 14 mmHg, m.p. 65°); purification of the 2-methylbenzotriazole *via* the picrate was unnecessary.

1-*Benzylbenzotriazole.*—This was obtained [15] in 59% yield; m.p. 115—116°.

Ethylbenzotriazoles.—Ethyl iodide (46·8 g) was added to benzotriazole (23·8 g) dissolved in a refluxing solution of sodium (4·6 g) in ethanol (200 ml), and the mixture was refluxed for 3 h. Water was added, and distillation of the dried ether extracts of the resulting solution gave 2-ethylbenzotriazole (10·3 g), b.p. 118—120 at 21 mmHg (lit.,[14] 108° at 14 mmHg), and 1-ethylbenzotriazole (14·3 g), b.p. 154—156° at 16 mmHg (lit.,[14] 149·5° at 12 mmHg).

[11] M. W. Foxton, D.Phil. Thesis, Oxford, 1965.
[12] R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
[13] G. M. Badger, R. S. Pearce, and R. Pettit, *J. Chem. Soc.*, 1951, 3199.
[14] F. Krollpfeiffer, A. Rosenberg, and C. Mühlhausen, *Annalen*, **1935**, **515**, 113.
[15] M. S. Gibson, *J. Chem. Soc.*, 1956, 1076.

Dialkylbenzotriazolium Salts.—1-Methylbenzotriazole (1·4 g), methyl iodide, and acetonitrile were refluxed for 2 h. The solvent was removed *in vacuo*, and the residue dissolved in the minimum of methanol. Addition of ether precipitated 1,3-dimethylbenzotriazolium iodide (0·63 g), yellow rods, m.p. 188·5—189° [lit.,[14] 185° (decomp.)]. The same compound was obtained in a similar alkylation of 2-methylbenzotriazole. 1-Ethyl-3-methylbenzotriazolium iodide, rods (precipitated from acetonitrile by ether), m.p. 140—140·5° (Found: C, 36·9; H, 4·2; N, 14·5. $C_9H_{12}IN_3$ requires C, 37·4; H, 4·2; N, 14·5%), was obtained similarly from both 1- and 2-ethylbenzotriazole and methyl iodide and from 1-methylbenzotriazole with ethyl iodide. The very deliquescent 1-benzyl-3-methylbenzotriazolium bromide, needles precipitated from acetonitrile solution with ether, m.p. 145—153°, was obtained from 1- and 2-methylbenzotriazoles with benzyl bromide.

Reaction of 1-*Methylbenzotriazole with Dimethyl Acetylenedicarboxylate.*—(i) With G. A. Taylor. Dimethyl acetylenedicarboxylate (18·5 ml) was added to the triazole (10·0 g) and tetrahydrofuran (20 ml; purified from cuprous chloride and dried with lithium aluminium hydride), and the mixture was shaken until homogeneous. After 72 h at room temperature the precipitate (8·5 g) was collected, washed with tetrahydrofuran, and recrystallised from benzene, toluene, or methanol to give *trimethyl* 4a,5,6,11-*tetrahydro*-4a-*methoxy*-6-*methyl*-5-*oxopyridazino*[2,3-a]*quinoxaline*-2,3,4-*tricarboxylate* (7), yellow rods, m.p. 178—179·5° (variable) (Found: C, 54·7; H, 4·6; N, 10·4; OMe, 29·1. $C_{19}H_{19}N_3O_8$ requires C, 54·7; H, 4·6; N, 10·1; OMe, 29·9%), $\nu_{max.}$ 1772, 1742, 1731, 1720, 1689infl, 1681, 1633, 1606, 1597, and 1515 cm^{-1}, *m/e* 417 (M^+, 3%), 388(3), 387(21), 386 (M − 31, 100), 358 (M − CO_2Me, 11), 328(20), 268(12), 169(8), 162(9), 156(11), 147(32), and 119(8) (other peaks <3%).

The filtrate and washings were combined and most of the solvent was evaporated off at room temperature. The residue on trituration with methanol (25 ml) solidified, and the solid (2·1 g) gave more of the pyridazinoquinoxaline (7). The filtrate was diluted with methanol (25 ml) and on cooling to *ca.* −20° for several days precipitated *tetramethyl* 5-*methyl*-5H-*pyridazino*[1,2-a]*benzotriazole*-7,8,9,10-*tetracarboxylate* (1), deep red plates (from methanol), m.p. 143—144° (Found: C, 54·9; H, 4·7; N, 9·9; OMe, 29·6. $C_{19}H_{19}N_3O_8$ requires C, 54·7; H, 4·6; N, 10·1; OMe 29·9%), $\nu_{max.}$ 1752, 1745, 1735, 1728, 1625, 1598, 1568, and 1561infl cm^{-1}, *m/e* 417 (M^+, 0·2%), 359(21), 358 (M − CO_2Me, 100), 327(1), 312(1), 300(4), and 182(4) (other peaks <1%).

From the mother liquors were isolated hexamethyl mellitate (0·1 g), m.p. and mixed m.p. 185—188°, *m/e* 426 (M^+, 2·5%), 395(100), 365(4), 350(5), 220(3·5), 182(7), 162(7·5), and 104(6·5), and a colourless compound, m.p. 136—137°.

(ii) The ester (12·9 g) was added to the triazole (6·0 g) in dry ether (50 ml) at room temperature and after 4 days the ether was allowed to evaporate. The residue was triturated with methanol (20 ml) and the precipitate, recrystallised from methanol, gave the pyridazinoquinoxaline (7) (3·57 g). Concentration of the mother liquors of the first recrystallisation gave a solid which was chromatographed on a thin layer with benzene–ethyl acetate (4 : 1 v/v) as developer. The slower moving band gave the pyridazinoquinoxaline (7), and the faster band *trimethyl*-4a,5,6,11-*tetrahydro*-4a-*hydroxy*-6-*methyl*-5-*oxopyridazino*-[2,3-a]*quinoxaline*-2,3,4-*tricarboxylate* (10), yellow plates (0·12 g) (from methanol), m.p. 182—183° (Found: C, 53·7; H, 4·2; N, 10·6. $C_{18}H_{17}N_3O_8$ requires C, 53·6; H, 4·2; N, 10·4%), $\nu_{max.}$ 3430 (OH), 1750, 1730, 1710, 1672, 1629, and 1565 cm^{-1}, *m/e* 403 (M^+, 1·7%), 386 (M − OH, 10), 345(15), 344 (M − CO_2Me, 75), 312(100), 228(12), and 227(85) (other peaks <2%). It gave no colour with iron(III) chloride in alcoholic solution. T.l.c. of the reaction mixture after removal of the pyridazinoquinoxaline (7) showed only traces of the pyridazinotriazole (1).

The methoxypyridazinoquinoxalinone (7) (0·83 g) in trifluoroacetic acid (0·5 ml) gave a dark orange-red solution which was placed in a desiccator (KOH) at 12 mmHg for 4 h. The red tar solidified on trituration with ice and water gave the hydroxypyridazinoquinoxalinone (10) (0·78 g), identical (n.m.r. and i.r. spectra) with an authentic specimen.

Reaction of 1-*Ethylbenzotriazole with Dimethyl Acetylenedicarboxylate.*—The ester (28·4 g) was added to the triazole (11·0 g) in tetrahydrofuran (30 ml) and after 5 days at room temperature the precipitate was collected, the filtrate being retained. Recrystallisation from methanol gave *trimethyl* 6-*ethyl*-4a,5,6,11-*tetrahydro*-4a-*methoxy*-5-*oxopyridazino*-[2,3-a]*quinoxaline*-2,3,4-*tricarboxylate* (8) (4·91 g) as yellow needles, m.p. 166—171°, resolidifying and remelting at 199—200° (Found: C, 56·0; H, 5·1; N, 9·9. $C_{20}H_{21}N_3O_8$ requires C, 55·7; H, 4·9; N, 9·7%), $\nu_{max.}$ 1749, 1725, 1688infl, 1677, 1653infl, 1648infl, 1625, and 1602 cm^{-1}, *m/e* 431 (M^+, 5%), 402(6), 407(28), 400 (M − OMe, 100%), 372(10), 343(7), and 282(3) (other peaks <3%). T.l.c. showed only one component and the n.m.r. spectrum showed no apparent impurities.

The filtrate was evaporated to dryness and chromatographed on alumina (1300 ml). Elution with benzene gave a red fraction. The constituents on recrystallisation from methanol gave more of the quinoxalinone (3·77 g), the mother liquor of which yielded *tetramethyl* 5-*ethyl*-5H-*pyridazino*[1,2-a]*benzotriazole*-7,8,9,10-*tetracarboxylate* (2), red needles (1·39 g) (from methanol), m.p. 144—146° (Found: C, 55·3; H, 5·1. $C_{20}H_{21}N_3O_8$ requires C, 55·7; H, 4·9%), $\nu_{max.}$ 1750, 1726, 1715infl, 1700infl, 1696infl, and 1675 cm^{-1}, *m/e* 431 (M^+, 1%), 400 (M − OMe, 13), 374(5), 373(22), 372 (M − CO_2Me, 100), 312(15), and 227(4) (other peaks <4%).

The pyridazinotriazole (2) (44 mg) gave a dark solution in trifluoroacetic acid (2 ml) which was immediately poured into excess of methanol. The solution was evaporated to dryness *in vacuo* and the residue dried (P_2O_5 and KOH) at 12 mmHg for 2 days. Recrystallisation from methanol gave the methoxypyridazinoquinoxalinone (8) (32 mg), identical (m.p., mixed m.p., and i.r. spectrum) with an analysed specimen.

Reaction of 1-*Benzylbenzotriazole with Dimethyl Acetylenedicarboxylate.*—(i) The triazole (15 g), the ester (20·4 g), and acetonitrile (500 ml) were refluxed for 15 h, the solvent was removed *in vacuo*, and the residual oil was chromatographed on alumina (600 ml). Elution with benzene (3·5 l) gave a single yellow fraction yielding *trimethyl* 6-*benzyl*-4a,5,6,11-*tetrahydro*-4a-*methoxy*-5-*oxopyridazino*[2,3-a]*quinoxaline*-2,3,4-*tricarboxylate* (9), yellow needles (9·5 g) (from methanol), m.p. 159—160° (Found: C, 60·6; H, 4·8; N, 8·5; OMe, 25·2. $C_{25}H_{23}N_3O_8$ requires C, 60·8; H, 4·7; N, 8·5; 4 × OMe, 25·1%), $\nu_{max.}$ 1755infl, 1750, 1741infl, 1725, 1685, 1678infl, 1670infl, 1653infl, 1645infl, 1624, and 1602 cm^{-1}, *m/e* 493 (M^+, 3%), 464(6), 463(38), 462 (M − OMe, 100), 434 (M − CO_2Me, 7), 405(3), 404(14), 402(13), 340(3), 227(3), 92(10), and 91(tropylium ion, 90) (other peaks

<3%). This compound was stable to refluxing in pyridine for 6 h.

(ii) The triazole (15·7 g), the ester (28·4 g), and tetrahydrofuran (130 ml) were refluxed for 17 h; the solvent was removed *in vacuo* and the residue triturated with methanol and filtered. Recrystallisation of the resulting solid (methanol) gave the pyridazinoquinoxalinone (9) (8·05 g), m.p. 157—161°. The filtrate was evaporated and chromatographed on alumina (150 ml). Elution with benzene–ethyl acetate (4 : 1 v/v) gave a mixture which on fractional crystallisation from methanol yielded as the less soluble component the quinoxalinone (9) (1·42 g) and as the more soluble component *tetramethyl 5-benzyl-5H-pyridazino*[1,2-a]*benzotriazole-7,8,9,10-tetracarboxylate* (3), red needles (0·32 g), m.p. 166—168° (Found: C, 60·6; H, 4·6. $C_{25}H_{23}N_3O_8$ requires C, 60·9; H, 4·7%), $\nu_{max.}$ 1748, 1739, 1735infl, 1719infl, 1710, 1700infl, 1695infl, 1682infl, and 1650infl cm^{-1}, *m/e* 493 (M^+, 1%), 463(3), 462 (M — OMe, 10), 436(5), 435(30), 434 (M — CO_2Me, 100), 404(3), 376(3), 316(3), 312(4), 100(3), 92(8), and 91(tropylium ion, 99) (other peaks <3%).

The methoxy-compound (9) (1·08 g) in trifluoroacetic acid (1·25 ml) was placed *in vacuo* over potassium hydroxide for 2 days and then treated with ice and water. Recrystallisation of the solid residue from toluene gave the corresponding *hydroxy-compound* (11) as yellow needles (0·56 g), m.p. 193—194° (Found: C, 60·7; H, 4·7; N, 8·7. $C_{24}H_{21}N_3O_8$ requires C, 60·1; H, 4·4; N, 8·8%), $\nu_{max.}$ 3442 (OH), 1769, 1750infl, 1732infl, 1720, 1713infl, 1704infl, 1696infl, 1682infl, 1675, 1631infl, 1629, and 1612 cm^{-1}, *m/e* 479 (M^+, 1%), 477(4), 463(6), 462 (M — OH, 12), 448 (M — OMe, 4), 421(5), 420 (M — CO_2Me, 22), 416(5), 404(12), 391(14), 388 (M — CH_2Ph, 5), 386(4), 360(15), 359(32), 344(4), 343(5), 312(11), 244(5), 227(4), 106(5), 105(6), 103(26), 92(11), and 91(tropylium ion, 100) (other peaks <4%).

The hydroxypyridazinoquinoxalinone (11) (100 mg) was refluxed in methanol (50 ml) for 4 h and the solvent was removed *in vacuo*. Recrystallisation of the residue from methanol gave the methoxypyridazinoquinoxalinone (9) (94 mg), identical (m.p., mixed m.p., and i.r. spectrum) with an analysed specimen.

Reduction of the Methoxymethylpyridazinoquinoxalinone (7).—(i) This compound (1·0 g) was shaken in methanol (200 ml) with 10% palladised charcoal (0·5 g) for 15 h under hydrogen (4 atmos); the solution was then filtered and concentrated to *ca.* 10 ml. The *dihydro-derivative* (12) separated and formed parallelepipeds (0·51 g) (from methanol), m.p. 167° (Found: C, 54·3; H, 5·6; N, 9·8; OMe, 30·0. $C_{18}H_{21}N_3O_8$ requires C, 54·4; H, 5·1; N, 10·0; 4 × OMe, 29·6%), $\nu_{max.}$ 1740, 1724, 1695, 1672, 1605, 1582, and 1502 cm^{-1}.

The filtrate was concentrated to *ca.* 4 ml and the *triester* (19) separated as yellow needles (0·25 g) (from methanol), m.p. 178—179° (Found: C, 55·8; H, 4·4. $C_{18}H_{17}N_3O_7$ requires C, 55·7; H, 4·4%), $\nu_{max.}$ 1715, 1675, 1634, 1608, 1577, and 1504 cm^{-1}.

(ii) A suspension of the quinoxalinone (7) (0·5 g) and anhydrous tin(II) chloride (5·0 g) in dry ether (100 ml) was saturated with dry hydrogen chloride and stirred for 24 h at room temperature. The mixture was neutralised with concentrated aqueous ammonia (*d* 0·88) and extracted with chloroform (3 × 100 ml), and the dried extracts were evaporated to dryness and triturated with methanol (10 ml). The precipitate crystallised from methanol giving *trimethyl 4,5-dihydro-5-methyl-4-oxopyrrolo*[1,2-a]*quinoxaline-1,2,3-tricarboxylate* (18) as needles (0·27 g), m.p. 169—170° (Found: C, 58·0; H, 4·3; N, 7·6; OMe, 25·6. $C_{18}H_{16}N_2O_7$ requires C, 58·1; H, 4·3; N, 7·5; 3 × OMe, 25·0%), $\nu_{max.}$ 1736infl, 1720, 1660, 1612, 1589, 1558, and 1510 cm^{-1}, *m/e* 372 (M^+, 13%), 341 (M — OMe, 16) 307(24), 306(100), 288(25), 273(20), 208(30), 194(16), 193(80), 181(15), 180(78), 179(37), 175(19), 167(20), 165(30), 162(16), 152(21), 151(26), 149(41), 148(23), 147(80), 145(22), 140(22), 135(24), 134(22), 133(26), 131(21), 124(18), 123(25), 122(26), 121(41), 120(20), 119(38), 118(25), 111(18), 109(40), 108(50), 107(60), 106(25), and 105(60) (other peaks <15%).

Reduction of the Benzylmethoxyquinoxalinone (9).—(i) This compound (1·0 g) was hydrogenated as for the methyl analogue (7) and gave *trimethyl 6-benzyl-3,4,4a,5,6,11-hexahydro-5-oxopyridazino*[2,3-a]*quinoxaline-2,3,4-tricarboxylate* (13), rods (0·4 g) (from methanol), m.p. 164—165° (Found: C, 61·8; H, 5·0; N, 9·2; OMe, 19·9. $C_{24}H_{23}N_3O_7$ requires C, 61·9; H, 5·0; N, 9·0; 3 × OMe, 20·0%), $\nu_{max.}$ 1728, 1695, 1665, 1602, and 1502 cm^{-1}.

Tetramethyl Benzo[c]*pyridazino*[1,2-a]*cinnoline-6,7,8,9-tetracarboxylate* (22).—Benzo[*c*]cinnoline (m.p. 154·5—155·5°; 2·9 g; prepared from 2,2′-dinitrobiphenyl [16] and purified by chromatography over alumina), dimethyl acetylenedicarboxylate (4·0 g), and methanol (60 ml) were refluxed for 15 h. The red precipitate on recrystallisation from methanol–chloroform (1 : 1 v/v) gave the cinnoline (22) (0·5 g) as red plates, m.p. 173—175° [lit.,[4] 178—180° (decomp.)] (Found: C, 61·6; H, 4·3; N, 5·7. Calc. for $C_{24}H_{20}N_2O_8$: C, 62·0; H, 4·3; N, 6·0%), $\nu_{max.}$ 1739, 1710, 1594, 1578, and 1439 cm^{-1}, *m/e* 465(6%), 464 (M^+, 22), 406(28), 405 (M — CO_2Me, 100), 229(11), 178(13), and 177(10), *m** 354 (464→405).

3,8-Dimethylbenzo[c]*cinnoline.*— 4,4′-Dimethyl-2,2′-dinitrobiphenyl [17] (4·5 g) was reduced with lithium aluminium hydride by the method [16] used for 2,2′-dinitrobiphenyl. The crude product was chromatographed on alumina; elution with benzene gave the cinnoline (2·81 g, 82%), needles (from methanol), m.p. 185—187° (lit.,[18] for a sample from a different synthesis, 184—185°) (Found: C, 80·8; H, 5·8; N, 13·6. Calc. for $C_{14}H_{12}N_2$: C, 80·8; H, 5·8; N, 13·5%), *m/e* 209(17%), 208 (M^+, 100), 180 (M^+ — 28, 23), 179(37), 178(23), and 165(37), *m** 156(208→180).

Tetramethyl 3,12-Dimethylbenzo[c]*pyridazine*[1,2-a] *cinnoline-6,7,8,9-tetracarboxylate* (23).—3,8-Dimethylbenzo[*c*] cinnoline (1·0 g) and dimethyl acetylenedicarboxylate (5·0 g) were mixed at room temperature. Next day the dark red product was triturated with methanol (5 ml) and the solid recrystallised from methanol–chloroform (1 : 1 v/v) to give the *adduct* (23) as red plates (0·82 g), m.p. 166·5—168° (Found: C, 63·0; H, 5·0; N, 5·9; OMe, 25·3. $C_{26}H_{24}N_2O_8$ requires C, 63·4; H, 4·9; N, 5·7; 4 × OMe, 25·2%), $\nu_{max.}$ 1738, 1718infl, 1710, 1600, 1509, and 1488 cm^{-1}, *m/e* 493(32%), 492 (M^+, 100), 434(13), 433 (M — CO_2Me, 42), 257(12), 256(10), 206(12), and 190(16).

Compound (23) (0·4 g) in ethyl acetate (300 ml) was hydrogenated (3—4 atmos) over 5% palladium–charcoal for 15 h at room temperature. Filtration and evaporation gave a yellow oil which was chromatographed on alumina (60 ml). Elution with benzene gave *tetramethyl 6,9-dihydro-3,12-di-methylbenzo*[c]*pyridazino*[a]1,2-a]*cinnoline-6,7,8,9-tetracarboxylate* (26), pale yellow parallelepipeds (0·1 g) [from methanol–

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chloroform (10 : 1 v/v)], m.p. 215—217° (decomp.) (Found: C, 63·1; H, 5·4; N, 5·9; OMe, 24·8. $C_{26}H_{26}N_2O_8$ requires C, 63·2; H, 5·3; N, 5·7; 4 × OMe, 25·1%), $\nu_{max.}$ 1763, 1747infl, 1743, 1710, 1581, 1562, and 1516 cm^{-1}, *m/e* 495(31%), 494 (M^+, 100), 436(29), 435 ($M - CO_2Me$, 100), 375(11), 317(25), 227(14), 209(21), and 208(13), *m** 383(494→435).

Reaction of Benzo[c]*cinnolines with Diethyl Acetylenedicarboxylate in Ethanol.*—(i) Benzo[*c*]cinnoline (0·20 g), spectroscopically pure ethanol (10 ml), and the ester (0·60 g) were left at room temperature for 3 days, and then in a refrigerator for 5 days. The red precipitate crystallised from ethanol giving *tetraethyl* 6(*or* 7)-*ethoxy*-6,7-*dihydrobenzo*[c]*pyridazino*[1,2-a]*cinnoline*-6,7,8,9-*tetracarboxylate* (27) (0·15 g) as orange-red plates, m.p. 117—119° (Found: C, 64·0; H, 6·1; N, 5·5; OEt, 39·2. $C_{30}H_{34}N_2O_9$ requires C, 63·6; H, 6·0; N, 5·0; 5 × OEt, 39·7%), $\nu_{max.}$ 1756, 1745, 1697, 1608, 1598, and 1588 cm^{-1}, *m/e* 566 (M^+, 5%), 494(5), 493(17), 436(31), 435(100), 263(10), 180(15), and 152(19).

(ii) 3,8-Dimethylbenzo[*c*]cinnoline similarly gave the corresponding *adduct* (28), hexagonal orange plates (from ethanol) (0·22 g), m.p. 130—132° (Found: C, 64·5; H, 6·6; N, 4·8; OEt, 37·8. $C_{32}H_{38}N_2O_9$ requires C, 64·6; H, 6·4; N, 4·7; 5 × OEt, 37·9%), $\nu_{max.}$ 1743infl, 1740infl, 1736, 1687, 1590, and 1580 cm^{-1}, *m/e* 594 (M^+, 12%), 521 ($M - CO_2Et$, 21), 464(33), 463(100), 312(14), and 208(18), *m** 457(594→521).

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