Addition Reactions of Heterocyclic Compounds. Part LII.[1] Further Adducts from Substituted 2-Methylquinolines and Dimethyl Acetylenedicarboxylate

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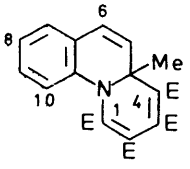
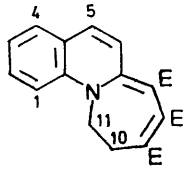
The ' dark red ' adducts from 2-methylquinolines and dimethyl acetylenedicarboxylate have been resolved into two types and identified as hexamethyl 6,7,7a,8-tetrahydrobenzo[*f*]cyclopenta[*a*]quinolizine-6,7,7a,8,9,10-hexacarboxylates [*e.g.* (12)], which are readily converted into tetramethyl 5-(2-quinolyl)cyclopenta-2,4-diene-1,2,3,4-tetracarboxylates. Other products from these reactions were also identified from their n.m.r., mass, and u.v. spectra, and included benzo[*c*]quinolizine-, azepino[1,2-*a*]quinoline-, and 2-propenylquinoline-carboxylic esters; 2-(trismethoxycarbonylphenyl)quinolines were also obtained from 2,8-dimethyl- and 2,4,6,8-tetramethyl-quinoline. The formation of these products is discussed.

2-METHYLQUINOLINE reacts[2] with dimethyl acetylenedicarboxylate in acetonitrile to give the 4a-methyl-4a*H*-benzo[*c*]quinolizine (1), the azepine (6), and small amounts of ' dark red ' and ' blue ' adducts. Two types of ' dark red ' adduct have now been isolated from 2-methylquinoline and some of its methyl derivatives, although others[3] give no trace of this sort of compound, and the structures of these substances, and of other compounds isolated from these reactions, are the subject of the present paper. The blue adducts are currently under investigation; an *X*-ray crystallographic structure determination is in progress.





(1)
(2) 10-Me
(3) 6,8,10-Me_3
(4) 8-Me
(5) 6,8-Me_2

(6) 10-E
(7) 1-Me-10-E
(8) 11-E
(9) 3-Me-10-E
(10) 3-Me-10-E (E = CO_2Et)
(11) 3,5-Me_2-10-E

E = CO_2Me in all formulae unless stated otherwise

2,6- and 2,8-Dimethyl-, 2,4,6-trimethyl-, and 2,4,6,8-tetramethyl-quinolines, with dimethyl and diethyl acetylenedicarboxylates in acetonitrile, gave the benzo[*c*]quinolizines (2)—(5), the azepines (7), (9)—(11), which were identified by comparison of their spectra[4] with those of numerous analogues,[2,3] and the 1 : 1 molar adducts (29)—(31), the spectra of which were similar to that[2] of (28). No other adducts were obtained from 2,6-dimethyl- and 2,4,6-trimethyl-quinolines, but additional compounds have been obtained from the other quinolines and these will be discussed.

If acetonitrile is employed as solvent for the reactions of 2-methyl- and 2,8-dimethyl-quinoline with dimethyl acetylenedicarboxylate, mixtures are formed. It was found almost impossible to separate the two types of red 1 : 3 molar adduct from each other, and from the azepines [(6) and (7) respectively], by chromatography over alumina. However, when methanol was used as reaction solvent, the red and blue adducts were the only isolable products. For both these quinolines the ' first ' red adducts precipitated first from the reaction mixtures in a fairly pure condition, although the ' second ' red adducts could not be resolved from their isomers. Complete separation of the corresponding red adducts from 2,6,8-trimethylquinoline was achieved chromatographically.

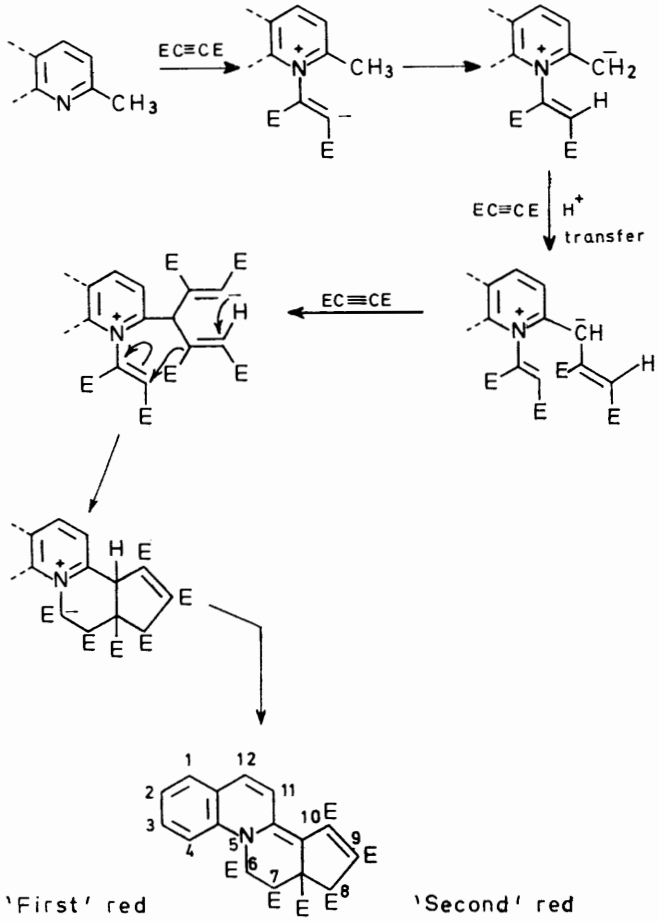
The ' first ' and ' second ' red adducts from the alkylquinolines are thought to be geometrical isomers of the benzo[*f*]cyclopenta[*a*]quinolizines (12)—(14). The n.m.r. spectra of the red adducts in deuteriochloroform showed that although the 2-methyl groups of the original quinoline had disappeared the remaining protons were present at their original positions; in trifluoroacetic acid reversible protonation occurred to give quinolinium cations with a low-field doublet assigned to the 12-proton. The remainder of the structure of the red adducts must therefore be attached to the 1- and 2-positions of the quinoline system. The doublets (*J ca.* 10 Hz) at about τ 3·4 and 2·9 are assigned to the 12- and 11-protons, the latter being deshielded by the 10-methoxycarbonyl group in a similar way to the 6-hydrogen atom of compounds (6)—(11).

The spectra of the ' first ' red adducts (12a)—(14a) possess one-proton singlets at τ *ca.* 4·5, assigned to the 8-protons, and doublets at *ca.* 5·1 and 6·1 (6-H and 7-H, respectively); the corresponding resonances for the ' second ' red adducts appear at τ *ca.* 4·9, 5·3, and 5·7. The ' first ' red adducts (12a)—(14a) show a fairly high-field ester resonance, assigned to the methoxycarbonyl group at position 6 which in one of its configurations could be shielded by the benzenoid ring; this type of shielding affects the 11-ester group of compound (8).[2]

In trifluoroacetic acid solution cations [*e.g.* (16)] are

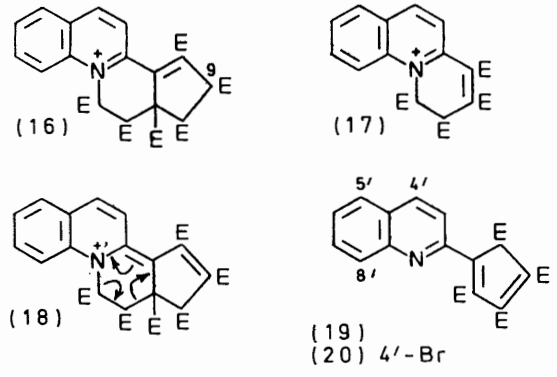
[1] Part XLI, R. M. Acheson, N. D. Wright, and P. A. Tasker, *J.C.S. Perkin I*, 1972, 2918.
[2] R. M. Acheson, J. M. F. Gagan, and D. R. Harrison, *J. Chem. Soc.* (*C*), 1968, 362.
[3] R. M. Acheson and D. F. Nisbet, *J. Chem. Soc.* (*C*), 1971, 3291.
[4] D. F. Nisbet, D.Phil. Thesis, Oxford University, 1971, Science Catalogue No. M.S. D.Phil., d. 5307. Photocopies may be obtained without reference to the author on payment of the library's standard fees for this work.

formed. No one-proton singlets now appear between τ 2·5 and 5·5 and the signals due to the 8-proton and the



SCHEME 1

added 9-proton cannot be observed clearly as they are obscured by the ester methyl resonances. The 6-



protons, adjacent to the cationic centre in the protonated 'first' red adducts, show a downfield shift of *ca.* 0·5 p.p.m. from their positions in deuteriochloroform solution. A smaller shift (*ca.* 0·3 p.p.m.), which is difficult to observe accurately because of the ester resonances, is shown by the higher field 7-protons. The 'second' red adduct (12b) shows a similar phenomenon, but the 7-proton signal is clearly below the ester region. However, for (13b) and (14b), where a 4-methyl group is present, the 6- and 7-protons appear as an apparent singlet at τ 5 and a relatively high field ester group, absent in (12b), is present. The presence of a 4-methyl group must affect the orientation of the 6-methoxycarbonyl group, changing it from that preferred in (12b) and thus causing the spectral changes. Otherwise the less likely explanations either that the 7-proton signal must move further downfield than that of the 6-proton when the molecule is protonated, or that the initial assignments for deuteriochloroform must be reversed, are necessary.

The u.v. spectra of all the red adducts in methanol are similar, particularly in the long-wavelength regions, and on acidification all change owing to the formation of yellow cations [*e.g.* (16)], showing conjugation (Table 2) similar to that [5] of the quinolizinium ion (17).

The base peaks of the mass spectra of the pure red adducts all occur at M — 144, corresponding to loss of the elements of dimethyl fumarate; the important peaks appearing in the mass spectrum of dimethyl fumarate at *m/e* 114, 113, 85, and 59 are also observed. Loss of this fragment is readily accounted for by the electrocyclic process indicated in the ion-radical structure (18) to give the corresponding cation [*cf.* structure (19)]. Loss of one ester group also occurs from the molecular ion; loss of the 7a-ester group would give a vinylquinolinium cation.

The 'first' red adduct (12a) with bromine in boiling glacial acetic acid gave a yellow monobromo-derivative, assigned the quinoline structure (20), and dimethyl fumarate. The single proton of the cyclopentadienyl ring could by [1,5] thermal shifts move to any position in the ring [*e.g.* (23)], but the most conjugated structure shown is preferred on grounds of stability and colour. The u.v. spectrum of this bromoquinoline was almost unchanged on acidification. In the n.m.r. spectrum deshielding of the 5-proton by the *peri*-bromine atom is apparent.[6] The cyclopentadiene ring proton appears in the aromatic region.

Debromination of compound (20) gave the quinoline (19), which was also obtained by treating the 'first' red adduct (12a) with zinc in acetic acid. The n.m.r. spectrum in deuteriochloroform shows that an aromatic proton is no longer deshielded, while in trifluoroacetic acid the 3'- and 4'-protons appear as doublets in the positions expected for a quinolinium salt; the cyclopentadiene ring proton signal for both compounds (19) and (20) appears at τ 2·43 in this solvent.

[5] R. M. Acheson, N. J. Earl, P. Higham, R. E. Richards, G. A. Taylor, and J. M. Vernon, *Proc. Chem. Soc.*, 1960, 281.

[6] *Cf.* R. A. Heacock, O. Hutzinger, B. D. Scott, J. W. Daly, and B. Witkop, *J. Amer. Chem. Soc.*, 1963, **85**, 1825; L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy,' 2nd edn., Pergamon, London, 1969, p. 206.

TABLE 1

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

Compound	Frequency (MHz)		CO_2Me
(12a)	60	ArH(4), 2·7—3·1m; 12-H, 3·45d; 11-H, 2·99d; $J_{11,12}$ 10·4; 6-H, 5·02d; 7-H, 6·10d; $J_{6,7}$ 9·3; 8-H, 4·41	6·08, 6·23, 6·35, 6·37, 6·37, 6·71
(12a) [a,b]	60	4-H, 2·19d; [c] $J_{3,4}$ 8·7; ArH(3), 11-H, 1·43—2·0m; 12-H, 0·80d; $J_{11,12}$ 9·6; 6-H, 4·54d; $J_{6,7}$ 8·8; 7,8,9-H, 5·7—6·2 [d]	5·83, 6·02, 6·10, 6·10, 6·19, 6·63
(12b)	60	ArH(4), 2·6—3·1m; 12-H, 3·46d; 11-H, 2·89d; $J_{11,12}$ 10·4; 6-H 5·32d; 7-H, 5·89d; $J_{6,7}$ 8·7; 8-H, 4·81	6·12, 6·24, 6·31, 6·33, 6·38, 6·40
(12b) [a]	60	ArH(4), 11-H, 1·2—2·0m; 12-H, 0·81d; $J_{11,12}$ 8·8; 6-H, 4·74d; 7-H, 5·59d; $J_{6,7}$ 7·7; 8,9-H, 5·8—6·3 [d]	5·86, 5·91, 6·01—6·26 (12)
(13a)	60	4-Me, 7·88; ArH(3), 2·7—3·2m; 12-H, 3·46d; 11-H, 2·99d; $J_{11,12}$ 10·0; 6-H, 5·12d; 7-H, 6·20d; $J_{6,7}$ 8·4; 8-H, 4·51	6·11, 6·19, 6·31, 6·40, 6·40, 6·68
(13a) [a]	60	4-Me, 7·31; ArH(3), 11-H, 1·6—2·1m; 12-H, 0·89d; $J_{11,12}$ 8·4; 6-H, 4·56d; $J_{6,7}$ 8·0; 7,8,9-H, 5·8—6·5 [d]	5·9—6·3 (15), 6·43
(13b) [e]	60	4-Me, 7·88; ArH(3), 11-H, 2·7—3·2m; 12-H, 3·41d; $J_{11,12}$ 10·5; 6-H, 5·47d; 7-H, 5·84d; $J_{6,7}$ 10; 8-H, 4·95	6·1—6·5 (18)
(13b) [a]	60	6,7-H, 4·98 [e,f]	
(14a)	60	ArH(2), 3·10, 3·13; ArMe, 7·81, 7·91; 12-H, 3·46d; 11-H, 3·03d; $J_{11,12}$ 10·0; 6-H, 5·13d; 7-H, 6·20d; $J_{6,7}$ 8·5; 8-H, 4·55	6·10, 6·18, 6·31, 6·39, 6·43, 6·67
(14a) [a]	60	ArH(2), 7-H, 1·5—2·1m; ArMe(6), 7·37; 12-H, 0·98d; $J_{11,12}$ 8·7; 6-H, 4·58d; $J_{6,7}$ 7·3; 7,8,9-H, 5·8—6·5 [d]	5·9—6·3 (15), 6·47
(14b)	100	ArH(2), 3·08; ArMe, 7·78, 8·03; 12-H, 3·36d; 11-H, 2·95d; $J_{11,12}$ 10·0; 6-H, 5·26d; 7-H, 5·61d; $J_{6,7}$ 12·0; 8-H, 4·95	6·10, 6·30, 6·30, 6·39, 6·39, 6·52
(14b) [a]	60	ArH(2), 1·98—2·15; ArMe, 7·36, 7·41; 12-H, 1·01d; 11-H, 1·86d; $J_{11,12}$ 9·3; 6,7-H, 4·98; [f] 8,9-H, 5·9—6·5 [d]	5·89, 6·13, 6·13, 6·13, 6·23, 6·48
(15)	60	ArH, 2·41 (1), 2·6—3·3m (4); 12-maleate H, 3·63; [c] 12-CH_2, 6·1—6·4; [d] 6-H, 5·32d; 7-H, 5·90d; $J_{6,7}$ 9·0; 8-H, 4·78	6·18—6·42 (24)
(15) [a]	60	ArH(5), 1·1—2·0m; 12-maleate H, 2·78; 12-CH_2, 5·8—6·35; [d] 6-H, 4·74d; 7-H, 5·58d; $J_{6,7}$ 8; 8,9-H, 5·8—6·35 [d]	5·9—6·35 (24)
(19)	60	ArH(6), C*H*E, 2·15—3·1m	5·96, 6·25, 6·31, 6·49
(19) [a]	60	3′-H, 2·04d; 4′-H, 0·86d; $J_{3',4'}$ 8·9; 5′,6′,7′-H, 1·53—1·9m; 8′-H, 2·91br; C*H*E, 2·43	6·00, 6·00, 6·00, 6·23
(20)	60	ArH(4), C*H*E, 2·15—2·9m; 5′-H, 1·92m	5·95, 6·24, 6·27, 6·43
(20) [a]	60	3′,6′,7′-H, 1·72br; 5′-H, 1·1—1·5br,m; 8′-H, 2·98br; C*H*E, 2·43	5·98, 5·98, 5·98, 6·19
(24)	60	ArH(6) and C*H*E, 2·2—3·05m; N:N·CH_2, 4·45d, 4·74d, J 2·7, [h] and 5·02d, 5·32d, J 8·0 [h]	5·98, 6·19, [g] 6·34, 6·97
(25)	60	4-H, 3·76d; [c] $J_{3,4}$ 8·0; 1,2,3-H, 2·9—3·55m; 6(?)-H, 5·29d, J 8·8; aliphatic H, 5·9—7·14m (4) [d] and 7·31br (4)	6·30—6·38 (15), 6·73
(26)	60	4-H, 3·81d; [c] $J_{3,4}$ 7·6; 1,2,3-H, 3·0—3·6m; aliphatic H (11), 5·7—7·95m [d]	6·32—6·40 (15), 6·92
(27)	60	4-Me, 7·90; 1,2,3-H, 3·1—3·4m; aliphatic H (11), 5·6—8·1m [d]	6·33—6·40 (15), 7·03
(33)	60	ArH(3), 2·41, 2·47, 2·62br; ArMe, 7·30, 7·34, 7·50; 5′-H, 2·16; maleate H, 4·74	6·07, 6·07, 6·20, 6·40, 6·59
(34)	60	ArH(3), 5′-H, 2·42—2·7m; ArMe, 7·36, 7·36, 7·52; C*H*E·CH_2E, 4·81t; CHE·C*H*$_2$E, 7·18d; J 6·0	6·15, 6·17, 6·33, 6·52, 6·67
(35)	60	ArH(3), 5′-H, 2·4—2·72m; ArMe, 7·28, 7·34, 7·50	6·13, 6·13, 6·28
(36)	60	3-H, 2·92; [c] 4-Me, 7·78; 5,6,7,8-H(6), 7·0—9·0m; [d] 6,8-Me_2, 8·58d (J 6·7) and 8·88d (J 5·3); 5′-H, 2·56	6·15, 6·15, 6·27
(37)	60	3,5′-H, 2·53, 2·73; [d] 4-Me, 7·78; 5,6,7,8-H (6), 6·9—9·0m; [d] 6,8-Me, 8·68d (J 6·4) and 8·91d (J 5·0); 6′-OMe, 6·44	6·13, 6·19, 6·19
(38)	100	ArH(4), 5′-H, 2·2—2·53m; 4-H, 1·71d; $J_{3,4}$ 8·6; 8-Me, 7·17	6·05, 6·05, 6·20
(38a)	60	ArH(5), 1·7—2·01; 4-H, 0·80d; $J_{3,4}$ 8·6; 8-Me, 7·06	5·85, 5·85, 6·20
(39)	60	ArH(4), 5′-H, 2·3—2·7m; 4-H, 1·90d; $J_{3,4}$ 8·0; 8-Me, 7·30; 6′-OMe, 6·67	6·12, 6·17, 6·17
(40) [i]	100	1-Me, 7·38; ArH(3), 2·8—2·95m; 5-H, 3·08d; [j] 6-H, 2·07d; [j] $J_{5,6}$ 10·0; 10-H_B, 5·60m; [k] 11-H_c, 6·90m; [k] 11-H_A, 7·67t; $J_{10,11A}$ 10·2, $J_{11A,11B}$ −13·0; $J_{10,11B}$ 10·3	6·07, 6·27, 6·27, 6·31, 6·57, 6·62
(41)	100	2,4-H, 3·08, 3·15; 5-H, 3·17d; 6-H, 2·14d; $J_{5,6}$ 9·4; ArMe, 7·45, 7·71; C*H*$_2$·C*H*E, 5·68t, 6·92, [k] 7·7m; [d] J's 10—13	6·10, 6·29, 6·32, 6·35, 6·58, 6·61
(42)	60	2,4-H, 3·02br; 6-H, 2·29; [c] ArMe, 7·43, 7·68, 7·72; C*H*$_2$·C*H*E 5·73m, 6·94, [k] 7·7m; [d] J's 10—13	6·13, 6·30, 6·33, 6·33, 6·61, 6·61

[a] Solvent CF_3·CO_2H. [b] Identical spectrum in CF_3·CO_2D. [c] Broad, indicating further coupling. [d] Partly or largely obscured by other resonances. [e] Values obtained from spectrum of red adduct mixture. [f] Apparent singlet. [g] Shows splitting of *ca.* 0·9 Hz. [h] Two sets of doublets; complete pattern integrates for two protons. [i] The ABX system due to 10-H, 11-H_A, and 11-H_B was accurately simulated (worst agreement ±0·4 Hz) by our usual program,[2] using the parameters given. [j] These assignments could be reversed. [k] Four lines.

TABLE 2

U.v. spectra

Compd.	Solvent *	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$)
(12a)	M	228infl (1·60), 319 infl (0·39), 363 (0·98), 381 (1·31), 452infl (0·80), 477 (0·99), 507 (0·85), 541infl (0·42)
	MA	247 (2·48), 263 (1·66), 329 (1·21), 358 (1·45)
(12b) [a]	M	231 (0·88), 284 (0·42), 306infl (0·32), 323 (0·25), 349infl (0·42), 366 (0·92), 382 (1·26), 426infl (0·42), 456infl (0·77), 480 (0·99), 511 (0·87), 546infl (0·40)
	MA	252infl (0·65), 275 (1·00), 363 (0·89)
(13a	M	266 (0·94), 327infl (0·24), 366 (0·42), 383 (0·65), 448infl (0·58), 472 (0·75), 501 (0·69), 534 (0·35)
	MA	258 (1·15), 275infl (1·00), 281 (1·09), 288 (1·10), 331 infl (0·48), 368 (0·72)
(14a)	M	240 (1·51), 261 (1·49), 360infl (0·98), 384 (1·46), 451infl (1·10), 475 (1·53), 506 (1·50), 540 infl (0·81)
	MA	260 (1·49), 286infl (1·97), 292 (2·13), 339infl (0·71), 372 (1·44)
(14b)	M	240 (1·55), 285 (0·67), 318 (0·55), 332 (0·61), 368 (1·34), 384 (2·12), 453infl (1·29), 479 (2·02), 509 (2·14), 545 (1·11)
	MA	296 (2·49), 369infl (1·74), 375 (1·91)
(15)	M	234 (2·24), 323 (1·00), 368 (2·30), 384 (3·09), 502br (1·57)
	MA	280 (2·40), 367 (2·10)
(17) [b]	P	265 (1·93), 362 (1·64)
(19)	M [c]	245 (3·48), 343 (0·92)
(20)	M [c]	247 (3·42), 278infl (1·53), 285infl (1·31), 356 (0·96), 382 (0·54)
(24)	M [c]	228 (2·62), 247 (3·48), 337 (0·98), 352infl (0·75)
(25)	M	271 (1·47), 282 (1·57)
	P	240infl (0·62), 271 (0·74), 288 (0·92)
(26)	M [d]	259 (0·89), 299 (0·18)
(27) [e]	M [c]	219 (1·25), 264 (0·50), 297infl (0·12)
(33)	M	233 (4·49), 267infl (2·60), 317 (1·17)
	MA	252 (4·80), 328 (1·15)
(34)	M	241 (1·45), 265infl (0·93), 320 (0·47)
	MA	252 (2·02), 328 (0·47)
(35)	M	216 (4·35), 251 (4·39), 270infl (2·92), 324br (1·36)
	MA	213 (4·92), 252 (6·10), 328 (1·47)
	B	230 (3·76), 247infl (4·38), 256 (4·76), 302 (1·91), 343 (1·11)
(36) [a]	M	220 (0·70), 243infl (0·48), 323br (0·19)
	MA	220 (0·76), 250 (0·37), 290 (0·25), 318 (0·15)
	B	240 (0·47), 257 (0·42), 278 (0·29), 300 (0·29)
(37) [a]	M	221 (0·85), 246infl (0·40), 289 (0·26), 306 (0·19)
	MA	221 (0·85), 291 (0·30), 309 (0·15)
(38)	M	208 (4·20), 246 (3·78), 271infl (2·03), 325br (1·06)
	MA	208 (4·28), 249 (4·93), 325br (1·02)
	B	254 (4·50), 300 (1·49), 355 (0·71)
(39)	M	240 (3·68), 263infl (2·23), 319 (1·12)
	MA	248 (5·08), 323 (1·08)
(40)	M	233 (1·94), 256infl (1·37), 356 (0·69), 404 (0·71)
	P	232 (1·77), 253 (1·72), 361 (0·80), 400 (0·72)
(41)	M	238 (2·22), 259 (1·27), 339 (0·38), 362 (0·57), 407 (0·65)
	P	228infl (2·02), 254 (1·61), 358 (0·88), 374 (0·13), 413 (0·70)
(42)	M	236 (1·77), 256infl (1·33), 285infl (0·77), 350 (0·73), 409 (0·66)
	P	236 (1·73), 255 (1·48), 359 (0·82), 416 (0·77)

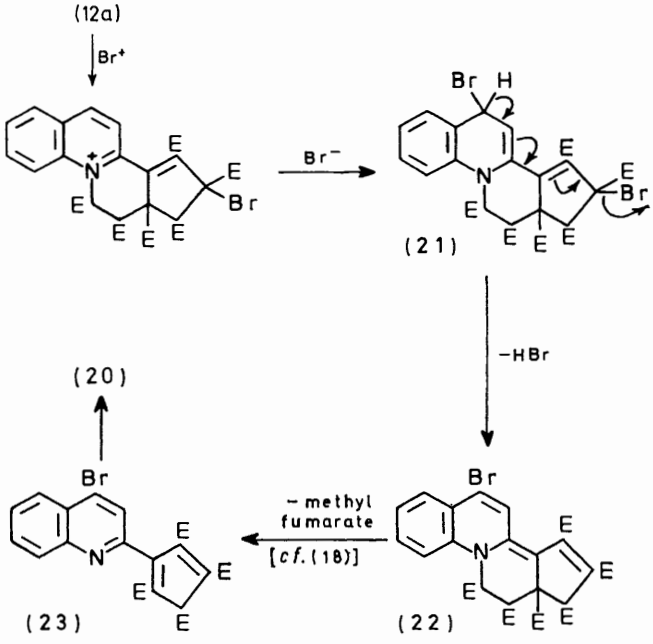
* M, MeOH; MA, MeOH acidified with 3 drops of 72% perchloric acid; P, MeOH–72% perchloric acid (2 : 1 v/v); B, MeOH–0·2N-NaOH (1 : 1 v/v).

[a] Optical densities in parentheses. [b] Ref. 4. [c] No change in P. [d] No change in MA. [e] Ref. 18.

The cracking pattern of the mass spectrum of the quinoline (19) is very similar to both that of (20), if the presence of bromine atoms is allowed for, and that of the parent red adduct (12a) in the range below *m/e* 425 $(M - 144)^+$. It thus appears that the red adducts readily eliminate dimethyl fumarate (or maleate) in the mass spectrometer and in the course of chemical reactions, and the losses may occur through concerted electrocyclic processes.

The introduction of a bromine atom to give compound (20) appears to be an independent substitution reaction, for which the course in Scheme 2 is suggested. The initial attack by bromonium ion is analogous to protonation; then nucleophilic attack by bromide ion at the 4-position of the quinoline nucleus occurs to give (21) which loses hydrogen bromide to give (22). The elimination of dimethyl fumarate *via* a reverse Diels-Alder reaction could then occur, but an alternative concerted loss of hydrogen bromide and the dimethyl fumarate could give the same product (23). Comparable reactions in the indole series, resulting in brominations in unexpected positions, have been described.[7]

The cyclopentadiene (19) with ethereal diazomethane gave a mixture of pyrazolines [*e.g.* (24)], the n.m.r.



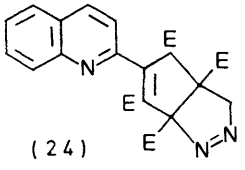
SCHEME 2

spectrum of which showed six aromatic protons, thereby excluding the possibility of pyrazoline formation across the 3- and 4-positions of the quinoline ring. Two sets of doublets in the τ 4·4—5·4 region (integral two protons) indicate that the substance, in spite of its sharp m.p., is a mixture of perhaps two of the possible pyrazolines; the substance gave an extremely weak molecular ion in its mass spectrum, the base peak corresponding to the

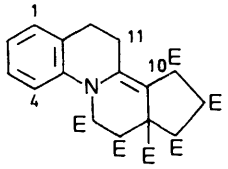
[7] W. I. Taylor, *Proc. Chem. Soc.*, 1962, 247.

loss of a molecule of nitrogen. An analogous reaction sequence in the stilbazole series has been reported.[8]

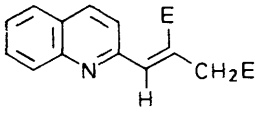
Hydrogenation of the 'first' red adduct (12a) in methanol over 10% palladised charcoal, or in acetic acid over Adams catalyst, gave a decahydro-compound (26); hydrogenation in acetic acid over 5% palladised charcoal gave a colourless octahydro-compound (25) different



(24)



(25)
(26) 10a,10b-dihydro
(27) 4-Me-10a,10b-dihydro



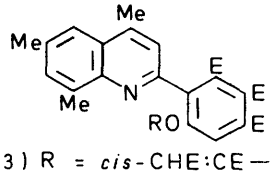
(28) 8-Br
(29) 8-Me
(30) 6,8-Me_2
(31) 4,6,8-Me_3
(32) 4,6,8-Me_3-2-(*trans*-CHE:CE—CH_2—)

from a yellow isomer, m.p. 148°, previously reported.[2] The mass spectra of these isomers (25) were almost identical and their u.v. spectra were similar, but the compound described earlier did not possess a high field ester group or aromatic proton; the compounds are therefore probably geometrical isomers. The u.v. spectra of the decahydro-compounds (26) and (27) are similar to that of *NN*-diethylaniline;[9] the u.v. spectrum of the octahydro-compound (25) shows less conjugation than those of ethyl β-anilinocrotonate[10] and dimethyl *N*-methylanilinomaleate.[11] The n.m.r. spectra of all the hydrogenated derivatives described here show high field ester methyl resonances, assigned as with the parent red adducts to the 6-ester methyl groups; those of (25) and (26) show only four aromatic protons, one of which appears as a high field doublet. This doublet, which is absent from the spectrum of the decahydro-compound (27), is assigned to the 4-proton; the stereochemistry of the molecules seemingly permits greater shielding of this proton than in the parent adduct. The dominant loss in the mass spectra of these derivatives is that of an ester group, but all show fragment ions at $M - 144$.

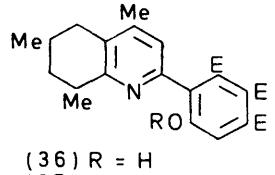
2,4-Dimethylquinoline with dimethyl acetylenedicarboxylate in methanol gave a low yield of a deep red 1 : 4 molar adduct, which appeared from its spectra to possess structure (15).

Scheme 1 is put forward to account for the formation of the red adducts. It follows earlier ideas[2,12] and there is ample opportunity for the formation of geometrical isomers. The easy formation of the red adducts in methanol, which is a good proton donor, is noteworthy.

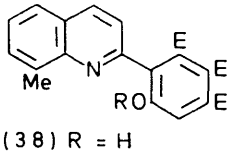
2,4,6,8-Tetramethylquinoline gave two more compounds on treatment with the ester. One of these is an isomer of (31) which shows markedly less conjugation than (31) itself; its spectra are compatible with structure (32) although transposition of the 2- and 4-substituents, as for (31) itself, is not excluded. The other compound is assigned structure (33); no analogues were obtained from any other 2-methylquinoline. The u.v. spectrum was essentially that of a quinoline and was only slightly changed by acid. The n.m.r. spectrum showed all the features required of this structure, and the vinyl proton signal appeared at τ 4·74, corresponding to that of dimethyl methoxymaleate (4·85), and not the methoxyfumarate (3·90).[13] Hydrogenation of compound (33) over palladium–charcoal gave the succinate (34), identified from its n.m.r. spectrum and the virtual identity of its u.v. spectrum with that of (33). Hydrogenation over Adams catalyst gave the phenol (35), the u.v. spectrum of which showed a bathochromic shift in alkaline solution; on another occasion the reduced phenol (36) was also formed. The phenol (35) gave no colouration with iron(III) chloride, excluding structures of the methyl salicylate type. No phenolic hydroxy-absorption was detected in its i.r. or n.m.r. spectra,



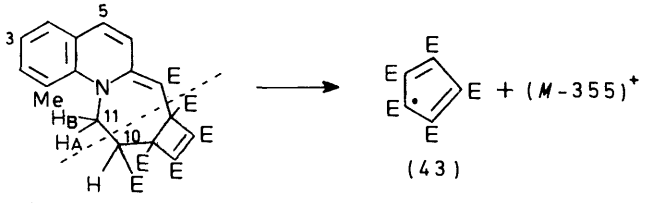
(33) R = *cis*-CHE:CE—
(34) R = CH_2E·CHE—
(35) R = H



(36) R = H
(37) R = Me



(38) R = H
(39) R = Me



(40)
(41) 3-Me
(42) 3,5-Me_2

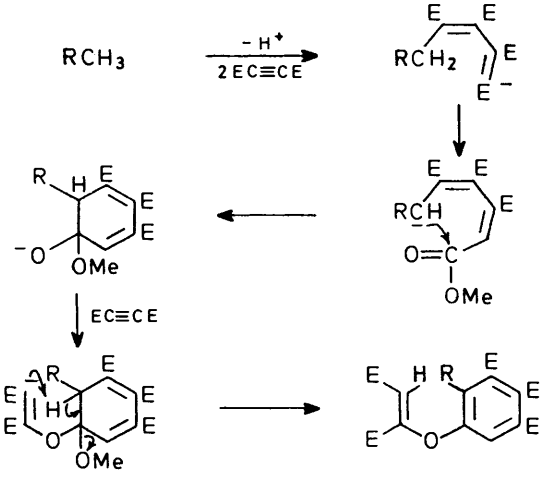
(43)

although a search was made down to τ −30. This is consistent with the presence of a strong hydrogen bond, associated possibly with line broadening in the n.m.r.

[8] R. M. Acheson and R. S. Feinberg, *J. Chem. Soc.* (*C*), 1968, 351.
[9] DMS UV Atlas of Organic Compounds, Butterworths and Verlag Chemie/Weinheim, vol. III, 1967.
[10] R. Huisgen and K. Herbig, *Annalen*, 1965, **688**, 98.
[11] R. Huisgen, K. Herbig, A. Seigl, and H. Hübner, *Chem. Ber.*, 1969, **99**, 2526.
[12] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.
[13] E. Winterfeld and H. Preuss, *Chem. Ber.*, 1966, **99**, 450.

spectrum due to the nitrogen atom. The n.m.r. spectrum of the second reduction product (36) showed clearly that the carbocyclic ring of the quinoline ring has been reduced. The phenolic proton could still not be detected but reaction with diazomethane gave the expected ether (37).

On one occasion only, the phenol (38) was isolated from the reaction of the acetylenic ester with 2,8-dimethylquinoline in tetrahydrofuran. Its n.m.r. spectrum, and that of the ether (39) formed with diazomethane, showed low field doublets characteristic of the 4-hydrogen atom of the quinoline system. Phenols of this type, and of type (33), can be formed as outlined in



SCHEME 3

Scheme 3, which has resemblances to other schemes used to account for the formation of benzene derivatives from acetylenic esters and other carbanions.[14,15]

The configuration shown for the vinyl proton of the ether (33) is expected in terms of this scheme, as the migration of the ring hydrogen atom to the carbanion can take place through a six-membered transition state leading to the observed *cis* arrangement of the ester groups.

Minor products from 2,8-dimethyl-, 2,6,8-trimethyl-, and 2,4,6,8-tetramethyl-quinoline and the acetylenic ester in acetonitrile are assigned structures (40)—(42) from the available spectral evidence. The n.m.r. spectra (Table 1) of compounds (40) and (41) show one-proton doublets at τ *ca.* 2·1 and 3·1, and (42) possesses a singlet at τ 2·3 showing that the 6-proton is strongly deshielded. This deshielding is consistent with the presence of a *peri*-ester group, as in the azepines (6)—(11). The aliphatic three-spin system for (40) has been accurately simulated and closely resembles that [2] for the ethyl ester analogue of (6) except for small differences in chemical shifts. The u.v. spectra show less conjugation than azepines such as (6), and in contrast do not appear to be protonated in methanol–perchloric acid. The most interesting feature of the mass spectra is the loss of a fragment of mass 355 from the molecular ion to give a very large peak, or the base peak. This fragment corresponds to the pentakismethoxycarbonylcyclopentadienyl radical (43), and could be formed as indicated. Cyclobutenecarboxylic esters have been obtained from enamines with dimethyl acetylenedicarboxylate.[1,16]

[14] R. M. Acheson and W. R. Tully, *J. Chem. Soc.* (*C*), 1968, 1623.

EXPERIMENTAL

The instruments and general procedures employed have been described.[1,3] Peaks $\leqslant$10% of the base peaks in the mass spectra are usually omitted, but full details are available.[4] Alumina (deactivated) chromatographic columns were prepared in benzene and eluted with benzene, benzene–chloroform mixtures, and finally chloroform, unless stated otherwise. Columns prepared in light petroleum (b.p. 60—80°) were eluted first with this solvent, containing increasing proportions of benzene, and then with pure benzene gradually changing to chloroform. The products from columns are described in their order of elution. The acetic acid used was glacial.

2-*Methylquinoline with Dimethyl Acetylenedicarboxylate in Methanol*.—The quinoline (20 ml) in dry methanol (20 ml) was added to the ester (52 ml) in dry methanol (230 ml) at 0°. The solution darkened rapidly and began to deposit crystals after 1 h. After 24 h at 0° and 48 h at room temperature the solid was collected, washed with methanol, and dissolved in chloroform (100 ml) by heating; the solution was chromatographed on alumina (1300 ml). Unchanged acetylene, dimethyl fumarate, a deep red tar, and a blue compound were successively obtained.

The red tar crystallised on trituration with methanol; recrystallisation from methanol–acetonitrile gave the '*first*' *red adduct* (*hexamethyl* 6,7,7a,8-*tetrahydrobenzo*[f]*cyclopenta*[a]*quinolizine*-6,7,7a,8,9,10-*hexacarboxylate*) (12a) as red prisms (2·0 g), m.p. 241° (lit.,[2] 236°) (Found: C, 59·3; H, 4·9; N, 2·6. Calc. for $C_{28}H_{27}NO_{12}$: C, 59·1; H, 4·8; N, 2·5%), $\nu_{max.}$ 1749, 1731, 1702, 1618, 1550, and 1535.

Chromatography of the combined filtrate and methanol washings from the original reaction gave a mixture of the 'first' (12a) and 'second' (12b) red adducts, the ratio (*ca.* 3 : 1 from n.m.r.) of which could not be appreciably altered by repeated crystallisation, and further blue adduct.

Reactions of the 'First' Red Adduct (12a).—(i) Bromine (0·8 ml) in acetic acid (5 ml) was added to the adduct (12a) (2·0 g) in boiling acetic acid, the mixture was refluxed for 5 min, and the solvent was removed *in vacuo*. The remaining acetic acid was removed by adding benzene and evaporating to dryness, several times, and the residue in chloroform was chromatographed on alumina (200 ml). A faint yellow band yielded a compound (5 mg), fine rods (from methanol), m.p. 208—211°, the mother liquors from which gave dimethyl fumarate (6 mg).

A pale yellow band gave *tetramethyl* 5-(4-*bromo*-2-*quinolyl*)*cyclopenta*-2,4-*diene*-1,2,3,4-*tetracarboxylate* (20), yellow rods (0·50 g) (from methanol), m.p. 186—188° (Found: C, 52·2; H, 3·8; Br, 15·5; N, 2·8. $C_{22}H_{18}BrNO_8$ requires C, 52·4; H, 3·6; Br, 15·8; N, 2·8%), $\nu_{max.}$ 1747, 1730, 1648w, 1611w, 1550w, and 1510 cm^{-1}.

A red band gave unchanged (12a) (0·1 g).

The recovered red adduct from the bromination of the

[15] V. Boekelheide and J. E. Notte, *J. Org. Chem.*, 1969, **34**, 4134.

[16] R. M. Acheson and N. D. Wright, *Chem. Comm.*, 1971, 1421.

TABLE 3

Mass spectra

Compd.	*m/e* (%) (peaks ⩽10% usually not recorded)
(12a)	569 (M^+, 4), 510 (3), 425 (100), 366 (16), 334 (12), 114 (5), 113 (30), 85 (16), 59 (26), *m** 457 (569 → 510), 315·5 (425 → 366), 304·5 (355 → 334)
(13a)	583 (M^+, 7·5), 568 (21), 524 (7), 439 (100), 380 (15), 348 (65), 320 (24), 316 (22·5), 288 (12), 202 (14), 114 (17·5), 113 (100), 85 (25), 59 (15), (other peaks <6%), *m** 483 (568 → 524), 328 (439 → 380), 319 (380 → 348)
(14a)	597 (M^+, 2), 582 (9), 538 (6), 453 (100), 394 (19), 362 (71), 334 (21), 330 (23), 302 (11), 272 (21), 218 (17), 217 (24), 216 (45), 215 (19), 202 (21), 113 (42), 85 (40), 59 (39), *m** 497 (582 → 538), 342 (453 → 394)
(14b)	597 (M^+, 7), 582 (18), 566 (4), 538 (11), 453 (100), 422 (6), 394 (9), 362 (40), 330 (11), 113 (32), 85 (3), 59 (7), *m** 567 (597 → 582), 497 (582 → 438), 393 (453 → 422), 342 (453 → 394), 301 (362 → 330)
(15)	725 (M^+, 4), 694 (5), 693 (4), 666 (5), 634 (4), 606 (6), 581 (79), 439 (19), 113 (100), 85 (63), 59 (39), *m** 663br (725 → 694, 693), 640 (694 → 666), 612·5 (725 → 666), 603·6 (666 → 634), 579·3 (634 → 606)
(19)	425 (M^+, 100), 366 (15), 334 (10), *m** 315·5 (425 → 366), 304·8 (366 → 334)
(20)	505 (M^+, 100), 503 (M^+, 100), 446 (18), 444 (16), 414 (11), 412 (10), 254 (10), *m** 343br (505 → 446, 503 → 444), 303br (446 → 414, 444 → 412)
(24)	467 (M^+, 0·2), 439 (100), 407 (9), 380 (29), 375 (6), 364 (19), 348 (39), 320 (11), 310 (15), 204 (24), 203 (11), 128 (11), 59 (26), *m** 377·5 (439 → 407), 345·4 (407 → 375), 329 (439 → 380), 319 (380 → 348)
(25)	573 (M^+, 35), 542 (1), 541 (1), 514 (35), 482 (9), 454 (13), 429 (28), 422 (19), 397 (25), 369 (93), 338 (67), 337 (99), 284 (28), 278 (25), 252 (18), 193 (11), 113 (58), 85 (12), 59 (100), *m** 461 (573 → 514), 511br (573 → 542, 541), 452 (514 → 482), 392 (454 → 422), 367 (429 → 397), 343·0 (397 → 369), 308 (369 → 337), 229 (337 → 278)
(26)	575 (M^+, 56), 544 (4), 516 (49), 484 (13), 431 (11), 302 (26), 286 (100), 280 (20), 278 (12), 254 (63), 242 (16), 196 (12), 168 (11), 131 (20), 130 (18), 113 (18), 105 (23), 85 (5), 59 (27), 55 (21), *m** 514 (575 → 544), 463 (575 → 516), 454 (516 → 484), 323 (575 → 431), 225·5 (286 → 254)
(36)	579 (M^+, 69), 564 (100), 549 (28), 548 (89), 547 (77), 520 (90), 461 (20), 460 (25), (other peaks <20%), *m** 467 (579 → 520)
(37)	581 (M^+, 66), 550 (25), 522 (100), 490 (27), 446 (26), 438 (21), 437 (78), 406 (68), 405 (43), 404 (22), 389 (20), 376 (14), 346 (20), 259 (12), 232 (12), 231 (11), 113 (62), 105 (12), 91 (19), 85 (36), 77 (17), 59 (47), 55 (28), *m** 469 (581 → 522), 460 (522 → 490), 329 (581 → 437)
(38)	437 (M^+, 100), 406 (29), 405 (27), 378 (2), *m** 375·5 (437 → 405), 327 (437 → 378)
(44)	583 (M^+, 30·5), 552 (11·5), 524 (100), 492 (21·5), 460 (16·5), 374 (13), 228 (81), 215 (17·5); *m** 498 (552 → 524), 471 (583 → 524), 462 (524 → 492), 430 (492 → 460), 405 (460 → 432), 89 (583 → 228)
(45)	597 (M^+, 16), 566 (6), 538 (40), 506 (9), 474 (7), 242 (100), 229 (14), 59 (8), *m** 511 (566 → 538), 485 (597 → 538), 476 (538 → 506), 440 (506 → 474), 420 (474 → 446), 98 (597 → 242)
(46)	611 (M^+, 12), 552 (39), 520 (5), 402 (7), 256 (100), 243 (30), *m** 498·6 (611 → 552), 490 (552 → 520), 372·5 (434 → 402), 107 (611 → 256)

3 : 1 mixture (5 g) of (12a) and (12b) proved, from n.m.r., to be mainly the 'second' red adduct, red needles (0·15 g) (from methanol), m.p. 230°.

The bromoquinoline (20) (0·4 g) in methanol (100 ml) was shaken under hydrogen (2 atm) for 5 h with 10% palladium–charcoal. Filtration and evaporation gave *tetramethyl 5-(2-quinolyl)cyclopenta-2,4-diene-1,2,3,4-tetracarboxylate* (19), yellow rods (0·18 g) (from methanol), m.p. 138—140° (Found: C, 62·1; H, 4·4; N, 3·1. $C_{22}H_{19}NO_8$ requires C, 62·1; H, 4·5; N, 3·3%), $\nu_{max.}$ ($CHCl_3$) 1721, 1638w, 1611w, 1559w and 1508 cm^{-1}. The quinolines (19) and (20) did not react with methyl iodide in refluxing acetonitrile.

(ii) Zinc dust was added in portions to the 'first' red adduct (12a) (1·9 g) in acetic acid (50 ml), and the mixture was stirred for 1 h and filtered. The filtrate was diluted with water (100 ml) and extracted with chloroform; the extracts were washed, dried, and evaporated. Acetic acid was removed from the residue by repeated extraction with benzene, and the involatile material in benzene was chromatographed on alumina (120 ml). A pale yellow band gave a solid (160 mg), recrystallised from methanol to give a mixture of yellow and colourless crystals. Some of the yellow crystals were picked out, and used to seed a solution of the mixture in methanol. The quinoline (19) (30 mg), m.p. 134—136°, identical (n.m.r., i.r., u.v., and mass spectra) with the analysed sample, was thus obtained.

Reduction of (12a) with sodium amalgam and methanol gave tar.

(iii) The adduct (12a) (0·5 g) in acetic acid (100 ml) was hydrogenated (5 atm) for 9 h over 5% palladium–charcoal (0·3 g). Filtration, evaporation, and repeated evaporation with methanol gave an oil which yielded *hexamethyl 6,7,7a,8,9,10,11,12-octahydrobenzo[f]cyclopenta[a]quinolizine-6,7,7a,8,9,10-hexacarboxylate* (25) (60 mg) as plates (from methanol), m.p. 60—63° (Found: C, 58·7; H, 5·6; N, 2·3. $C_{28}H_{31}NO_{12}$ requires C, 58·6; H, 5·5; N, 2·4%), $\nu_{max.}$ ($CHCl_3$) 1731br and 1602w cm^{-1}.

(iv) The adduct (12a) (0·5 g) was hydrogenated as in (iii) but over Adams catalyst (0·25 g) for 24 h, and gave the *decahydro-compound* (26) (0·12 g), as thick rods (from methanol–acetonitrile), m.p. 196—198° (Found: C, 58·6; H, 5·8; N, 2·5. $C_{28}H_{33}NO_{12}$ requires C, 58·4; H, 5·8; N, 2·4%), $\nu_{max.}$ 1730br, 1606, and 1580 cm^{-1}.

2,8-*Dimethylquinoline with Dimethyl Acetylenedicarboxylate.*—(i) The quinoline (20 g) in acetonitrile (50 ml) was added to the ester (46 ml) in acetonitrile (150 ml). The mixture was refluxed for 3 h and the acetonitrile was evaporated off. After 3 months the residual oil in benzene was chromatographed on alumina (1500 ml). The products were unchanged ester, a yellow band yielding *tetramethyl 4a,10-dimethyl-4aH-benzo[c]quinolizine-1,2,3,4-tetracarboxylate* (2) (1·0 g), yellow rods (from methanol), m.p. 98—100° (Found: C, 62·2; H, 5·5; N, 3·1. $C_{23}H_{23}NO_8$ requires C, 62·6; H, 5·3; N, 3·2%), $\nu_{max.}$ 1751, 1745, 1718, 1641, 1631, 1580, and 1552 cm^{-1}, an orange band yielding *tetramethyl 10,11-dihydro-1-methylazepino[1,2-a]quinoline-7,8,9,10-tetracarboxylate* (7) as yellow-orange rods (0·61 g) (from methanol), m.p. 158—159·5° (Found: C, 63·0; H, 5·3; N, 3·2. $C_{23}H_{23}NO_8$ requires C, 62·6; H, 5·3; N, 3·2%), $\nu_{max.}$ 1760, 1743, 1730, 1679, 1634, 1606w, and 1567 cm^{-1}, and a red band yielding a mixture (1·0 g) of the 'first' (13a) and 'second' (13b) red adducts in *ca.* 3 : 1 ratio (unchanged after repeated recrystallisation).

The column was run dry and extruded, and a dark blue band was extracted with chloroform–acetone to give a

blue adduct, deep blue prisms (0·29 g) (from methanol), m.p. 272—274° (turning green) (Found: C, 59·2; H, 4·8; N, 2·1. Calc. for $C_{34}H_{31}NO_{15}$: C, 58·9; H, 4·5; N, 2·0. Calc. for $C_{35}H_{33}NO_{15}$: C, 59·4; H, 4·7; N, 2·0%).

(ii) On another occasion chromatographing the product from 8·0 g of the quinoline on alumina (400 ml) prepared in petroleum gave: *dimethyl* 2-(8-*methyl*-2-*quinolylmethylene*)-*succinate* (29), needles (1·4 g) (from methanol), m.p. 107—107·5° (Found: C, 67·8; H, 5·7. $C_{17}H_{17}NO_4$ requires C, 68·2; H, 5·7%), $\nu_{max.}$ 1738 and 1700 cm^{-1}; and the quinolizine (2) (0·5 g). The remaining fractions were combined and rechromatographed on alumina (70 ml) made up in benzene. A pale red band gave a yellow 1 : 3 molar *adduct* (*hexamethyl* 7a,9a,10,11-*tetrahydro*-1-*methylcyclobut*[4,5]*azepino*[1,2-a]*quinoline*-7,7a,8,9,9a,10-*hexacarboxylate*) (40), yellow prisms, m.p. 186—189° (Found: C, 60·0; H, 5·0; N, 2·5. $C_{29}H_{29}NO_{12}$ requires C, 59·7; H, 5·0; N, 2·4%), $\nu_{max.}$ ($CHCl_3$) 1741, 1614w, 1573w, 1565w, and 1546w cm^{-1}, and a subsequent dark band gave a thick tar, which yielded 2-(6-*hydroxy*-2,3,4-*trismethoxycarbonylphenyl*)-8-*methylquinoline* (38), yellow needles (0·15 g) (from methanol), m.p. 173—175° (Found: C, 64·3; H, 4·9; N, 3·6; OMe, 22·6. $C_{22}H_{19}NO_7$ requires C, 64·5; H, 4·7; N, 3·4; 3OMe, 22·8%), $\nu_{max.}$ 1731, 1720, 1615w, 1597, 1590, and 1554w cm^{-1}. The corresponding *methyl ester* (39), obtained with ethereal diazomethane, needles (70% yield) (from methanol), had m.p. 168—171° (Found: C, 65·3; H, 5·1; N, 3·4. $C_{23}H_{21}NO_7$ requires C, 65·2; H, 5·0; N, 3·3%), $\nu_{max.}$ 1747, 1733, 1724, 1612w, 1600, 1590, and 1502 cm^{-1}.

(iii) The ester (19 g) and the quinoline (8·0 g) in dry [17] tetrahydrofuran (170 ml) were refluxed for 6 days; the solvent was then removed and the residue in chloroform was chromatographed on alumina (400 ml) prepared in petroleum. The ' first ' red adduct (13a) (0·25 g), the phenol (38) (0·19 g), and the propene (29) (0·4 g) were obtained.

(iv) (With J. M. F. Gagan [18]). The ester (20 ml), the quinoline (10 g), and benzene (200 ml) were refluxed for 3 h, the solvent was removed, and the residue after 6 weeks was chromatographed on alumina to give the ' first ' red adduct (4·2 g), and the blue adduct (0·3 g).

(v) The quinoline (19·2 g) and the ester (46 ml) in methanol (250 ml) were refluxed for 24 h. After 14 weeks the precipitate was collected and gave the ' *first* ' *red adduct* (13a) as prisms (5·5 g) (from methanol–acetonitrile), m.p. 237—238° (Found: C, 59·9; H, 5·1; N, 2·3. $C_{29}H_{29}NO_{12}$ requires C, 59·7; H, 5·0; N, 2·4%), $\nu_{max.}$ 1751, 1741, 1699, and 1632 cm^{-1}. The original filtrate contained (13a), (13b), and the blue adduct, according to t.l.c.

Reaction of the Quinoline (19) *with Diazomethane*.—The quinoline (19) (100 mg) in ether (100 ml) was treated with ethereal diazomethane, and after 10 h acetic acid was added to decompose unchanged diazomethane. Excess of acetic acid was removed by repeated addition and evaporation of methanol, the solution was filtered, and the residue gave *tetramethyl* 3,3a,4,6a-*tetrahydro*-5-(2-*quinolyl*)*cyclopentapyrazole*-3a,4,6,6a-*tetracarboxylate* (24) as pale yellow hexagonal plates (42 mg) (from methanol), m.p. 140—141° (decomp.) (Found: C, 59·1; H, 4·5; N, 8·7. $C_{23}H_{21}N_3O_8$ requires C, 59·1; H, 4·5; N, 9·0%), $\nu_{max.}$ ($CHCl_3$) 1720br, 1608w, 1558, 1547, and 1504 cm^{-1}.

The pyrazoline was heated at 150° in an oil-bath for 5 min; no more nitrogen was then evolved. The resulting melt was triturated with methanol, and the methanol was evaporated off, giving an oil, presumably the cyclopropane, which solidified. The mass spectrum was almost identical with that of the pyrazoline.

2,6,8-*Trimethylquinoline with Dimethyl Acetylenedicarboxylate in Acetonitrile*.—2,6,8-Trimethylquinoline (10 g) in acetonitrile (30 ml) was added to the ester (22 ml) in acetonitrile (120 ml). The mixture was refluxed for 6 days and left for 7 weeks at room temperature. The acetonitrile was evaporated off and the tarry residue in benzene–chloroform was chromatographed on alumina (700 ml) prepared in petroleum. A pale yellow band yielded *dimethyl* 2-(6,8-*dimethyl*-2-*quinolylmethylene*)*succinate* (30), plates (0·96 g) (from methanol), m.p. 107—108° (Found: C, 69·0; H, 6·3. $C_{18}H_{19}NO_4$ requires C, 69·0; H, 6·1%), $\nu_{max.}$ 1737, 1710br, 1642w, and 1618w cm^{-1}. The deep yellow band gave the 1 : 3 molar *yellow adduct* (41), parallelepipeds (100 mg) (from methanol–acetonitrile), m.p. 199·5—201° (Found: C, 60·9; H, 5·4; N, 2·3. $C_{30}H_{31}NO_{12}$ requires C, 60·3; H, 5·2; N, 2·3%), $\nu_{max.}$ 1736br, 1713, 1634w, 1600, 1567, and 1559 cm^{-1}. A red band gave the ' *first* ' *red adduct* (14a) obtained as deep crimson rods (0·78 g) (from methanol–acetonitrile), m.p. 224° (Found: C, 60·1; H, 5·3; N, 2·5. $C_{30}H_{31}NO_{12}$ requires C, 60·3; H, 5·2; N, 2·3%), $\nu_{max.}$ 1749, 1740, 1688, 1622, 1609, 1573w, and 1523 cm^{-1}. The mother liquor yielded more (0·16 g) of (41).

A thick, deep red band yielded the ' *second* ' *red adduct* (14b), obtained as bright red needles (80 mg) (from methanol–acetonitrile), m.p. 252—252·5° (Found: C, 60·2; H, 5·2; N, 2·3. $C_{30}H_{31}NO_{12}$ requires C, 60·3; H, 5·2; N, 2·3%), $\nu_{max.}$ 1743, 1739, 1692, 1630, and 1521 cm^{-1}. A blue band yielded the dark blue adduct (30 mg), tiny rods, m.p. 272—276° (Found: C, 59·7; H, 4·7; N, 2·1. Calc. for $C_{35}H_{33}NO_{15}$: C, 59·4; H, 4·7; N, 2·0. Calc. for $C_{36}H_{35}NO_{15}$: C, 59·9; H, 4·9; N, 1·9%).

2,4-*Dimethylquinoline with Dimethyl Acetylenedicarboxylate in Methanol*.—2,4-Dimethylquinoline (8·2 ml) in methanol (20 ml) was added slowly to the ester (19 ml) in methanol (150 ml), and the mixture was kept at 0° for 24 h. After 3 months at room temperature, the precipitated tar was washed with methanol, dissolved in benzene–chloroform, and chromatographed on alumina (570 ml prepared in benzene). A pale yellow band yielded dimethyl fumarate (100 mg). A deep red band gave a tar which yielded the *red adduct* (15) (90 mg), deep red matted rods (from methanol, m.p. 143—147° (Found: C, 58·1; H, 5·0; N, 2·0. $C_{35}H_{35}NO_{16}$ requires C, 57·9; H, 4·9; N, 1·9%), $\nu_{max.}$ 1729br, 1610w, 1540, and 1518 cm^{-1}.

2,4,6,8-*Tetramethylquinoline with Dimethyl Acetylenedicarboxylate*.—2,4,6,8-Tetramethylquinoline (71 g), the ester (126 ml), and acetonitrile (600 ml) were refluxed for 1 week. After a further week at room temperature the acetonitrile was evaporated off, and the tarry residue largely solidified over the next 2 months. The solid was triturated and washed with methanol, and the washings and filtrate were combined and evaporated; the residue (A) was retained.

The solid mixture of thick, brown crystals and fine, yellow ones was readily separated, since the yellow, but not the brown crystals, adhered to the damp filter paper. The yellow crystals gave the *adduct* (42), thick prisms (2·4 g) (from methanol–acetonitrile), m.p. 216—216·5° (Found: C, 61·3; H, 5·4; N, 2·3. $C_{31}H_{33}NO_{12}$ requires C, 60·9; H, 5·4; N, 2·3%), $\nu_{max.}$ 1744, 1731, 1713, 1603, and 1568 cm^{-1}.

[17] L. F. Fieser and M. Fieser, ' Reagents for Organic Syntheses,' Wiley, New York, 1967, p. 1140.

[18] J. M. F. Gagan, D. Phil. Thesis, Oxford University, 1965.

The brown crystals on recrystallisation from acetonitrile gave *dimethyl* 2-(4,6,8-*trimethyl*-2-*quinolylmethylene*)*succinate* (31), pale brown needles (13·8 g) (from acetonitrile), m.p. 136·5—137·5° (Found: C, 69·8; H, 6·5; N, 4·3. $C_{19}H_{21}NO_4$ requires C, 69·7; H, 6·5; N, 4·3%), $\nu_{max.}$ 1740, 1712, 1640, 1620, and 1597 cm^{-1}.

The residue (A) in benzene–chloroform was chromatographed on alumina (3600 ml). A yellow band yielded the *quinoline* (33) as flocculent, fine white rods (2·7 g) (from methanol–acetonitrile), m.p. 194·5—196·5° (Found: C, 62·4; H, 5·2; N, 2·6. $C_{30}H_{29}NO_{11}$ requires C, 62·2; H, 5·0; N, 2·4%), $\nu_{max.}$ 1741, 1722, 1645, and 1597w cm^{-1}. A deep orange band yielded a mixture which on fractional crystallisation from methanol–acetonitrile gave compound (42) (1·3 g) and then a further crop of the white adduct (33) (3·0 g).

The mother liquors from the foregoing crystallisations were combined and evaporated, and the resulting tar in benzene was chromatographed on alumina (4 l) prepared in 1 : 1 petroleum (b.p. 40—60°)–benzene. The first eluate contained 2,4,6,8-tetramethylquinoline (4·5 g). A pale yellow band yielded compound (31) (0·9 g), m.p. 136—137°. The mother liquor was evaporated and the residue after two recrystallisations from hexane gave the 1 : 1 *adduct* (32) (140 mg) as white needles, m.p. 100—101° (Found: C, 69·9; H, 6·2; N, 4·4. $C_{19}H_{21}NO_4$ requires C, 69·7; H, 6·5; N, 4·3%), $\nu_{max.}$ 1717, 1631w, 1619w, 1595w, 1567w, and 1561w cm^{-1}.

A yellow band yielded more compound (31) (0·85 g). A deep yellow band gave *tetramethyl* 4a,6,8,10-*tetramethyl*-4aH-*benzo*[c]*quinolizine*-1,2,3,4-*tetracarboxylate* (3), pale yellow prisms (17 g) (from methanol), m.p. 151—153° (Found: C, 64·0; H, 5·6; N, 3·1. $C_{25}H_{27}NO_8$ requires C, 64·0; H, 5·8; N, 3·0%), $\nu_{max.}$ 1740, 1709, 1623, 1601w, and 1539 cm^{-1}. A deep red band gave compound (42) (70 mg).

Compounds (31), (32), and (33) did not form methiodides with methyl iodide in boiling acetonitrile.

Reduction of the Ether (33).—(i) The ether (33) (0·5 g) in glacial acetic acid (150 ml) was shaken under hydrogen (5 atm) with 10% palladium–charcoal (0·3 g) for 48 h. After filtration and evaporation, residual acetic acid was removed by repeated addition and evaporation of methanol. The residue gave the *quinoline* (34) as brilliant white needles (0·34 g) [from methanol–acetonitrile (charcoal)], m.p. 160—162° (Found: C, 61·8; H, 5·4; N, 2·4. $C_{30}H_{31}NO_{11}$ requires C, 62·0; H, 5·4; N, 2·4%), $\nu_{max.}$ 1752, 1737, 1721, 1615w, 1590, 1574w, and 1558w cm^{-1}.

(ii) The ether (33) (0·3 g) was hydrogenated as in (i) but with Adams catalyst (0·15 g) for 24 h. The product was the *phenol* (35), pale yellow rods (50 mg) (from methanol), m.p. 152—156° (Found: C, 66·1; H, 5·3; N, 3·3. $C_{24}H_{23}NO_7$ requires C, 65·9; H, 5·3; N, 3·2%), $\nu_{max.}$ ($CHCl_3$) 1730, 1600w, 1583w, 1554w, and 1540w cm^{-1}.

(iii) Repetition of experiment (ii) with a newly-opened batch of Adams catalyst gave the phenol (36), brown rods (70 mg) (from methanol), m.p. 156—160°, $\nu_{max.}$ 1738, 1721, and 1581 cm^{-1}. With ethereal diazomethane the methoxy-compound (37) (24 mg) was obtained as prisms (from methanol), m.p. 141—142°, $\nu_{max.}$ ($CHCl_3$) 1736, 1728, and 1590br cm^{-1}.

2,6-*Dimethylquinoline with Dimethyl Acetylenedicarboxylate* (with J. A. L. B. Caterer).—The quinoline (10 g) was added slowly to a stirred solution of the ester (20 ml) in acetonitrile (50 ml) at 0°, and after 4 days at room temperature the solvent was removed *in vacuo* and the residue chromatographed. The products were *tetramethyl* 4a,8-*dimethyl*-4aH-*benzo*[c]*quinolizine*-1,2,3,4-*tetracarboxylate* (4), yellow needles (2·6 g) (from methanol), m.p. 149° (Found: C, 62·5; H, 5·5; N, 3·4. $C_{23}H_{23}NO_8$ requires C, 62·6; H, 5·3; N, 3·2%), $\nu_{max.}$ 1740, 1618, and 1538 cm^{-1}; *tetramethyl* 10,11-*dihydro*-3-*methylazepino*[1,2-a]*quinoline*-7,8,9,10-*tetracarboxylate* (9), orange crystals (1·3 g) (from acetonitrile), m.p. 260·5° (Found: C, 62·5; H, 5·3; N, 3·1. $C_{23}H_{23}NO_8$ requires C, 62·6; H, 5·3; N, 3·2%), $\nu_{max.}$ 1757, 1742, 1669, 1613, and 1553 cm^{-1}, and traces of dark red and blue adducts.

A similar experiment with diethyl acetylenedicarboxylate gave as sole crystalline product *tetraethyl* 10,11-*dihydro*-3-*methylazepino*[1,2-a]*quinoline*-7,8,9,10-*tetracarboxylate* (10), orange crystals (1·0 g) (from acetonitrile), m.p. 145·5° (Found: C, 65·4; H, 6·0; N, 3·2. $C_{27}H_{31}NO_8$ requires C, 65·2; H, 6·3; N, 2·8%).

2,4,6-*Trimethylquinoline with Dimethyl Acetylenedicarboxylate* (with J. A. L. B. Caterer).—The quinoline (10 g) was treated as in the previous experiment and gave *tetramethyl* 4a,6,8-*trimethyl*-4aH-*benzo*[c]*quinolizine*-1,2,3,4-*tetracarboxylate* (5), yellow prisms (2·7 g) (from methanol), m.p. 154—155° (Found: C, 63·7; H, 5·6; N, 3·2. $C_{24}H_{25}NO_8$ requires C, 63·3; H, 5·5; N, 3·1%) and *tetramethyl* 10,11-*dihydro*-3,5-*dimethylazepino*[1,2-a]*quinoline*-7,8,9,10-*tetracarboxylate* (11), orange crystals (from acetonitrile), m.p. 277—278° (Found: C, 63·7; H, 5·5; N, 3·4. $C_{24}H_{25}NO_8$ requires C, 63·3; H, 5·5; N, 3·1%). No blue or red compounds were detected.

We thank the S.R.C. for a Studentship (to D. F. N.), Mrs. E. E. Richards for the 100 MHz n.m.r. spectra, and Mr. N. M. Sinclair for the mass spectra.

[2/2180 *Received*, 18*th September*, 1972]