Addition Reactions of Heterocyclic Compounds. Part XLVIII.[1] Reactions of Indoles with Dimethyl Acetylenedicarboxylate in the Presence and Absence of Solvents

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Treatment of indole with dimethyl acetylenedicarboxylate alone gave a mixture from which the major components tetramethyl carbazole-1,2,3,4-tetracarboxylate, tetramethyl 9-(*cis*-1,2-dimethoxycarbonylvinyl)-1,2-dihydrocarbazole-1,2,3,4-tetracarboxylate, trimethyl 5,6-dihydro-6-oxophenanthridine-7,8,9-tricarboxylate and dimethyl 2,3-dihydro-2-(indol-3-yl)[1]benzazepine-3,4-dicarboxylate, and ten other indole derivatives, were isolated by chromatography and identified from their spectra. Fewer products were obtained when benzene or toluene was used as solvent; the main products in methanol and in acetic acid were, respectively, dimethyl indol-3-ylfumarate and dimethyl 2,2-di(indol-3-yl)succinate. Reactions involving 1- and 2-methylindole and diethyl acetylenedicarboxylate were also investigated.

THE formation of benzazepines from indoles and dimethyl acetylenedicarboxylate in acetonitrile was discussed, along with earlier work in this area in Part XLVII.[1] Treatment of indole with the acetylenic ester alone at room temperature for 74 days is reported [2] to give tetramethyl carbazole-1,2,3,4-tetracarboxylate (16), identified by conversion into carbazole, and three other compounds which were not identified. Dimethyl indol-3-ylfumarate (4) was the main product when the reaction medium was boiling methanol,[3] while the di-indolylsuccinate (7) was obtained from the appropriate molar ratio of reactants, or from the fumarate (4) and more indole, in acetic acid.[3] We have methylated the succinate by use of sodium hydride with

[1] Part XLVII, R. M. Acheson, J. N. Bridson, and T. S. Cameron, *J.C.S. Perkin I*, 1972, 968; see also R. M. Acheson and J. N. Bridson, *Chem. Comm.*, 1971, 1225; F. Fried, J. B. Taylor, and R. Westwood, *ibid.*, 1226.

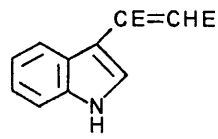
[2] W. E. Noland, W. C. Kuryla, and R. F. Lange, *J. Amer. Chem. Soc.*, 1959, **81**, 6010.

[3] D. C. Johnson, Ph.D. Thesis, University of Minnesota, 1961; see also *Diss. Abs.*, 1962, **23**, 834.

methyl iodide to give the *NN'*-dimethyl compound (8); the n.m.r. spectra of these compounds support their structures.

A preliminary re-examination of the product from the room temperature indole–dimethyl acetylenedicarboxylate reaction showed it to contain many more products

E = CO_2Me in all formulae unless otherwise stated

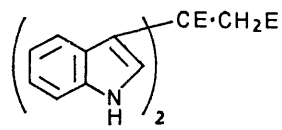


cis *trans*

(1) (4)

(2) 1-Me (5) 1-Me

(3) 2-Me (6) 2-Me



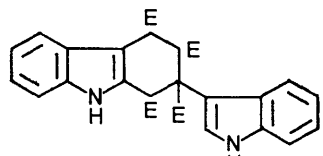
(7)

(8) 1,1'-Me_2

(9) E = CO_2Et

than previously noted. Large-scale reactions were carried out and the products were separated by chromatography on alumina; chromatographic methods and n.m.r. spectrometry do not appear to have been employed by earlier workers. Fourteen compounds were in fact resolved and identified, although complete separation of some of the minor products could not be guaranteed on every occasion. The reaction was also examined with benzene, toluene, acetic acid, and methanol as solvents, and parallel investigations were made with 1-methylindole, which gave fewer products.

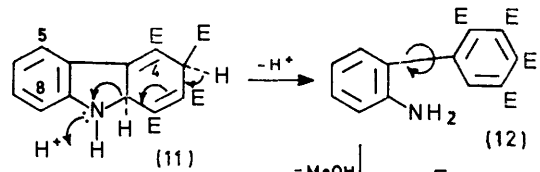
It is thought that all the products from indole are obtained *via* the indol-3-yl-maleate (1) or -fumarate (4), the formation of which has been considered earlier.[1] A small amount of the fumarate was isolated, and also the succinate (7), which has been obtained from the fumarate by treatment with a second molar proportion of indole.[3] We have confirmed that treatment of the fumarate with methanol and a trace of acid yields a dimer (10),[4] the



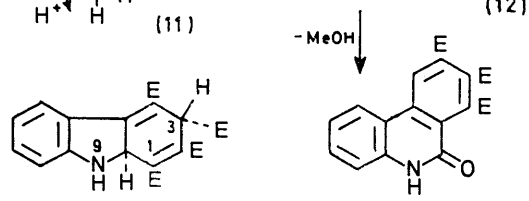
(10)

structure of which is in accord with its n.m.r. spectrum, but this dimer was not found in our complex mixture.

Diels–Alder additions of the maleate (1) and fumarate (4) to dimethyl acetylenedicarboxylate are expected to yield compounds (11) and (13), respectively. Dehydrogenation of each of these would give tetramethyl carbazole-1,2,3,4-tetracarboxylate (16), which is the main product of our reaction. Although Campbell[4] observed that the fumarate (4) and maleate (1), on treatment with dimethyl acetylenedicarboxylate under identical conditions, gave different product distributions, the differing stereochemistry of the expected intermediates, (11) and (13), respectively, was not pointed out. The fumarate gave mainly the carbazole (16), and this could be formed by the loss of the 3-hydrogen atom of the intermediate (13) as a proton while the *trans*-9a-hydrogen atom is transferred as a hydride ion; hydride transfers from carbon atoms bonded to nitrogen are known in the Sommelet reaction.[5] The alternative loss of a hydride ion from position 3 and a proton from position 9a has been suggested.[6] The maleate (1) in methanol gave mainly the phenanthridone (14); this reaction could take place *via* intermediate (11), essentially



(11) (12)

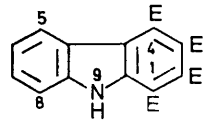


(13) (14)

(15) E = CO_2Et

as outlined,[7] but with a *trans*-elimination involving the 3-hydrogen atom and the protonated amino-group leading to the biphenyl (12), which could then cyclise to the phenanthridone (14).

The acceptor of the hydride ion could in part be dimethyl acetylenedicarboxylate, as both dimethyl fumarate and 9-methylcarbazole (17) are formed from 1-methylindole and the acetylenic ester.



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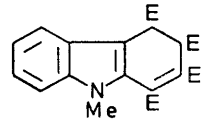


(22)

(17) 9-Me

(18) 9-CE=CHE (*cis*)

(19) E = CO_2Et

(20) 6-Br-9-Me

(21) 6-Br-9-CE=CHE (*cis*)

Compounds corresponding to structures (11) and (13), or *N*-substituted analogues, have not been found by us or earlier investigators. However, a compound allocated [3] structure (22) has been obtained from 1-methyl-

[4] R. W. Campbell, Ph.D. Thesis, University of Minnesota, 1961; see also *Diss. Abs.*, 1962, **22**, 3851.

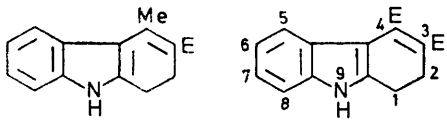
[5] S. J. Angyal, D. R. Penman, and G. P. Warwick, *J. Chem. Soc.*, 1953, 1742.

[6] W. E. Noland and K. Sivasankaran, quoted by R. A. Johnson in *Diss. Abs.*, 1966, **26**, 5719.

[7] R. A. Johnson, Ph.D. Thesis, University of Minnesota, 1965; see also *Diss. Abs.*, 1966, **26**, 5719.

indole, and we have isolated the same substance from reactions performed in acetonitrile or in the absence of solvent. We prefer the isomeric formulation (25) for this compound and have also isolated the *cis*-isomer (24), which yields the *trans*-compound (25) on treatment with base. The vicinal nature of the hydrogen atoms at positions 1 and 2 is shown by the n.m.r. spectra of the compounds, and their stereochemistry is deduced from the assumption that the more stable isomer will have the ester groups *trans*. The u.v. spectra of compounds (24) and (25) are very similar to those of the maleate (1) and compounds such as (23),[8] except that the long wavelength bands show a bathochromic shift. The long wavelength maximum for the *cis*-compound (24) is at shorter wavelength than that of the *trans*-isomer (25). We have found no spectral models for structure (22) in the literature, but feel that as the enamine system and the maleate grouping are cross-conjugated the longest wavelength absorption band for this type of structure should appear at markedly shorter wavelength than that for the indol-3-ylmaleate (1).

Adducts corresponding to (24) and (25) but lacking the *N*-methyl groups have not been isolated from reactions

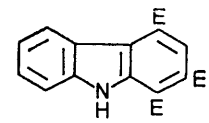


(23) (24) *cis*-1,2-E_2-9-Me
(25) *trans*-1,2-E_2-9-Me
(26) *trans*-1,2-E_2-9-(*cis*-1,2-E_2-vinyl)
(27) *cis*-1,2-E_2-9-(*cis*-1,2-E_2-vinyl)
(28) 1;2-E_2-9-(*trans*-1,2-E_2-vinyl)

involving indole, but the *N*-substituted analogues (26) and (27) have now been obtained from the fumarate (4) and the ester in the absence of solvent, and compound (27) yields (26) with base or on alumina. The stereochemical assignment has been made on this evidence and is consistent with the u.v. data for the compounds. Compound (28) has also been isolated. The vinyl proton of the 9-substituent in the carbazoles (18) and (21), and also that of the dihydrocarbazoles (26) and (27), appears at τ 3·31—3·44 in the n.m.r. spectra; that of the isomeric dihydrocarbazole (28) shows at τ 2·55. The maleate structure has been assigned to the group of compounds with the higher field resonance (diethyl maleate τ 3·72; fumarate τ 3·17).[9]

The adducts (24) and (25) could well be formed *via* tautomerisation of the *N*-methylated analogues of (11) and (13), and various reaction sequences are possible. As aromatic amines readily add to activated acetylenes to give vinylamines,[10] and the nitrogen atom of indole is only weakly nucleophilic, it is thought that compounds (26)—(28) are formed from (11) and/or (13) by *N*-vinylation followed by tautomerisation, rather than the reverse sequence.

The major product from treatment of the fumarate (5) with dimethyl acetylenedicarboxylate in toluene is stated [3] to be the triester (30). Indole and the acetylene in the absence of solvent, or in benzene [when a trace of compound (31) is also formed], give the analogue (29), which is converted into the *N*-methyl compound (30)



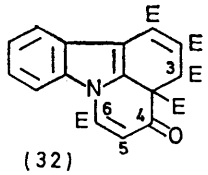
(29)
(30) 9-Me
(31) 9-CE=CHE (*cis*)

by sodium hydride and methyl iodide. A scheme [6] for the formation of the carbazole (30) from the *N*-methyl derivative of the carbazole (11) or (13) requires the abstraction of a proton from the 9a-position and elimination of the 3-ester group. This would be formally similar to the conversion of methyl 1,4-dihydro-2-methoxy-1-methylbenzoate by phenyl-lithium into 2-methoxytoluene.[11] The conclusion that the 3-ester group was lost depended mainly on a series of u.v. spectral comparisons and neglects consideration of any effect of the steric crowding due to the ester groups on the conjugated system. The 1- and 4-positions must be occupied by ester groups, as the compound lacking the 1-ester group is known [3] and the presence of a 4-ester group is shown by its deshielding of the *peri*-hydrogen atom. The possibility that the ester group has been lost from position 2 of compounds (16)—(18) cannot therefore be excluded, and although evidence from pyrolyses at 250° cannot be regarded as conclusive, the pyrolysis of the *trans*-compound (25), does give a trace of a triester, identical with that assigned structure (30), along with the expected dehydrogenation product (17). This is more easily understood on the basis of the loss of the 2-ester group.

Three compounds, (18), (32), and (33), have been obtained from indole and the acetylenic ester in benzene or without solvent. Compound (18) could come from the aromatisation of (26) or (27), and loss of methanol from the dihydrocarbazole (28) would give (32) and subsequent aromatisation the tetraester (33). Compounds (18) and (32) on alkaline hydrolysis and distillation from soda-lime gave carbazole. Compound (33) shows one low field aromatic signal (τ 1·59) assigned to the 8-proton. If the positions of the carbonyl group,

[8] T. Sakan, S. Matsubara, H. Takagi, Y. Tokunaga, and T. Miwa, *Tetrahedron Letters*, 1968, 4925.
[9] Varian High Resolution N.M.R. Catalog, Varian Associates, 1963, spectra nos. 212 and 213.
[10] R. Huisgen, K. Herbig, A. Siegl, and A. Huber, *Chem. Ber.*, 1966, **99**, 2526.
[11] R. M. Magid, C. R. Grayson, and D. R. Cowsar, *Tetrahedron Letters*, 1968, **47**, 4877.

double bond, and ester group had been reversed then the 8-proton signal would have been expected to appear at lower field.[12] Hydrogenation of compounds (28) and (33) over Raney nickel gives the dihydro-derivatives (34) and (35), which have almost identical u.v. spectra. The differences between the u.v. spectra of compound (28) and its cyclisation product (32) may be associated with the coplanarity of the *N*-substituent with the indole system in (32) but not in (28), because of interference by the 1-ester group; the u.v. spectra of compounds (18) and (33) differ for similar reasons.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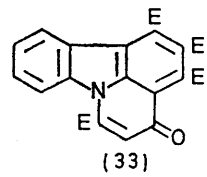
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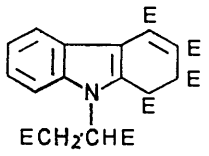
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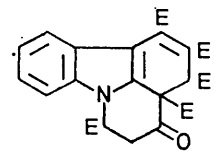
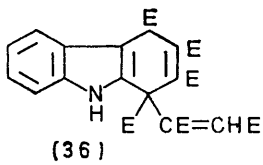
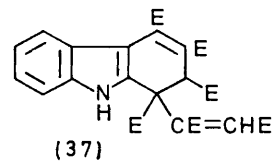

(35)

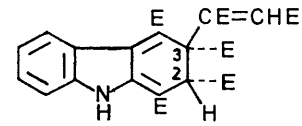
Four 1 : 3 molar adducts, which showed N–H absorption in the i.r. and which on hydrolysis and decarboxylation gave carbazole, have been isolated from


(36)

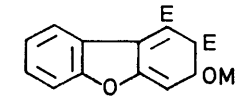

(37)

the neat indole–acetylenic ester reaction. The provisional structures proposed for compounds (36) and (37) are based mainly on the similarity of their u.v. spectra to those of simple indoles and the 1,2-dihydrocarbazoles shown in Table 2, respectively, and the conversion of (36) into the more conjugated (37) by acid. Unlike the other products from the indole reaction, the other two adducts provisionally given structures (38) and (39) are appreciably soluble in aqueous acid, and their similar u.v. spectra show corresponding reversible hypsochromic shifts on acidification. The most suitable model compound found in the literature[13] for u.v. comparisons is (40), and although at lower wavelengths its spectrum has the same form as those of (38) and (39), it lacks the N–C=C–C=O chromophore responsible for the long wavelength absorption of these compounds.

The fact that compound (39), but not (38), eliminates the 3-vinyl group and the 2-hydrogen atom in hot decalin with palladium–charcoal to give the carbazole (16) suggests that these substituents are *trans*. Compound (39) also absorbs at slightly shorter wavelengths in the u.v.; this is now expected as the greater steric interaction between the *cis* vinyl and ester substituents in


(38)

(39) 2,3-E *trans*

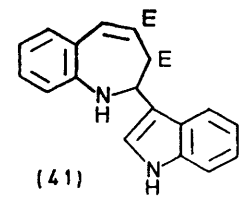

(40)

(39) will cause a greater distortion from planarity in the partially reduced ring. This could be associated with the upfield shift of the n.m.r. signal of one aromatic proton of (39), as compared with (38) where the 4-ester group is presumed to deshield the 5-hydrogen atom. None of the adducts derived from indole and three molecules of dimethyl acetylenedicarboxylate is formed *via* the carbazole (16); this compound is inert to the acetylene even when heated at 100° for 8 days.

The bromination of the dihydrocarbazoles (25)[3] and (26) caused aromatisation and substitution, presumably[14] at position 6, yielding compounds (20) and (21). Compound (20) was also obtained[3] from the bromination of the carbazole (17), and hydrogenation of compound (21) removed the bromine to give the carbazole (18).

In contrast to the dimethyl ester, diethyl acetylenedicarboxylate reacted with indole to give a mixture from which only three compounds, (9), (15), and (19), could be isolated, and these were identified by spectral comparison with the analogous methyl esters.

The benzazepines (41) and (43) are described in ref. 1. The u.v. spectrum of compound (42) resembles those of (24) and (25), indicating a similar chromophore. The n.m.r. spectra show similar resonances, attributed to the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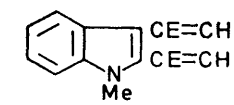
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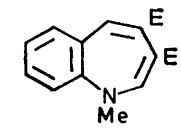
(43)

9-methyl groups, but compound (42) shows two singlets at low field assigned to the vinyl protons.

EXPERIMENTAL

The instruments, general procedures, and preparation of most reagents have been described.[1] Hydrocarbon solvents

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

[13] J. A. Elix and W. J. Davidson, *Tetrahedron Letters*, 1968, 4589.

[14] N. P. Buu-Hoi and R. Royer, *Rec. Trav. chim.*, 1947, **66**, 533.

were dried over sodium, and the methanol was distilled from magnesium methoxide. Light petroleum refers to the b.p. 40—60° fraction.

TABLE 1

N.m.r. spectra (100 MHz; τ values; J in Hz) with internal tetramethylsilane as reference

Compd.	Solvent	Proton resonance	Ester methyls
(1)	$CDCl_3$	ArH_4, 2·75—3·00(m); 1-H 1·39;[a] 2-H, 2·69(d); vinyl H, 3·10; $J_{1,2}$ 2·5	6·21, 6·40
(7)	$(CD_3)_2SO$	ArH_{10}, 2·4—3·5(m); 1,1′-H_2, −1·0;[b] CH_2, 6·33	6·42, 6·58
(7; 5,5′-Br_2)	$(CD_3)_2SO$	1-H, −0·9;[b] 2-H, 2·37;[c] 4-H, 2·93(d); 6-H, 2·89(q); 7-H, 2·65(d); $J_{4,6}$ 1·8; $J_{6,7}$ 9·0; CH_2, 6·38[d]	6·38, 6·54
(8)	$(CD_3)_2SO$	ArH_{10}, 2·4—3·5(m); 1,1′-Me_2 6·23; CH_2, 6·37	6·44, 6·56
(10)	$(CD_3)_2SO$	ArH_8, 2·3—3·2(m); 1-H, 5·02; 3-H, 6·56(d);[d,e] 4-H, 6·85(d);[e] 9-H, −1·02;[b,f] 1′-H, −1·29;[b,f] $J_{3,4}$ 10·5	6·33, 6·41[c] (6H) 6·63
(14)	$(CD_3)_2SO$	ArH_3, 2·2—2·8(m); 1-H, 1·50(d); 5-H, −2·00; 10-H, 1·04	6·05, 6·15, 6·15
(16)	Me_2SO[g]	ArH_4, 1·9—2·7(m); 9-H −2·00	5·96, 6·00, 6·14, 6·16
(18)	$CDCl_3$[g]	ArH_3, 2·43—2·79; 5-H, 1·90—2·11(m); vinyl H 3·41	5·95, 6·11, 6·11, 6·14, 6·14, 6·37
(21)	$CDCl_3$	5-H, 1·82(d); 7-H, 2·33(q); 8-H, 2·76(d); vinyl H, 3·31; $J_{5,7}$ 1·9; $J_{7,8}$ 8·8	5·89, 6·0—6·1 (12H), 6·30
(24)	$CDCl_3$	ArH_4, 2·4—3·0(m); 1-H, 5·34(d);[e] 2-H, 5·51(d);[e] 9-Me, 6·52;[f] $J_{1,2}$ 1·3	6·12, 6·20, 6·24, 6·37[f]
(25)	$CDCl_3$	ArH_4, 2·4—3·0(m); 1-H, 5·20(d);[e] 2-H, 5·29(d);[e] 9-Me, 6·42;[f] $J_{1,2}$ 1·3	6·02, 6·19, 6·22, 6·37[f]
(26)	$CDCl_3$	ArH_4, 2·42—2·84(m); 1-H, 5·24(d);[e] 2-H, 5·32(d);[e] vinyl H, 3·40; $J_{1,2}$ 1·5	5·99, 6·11, 6·15 (6H), 6·18, 6·35
(27)	$CDCl_3$	ArH_4, 2·4—2·9(m); 1-H, 5·28(d);[e] 2-H, 5·31(d);[e] vinyl H, 3·44; $J_{1,2}$ 2·2	5·96, 6·18 (9H), 6·34, 6·45
(28)	$CDCl_3$	ArH_4, 2·4—3·0(m); 1-H, 5·33;[e,h] 2-H, 5·61;[e,h] vinyl H, 2·56	5·97, 6·17, 6·35, 6·46
(29)	$CDCl_3$	ArH_3, 2·3—2·8(m); 3-H, 2·00; 5-H, 1·08(d); 9-H, 0·09;[b] $J_{5,6}$ 8·5	5·92, 5·98, 6·01
(32)	$CDCl_3$	ArH_3, 2·3—2·9(m); 5-H, 2·94; 3-H, 4·53; 8-H, 1·59(d)[c]	6·04, 6·10, 6·17, 6·50, 6·58
(38)	$CDCl_3$	ArH_3, 2·65—3·12(m); 3-H, 4·73; vinyl H, 3·30; 5-H, 2·12(d); 9-H, −0·12	6·17, 6·25 (9H), 6·31, 6·57
(39)	$CDCl_3$[g]	ArH_4, 2·55—3·19(m); 3-H, 5·45; vinyl H, 3·94; 9-H, −0·64	6·15, 6·21 (9H), 6·36, 6·57
(42)	$CDCl_3$	ArH_4, 2·3—3·0(m); vinyl H_2, 2·64 and 3·02; 1-Me, 6·53	6·15, 6·21, 6·38, 6·43

[a] Broad. [b] Broad peak, disappears on addition of D_2O. [c] Shows signs of further splitting. [d] Partially obscured by OMe absorptions. [e,f] These assignments may be the reverse. [g] At 60 MHz. [h] Signs of splitting.

T.l.c. was performed on either (i) 20 × 20 cm glass plates prepared by slurrying Kieselgel PF_{254} (Merck) (30 g) with distilled water (45 ml) for 1 min, and then with a further 25 ml for 45 s, and spreading this mixture to a depth of 30 μm (apparatus supplied by Shandon); layers were allowed to set, and then dried for 40 min at 105°; or (ii) precoated plastic sheets [Polygram SIL N-HR/UV_{254} (Machery–Nagel and Co., Düren)]. One example of the chromatography is given, for the case of indole with dimethyl acetylenedicarboxylate.

Full details of the chromatographic separations, i.r. spectra, and the mass spectra of compounds (15), (16), (21), (29), (31), (33), and (36)—(39) are available.[15]

Indole and Dimethyl Acetylenedicarboxylate Alone.—The reactants (50 and 120 g respectively) were warmed on a steam-bath until the mixture was homogeneous, and kept at room temperature in the dark for 112 days in a flask fitted with a calcium chloride guard tube. Benzene (200 ml) was added, and the solution (in three batches) was chromatographed on alumina (3 × 1800 g) prepared in benzene–petroleum (1 : 1). The column was eluted with solvents of increasing polarity.

TABLE 2

U.v. spectra (methanol)

Compd.	$\lambda_{max.}$/nm (10^{-4} ε)
(1)	219 (2·45), 274 (0·99), 340 (1·86)
(2)	227 (2·45), 275 (0·91), 347 (1·86)
(5)	219 (2·88), 277 (0·76), 284infl (0·65), 362 (0·50)
(7; 5,5′-Br_2)	224 (7·30), 282 (1·10), 290 (1·10), 300infl (0·73)
(9)	219 (7·16), 282 (1·50), 291 (1·30)
(15)	232 (3·63), 242infl (3·61), 275 (1·52), 320infl (0·62), 351 (0·78)
(18)	221 (3·70), 257 (2·98), 275 (4·16), 305infl (1·00), 355 (0·92)
(19)	222 (3·42), 264infl (2·68), 284 (4·42), 365 (0·60), 376 (0·60), 367 (0·51)
(21)	227 (3·57), 259 (2·82), 281 (3·08), 310infl (1·08), 355infl (0·39)
(23)	234 (2·40), 285 (0·91), 354 (1·35)
(24)	230 (2·36), 275 (1·10), 298infl (0·43), 365 (1·41)
(25)	229 (2·02), 276 (1·18), 301infl (0·42), 376 (1·27)
(26)	226 (3·00), 264 (1·64), 275infl (0·96), 364 (1·24)
(27)	214 (3·04), 226infl (2·14), 254 (1·35), 279infl (0·72), 353 (1·45)
(28)	223 (2·28), 264 (1·36), 361 (0·58)
(29)	224 (1·48), 275 (1·12), 332 (0·57), 384 (0·21)
(31)	229 (2·75), 264 (2·12), 321 (1·43), 369 (0·44)
(32)	232 (3·14), 261infl (2·20), 336 (0·78), 392infl (0·33)
(33)	218 (3·58), 259 (3·09), 320 (0·79), 376 (0·64)
(34)	235 (3·63), 267 (2·51), 365 (1·79)
(35)	230 (3·74), 267 (2·70), 362 (1·25)
(37)	240 (1·69), 292infl (1·13), 302 (1·56), 347 (1·48)
(38)	259 (2·03), 280infl (1·44), 333 (1·26), 431 (1·11)
(38)[a]	228 (2·01), 258infl (1·53), 287 (0·96), 342 (0·75), 423 (1·14)
(36)[b]	218 (2·82), 279 (0·69), 286 (0·62)
(39)	251 (2·94), 337 (1·76), 445 (1·25)
(39)[a]	228 (2·61), 258infl (1·54), 270 (1·35), 343 (0·92), 415 (0·58)
(40)	246 (1·78), 271 (0·54), 278 (0·51), 284 (0·39), 322 (0·45)
(42)	224 (2·63), 278infl (0·60), 379 (0·45)
(43)	260 (2·40), 283 (1·28), 315infl (0·38)
(43)[a]	240infl (1·94), 253 (2·48), 281infl (1·15), 289 (1·25), 328infl (0·30), 324 (0·30)

[a] Solution acidified with a trace of 70% $HClO_4$. [b] No change on acidification.

[15] J. N. Bridson, D.Phil. Thesis, Oxford, 1970, Science Catalogue no. M.S. D.Phil., d. 4943. Photocopies may be obtained without reference to the author on payment of the library's standard fees for this work.

The first fractions (eluted with benzene–petroleum) gave indole (0·85 g), m.p. 48—51° followed by yellow oils. One of these in ether (10 ml) deposited a mixture of yellow and red crystals which were separated by hand. Recrystallisation (methanol) then gave *pentamethyl* 3a,4-*dihydro*-4-*oxo*-3H-*pyrido*[3,2,1-jk]*carbazole*-1,2,3,3a,6-*pentacarboxylate* (32) as red prisms (9 mg), m.p. 216—218° (Found: C, 58·4; H, 4·1; N, 3·0. $C_{25}H_{21}NO_{11}$ requires C, 58·7; H, 4·1; N, 2·7%), and *tetramethyl* 1,2-*dihydro*-9-(cis-1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,trans-2,3,4-*tetracarboxylate* (26) as

TABLE 3

Mass spectra

Compd.	I [a]	*m/e* (%)
(15)	5	415 (8), 356 (19), 325 (18), 324 (100), 297 (7), 296 (7), 266 (10), 179 (9), 178 (6); *m* * 295, 249
(16)	5	399 (100), 368 (60), 367 (69), 322 (19), 251 (60), 193 (58), 168 (24)
(21)	9	622 (30), 621 (100), 620 (30), 619 (98), 590 (12), 588 (12), 547 (11), 546 (30), 545 (11), 544 (29), 518 (10), 516 (10), 500 (12), 498 (11), 472 (10), 470 (10); *m* * 560, 506, 480, 458, 431
(29)	10	341 (50), 310 (26), 309 (63), 252 (11), 251 (28), 224 (16), 223 (100), 192 (20), 155 (13), 118 (10), 117 (22); *m* * none
(31)	5	483 (100), 409 (6), 408 (22), 392 (11), 381 (6), 380 (23), 362 (9), 335 (13), 334 (13), 309 (8), 304 (6), 276 (6), 274 (5), 251 (5), 223 (12); *m* * 376, 374, 351, 344, 319·5, 299, 276, 280·5, 251, 204, 198·5
(33)	3	451 (68), 421 (25), 420 (100), 393 (4), 392 (15), 374 (8), 362 (3), 341 (5), 303 (7), 302 (3), 275 (5), 245 (4), 217 (3), 190 (3), 189 (5), 188 (5), 176 (3), 175 (3); *m* * 391, 341, 334
(36)	4	543 (32), 512 (11), 511 (24), 484 (5), 483 (6), 452 (100), 424 (7), 368 (16), 223 (6)
(37)	5	543 (27), 512 (13), 511 (25), 484 (5), 483 (5), 452 (100), 424 (5), 368 (17), 223 (6)
(38)	13	543 (78), 512 (29), 511 (28), 484 (52), 483 (13), 452 (100), 424 (28), 420 (17), 368 (43), 193 (21)
(39)	13	543 (86), 512 (26), 511 (22), 484 (39), 483 (13), 452 (100), 424 (24), 420 (17), 368 (80), 193 (22)

[a] Minimum intensity recorded (%).

pale yellow prisms (62 mg), m.p. 165—169° (Found: C, 57·6; H, 4·8; N, 2·8. $C_{26}H_{25}NO_{12}$ requires C, 57·5; H, 4·6; N, 2·6%). Elution with benzene gave more of compound (26) (3·1 g), followed by the carbazole (16) (0·9 g), m.p. 180—181° (from methanol) (lit.,[2] 182—182·5°), the mother liquors from which gave the azepine (41) [1] (0·02 g), m.p. 238—241°, $\nu_{max.}$ 3390, 3340, 2950, 2905, 2850, 1775, 1730, 1675, 1603, and 1540. Benzene–ether elution gave more compound (16) (6·0 g), along with the azepine (41) (1·2 g). The first eluates yielded a solid which contained seven components (t.l.c.); slow evaporation of a methanolic solution gave red and pale yellow crystals (1·1 g). Separation by hand gave the phenanthridone (14) (0·8 g), m.p. 270—272° (from acetonitrile) and *tetramethyl* 2,3-*dihydro*-3-(1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,cis-3,4-*tetracarboxylate* (38), red prisms (10 mg) (from methanol), m.p. 164—167° (Found: C, 57·5; H, 4·6; N, 2·9. $C_{26}H_{25}NO_{12}$ requires C, 57·5; H, 4·6; N, 2·6%). The first ether–methanol eluates on addition of acetonitrile (50 ml) gave a solid which [from methanol–nitromethane (10 : 1)] yielded compound (14) (0·4 g). The mother liquor slowly deposited *tetramethyl* 1,2-*dihydro*-1-(1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,3,4-*tetracarboxylate* (37), microcrystals (0·1 g) (from acetonitrile), m.p. 240—242° (decomp.) (Found: C, 57·6; H, 4·9; N, 2·5. $C_{26}H_{25}NO_{12}$ requires C, 57·5; H, 4·5; N, 2·6%). Further quantities of compounds (14), (37), and (38) were obtained from subsequent eluates.

Rechromatography of the combined mother liquors of the products from the (mainly) benzene eluates gave more indole (0·25 g) and compounds (26), (32), (4), and (7) (0·11 g), m.p. 196—198° (lit.,[3] 198—199°).

In a similar way, the mother liquors and non-crystalline residues from the benzene–ether and ether eluates were combined and rechromatographed to yield, in order of elution from the column, indole (0·15 g); (26) (0·54 g); (41) (0·05 g); (16) (1·9 g) (from methanol), the mother liquors of which yielded *trimethyl carbazole*-1,2,4-*tricarboxylate* (29) (17 mg), m.p. 162—165° (Found: C, 63·6; H, 4·6; N, 4·2. $C_{18}H_{15}NO_6$ requires C, 63·3; H, 4·4; N, 4·1%), $\nu_{max.}$ 3260s, 1798w, 1720s, 1708s, 1617w, 1565w, and 1511m cm^{-1}, and *tetramethyl* 9-(cis-1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,3,4-*tetracarboxylate* (18) (0·20 g), m.p. 160—162° (Found: C, 57·8; H, 4·2; N, 2·9. $C_{26}H_{23}NO_{12}$ requires C, 57·7; H, 4·3; N, 2·6%); a yellow tar which with methanol yielded more compound (29) (0·12 g), the mother liquors of which gave *tetramethyl* 4-*oxo*-4H-*pyrido*-[3,2,1-jk]*carbazole*-1,2,3,6-*tetracarboxylate* (33) (13 mg), m.p. 264—265° (Found: C, 61·3; H, 3·9; N, 3·3. $C_{23}H_{17}NO_9$ requires C, 61·2; H, 3·8; N, 3·1%), $\nu_{max.}$ 1731s, 1679s, 1621w, 1601w, 1583w, and 1533w cm^{-1}.

The combined yields of the various compounds were: compound (4) (2 mg); (7) (0·63 g); (14) (10·2 g); (16) (22·8 g); (18) (0·22 g); (26) (17·5 g); (29) (1·4 g); (32) (2 mg); (33) (75 mg); (37) (0·37 g); (38) (0·17 g); (41) (7·8 g); recovered indole (9·1 g).

On another occasion the benzene–ether eluate yielded *tetramethyl* 1,4-*dihydro*-1-(1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,3,4-*tetracarboxylate* (36) (0·37 g) (from acetonitrile–methanol), m.p. 244° (decomp.) (Found: C, 57·5; N, 4·6; N, 2·9. $C_{26}H_{25}NO_{12}$ requires C, 57·5; H, 4·6; N, 2·6%), which on refluxing in ethanol containing a trace of sulphuric acid yielded compound (37), and the methanol eluate gave also *tetramethyl* 2,3-*dihydro*-3-(1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,trans-3,4-*tetracarboxylate* (39) (from methanol), m.p. 198—200° (Found: C, 57·2; H, 5·0. $C_{20}H_{25}NO_{12}$ requires C, 57·5; H, 4·6%).

Indole and Diethyl Acetylenedicarboxylate.—The reactants (25 and 70 g respectively) were treated essentially as for the dimethyl ester but *diethyl* 2,2-*di*(*indol*-3-*yl*)*succinate* (9) crystallised and was collected and washed with cold ether (200 ml); it gave crystals (from ethanol) (30·0 g), m.p. 170—172° (Found: C, 71·3; H, 6·1; N, 6·9. $C_{24}H_{24}N_2O_4$ requires C, 71·3; H, 6·0; N, 6·9%), $\nu_{max.}$ 1707s, 1619w, and 1532w cm^{-1}. The filtrate was combined with the residue obtained by evaporating the ether, and chromatography gave indole (5·4 g); *tetraethyl carbazole*-1,2,3,4-*tetracarboxylate* (19) (19·7 g), needles (from ethanol), m.p. 140—141° (Found: C, 63·2; H, 5·3; N, 3·4. $C_{24}H_{25}NO_8$ requires C, 63·3; H, 5·5; N, 3·1%), $\nu_{max.}$ 3440m, 1730s, 1704s, 1625w, 1599m, and 1579m cm^{-1}; and *triethyl* 5,6-*dihydro*-6-*oxophenanthridine*-7,8,9-*tricarboxylate* (15) (7·5 g) [from ethanol–acetonitrile (4 : 1)], m.p. 203—206° (Found: C, 63·9; H, 5·2; N, 3·6. $C_{22}H_{21}NO_7$ requires C, 64·2; H, 5·1; N, 3·4%), $\nu_{max.}$ 3320w, 1750s, 1732s, 1674s, and 1609m cm^{-1}.

Hydrolyses and Decarboxylations to Carbazole.—Compounds (16), (18), (32), and (36)—(39) were refluxed with excess of potassium hydroxide in methanol for 12 h; in each

case the solvent was removed and the residue ground with soda-lime. The mixture was then heated at atmospheric pressure; carbazole, m.p. and mixed m.p. 243°, possessing the same u.v. spectrum as authentic material, was obtained.

Indole and Dimethyl Acetylenedicarboxylate in Benzene or Toluene.—The reactants (23·4 and 56·8 g respectively) were refluxed in benzene (250 ml) for 18 days; the solution was concentrated and chromatographed, and the products were: the indolylazepine (41) (15·2 g); *trimethyl* 9-(cis-1,2-*bismethoxycarbonylvinyl*)*carbazole*-1,2,4-*tricarboxylate* (31) (18 mg), plates (from acetonitrile–methanol), m.p. 238—240° (Found: C, 59·9; H, 4·3; N, 3·2. $C_{24}H_{21}NO_{10}$ requires C, 59·6; H, 4·4; N, 2·9%), $\nu_{max.}$ 1735s, 1727s, 1711s, 1640m, and 1608m cm^{-1}; the tetraester (16) (14·3 g); the triester (29) (0·95 g); the pyridocarbazole (33) (23 mg); the phenanthridone (14) (0·60 g); the hexaester (37) (0·86 g); and unchanged indole (1·26 g).

With toluene as solvent and 8 days refluxing the products were the hexaester (26) (4·3 g); the tetraester (16) (2·9 g); the phenanthridone (14) (0·60 g); and unchanged indole (1·4 g).

Indole and Dimethyl Acetylenedicarboxylate in Methanol.—The reactants (11·7 and 14·5 g respectively) were refluxed in methanol (100 ml) for 3 days; the solvent was removed, the residue was chromatographed, and the products were recrystallised to give: indole (3·3 g); the fumarate (4) (10·7 g) (from methanol), m.p. 106—108°; the azepine (41) (0·056 g), m.p. 238—239°; the hexaester (16) (1·35 g); and the phenanthridone (14), identified by t.l.c.

Indole and Dimethyl Acetylenedicarboxylate in Acetic Acid.—The reactants (5·86 and 3·55 g respectively) were refluxed in acetic acid (50 ml) for 7 h. The solution was cooled, neutralised with saturated aqueous sodium carbonate, and extracted with ether (3 × 100 ml). The ether layer was dried ($MgSO_4$) and evaporated and the residue was stored in methanol (150 ml) for 12 h at 0° to give the succinate (7), prisms (1·04 g) (from methanol), m.p. 195—197°. The mother liquors were combined, evaporated, and chromatographed. The products were the succinate (7) (0·95 g), the fumarate (4) (identified by t.l.c.), and di-indol-3-ylmethane (4 mg), plates (from chloroform), m.p. 163—165° (lit.,[16] 164—165°).

In similar experiments diethyl acetylenedicarboxylate gave *diethyl* 2,2-*di*(*indol*-3-*yl*)*succinate* (9) (44%), m.p. 174—176° (Found: C, 71·3; H, 6·1; N, 6·9. $C_{24}H_{24}N_2O_4$ requires C, 71·3; H, 6·0; N, 6·9%), $\nu_{max.}$ 3360s (N–H), 1707s, and 1619w cm^{-1}.

1-*Methylindole and Dimethyl Acetylenedicarboxylate.*—The reactants (28 and 60 g respectively) were mixed and treated essentially as for the indole reaction, ether being replaced by chloroform in the chromatography.

The products were dimethyl fumarate (0·45 g), m.p. 99—100° (lit.,[13] 102°); the azepine (43) [1] (14·1 g), m.p. 107—108°; the dihydrocarbazole (25) (7·3 g) (from methanol), m.p. 175—176° (lit.,[3] 175—176·5°); *tetramethyl* 1,2-*dihydro*-9-*methylcarbazole*-1,cis-2,3,4-*tetracarboxylate* (24) (0·01 g), yellow prisms (from methanol), m.p. 169—170° (Found: C, 60·7; H, 5·1; N, 3·4. $C_{21}H_{21}NO_8$ requires C, 60·7; H, 5·1; N, 3·4%), $\nu_{max.}$ 1742s, 1730s, 1700s, and 1664w cm^{-1}; the phenanthridone (14; 5-Me) (0·94 g), needles, m.p. 169—171° (from methanol) (lit.,[3] 171—172·5°); a compound which may be *tetramethyl* N-*methylindole*-2,3-*di*(*butenedioate*) (42) (0·02 g), orange prisms (from methanol), m.p. 139—140° (Found: C, 60·8; H, 5·0; N, 3·2. $C_{21}H_{21}NO_8$ requires C, 60·7; H, 5·2; N, 3·4%), $\nu_{max.}$ 1750s, 1737s, 1703s, 1656w, 1622w, 1605m, 1572w, 1542s, and 1518w cm^{-1}; and an unidentified compound (8 mg), needles, m.p. 169—170°.

1-Methylindole (6·50 g) with dimethyl acetylenedicarboxylate (3·55 g) in refluxing acetic acid gave the succinate (8) (5·16 g), prisms, m.p. 206—207° (lit.,[3] 208—209·5°); and 5-bromoindole (3·92 g) with dimethyl acetylenedicarboxylate (1·50 g) similarly gave *dimethyl* 2,2-*bis*-5-*bromoindol*-3-*ylsuccinate* (7; 5,5′-Br_2) (0·43 g), m.p. 280—282° (Found: C, 49·7; H, 3·5; Br, 29·7. $C_{22}H_{18}Br_2N_2O_4$ requires C, 49·5; H, 3·4; Br, 30·0%), $\nu_{max.}$ 3330s, 1730s, and 1702s cm^{-1}.

1-*Methylindole and Dimethyl Acetylenedicarboxylate in Toluene.*—The reactants (0·65 and 1·4 g respectively), heated in toluene (20 ml) at 100° for 4 days, gave compounds (42), (25), and (14; 5-Me) identified from their spectra and t.l.c.

2-*Methylindole and Dimethyl Acetylenedicarboxylate.*—These compounds (13·1 and 14·2 g respectively) were refluxed in benzene (50 ml) for 12 days; chromatography gave the *trans*-indole (6), orange prisms (8·0 g) (from methanol), m.p. 122—123° (lit.,[3] 122—124°); the *cis*-isomer (3), microneedles (8·94 g) (from methanol), m.p. 138—140° (lit.,[3] 138—139·5°); an unidentified compound (15 mg), m.p. 198—200° (Found: C, 58·4; H, 5·2; N, 2·4. $C_{27}H_{27}NO_{12}$ requires C, 58·2; H, 4·9; N, 2·5%), $\nu_{max.}$ 1747s, 1738s, 1712s, 1695s, 1642w, 1613m, 1594s, and 1540w cm^{-1}; and the phenanthridinone (14; 10-Me) (0·03 g), m.p. 269—271° (lit.,[3] 269—271°).

2-*Methylindole and Dimethyl Acetylenedicarboxylate in Methanol.*—The reactants (6·55 and 7·1 g respectively) were refluxed in methanol (35 ml) for 15 min. Next day the orange precipitate (2·2 g), m.p. 115—124°, of compounds (3) and (6) (i.r. comparisons with authentic samples) was collected, but recrystallisations (methanol) did not separate the mixture. Chromatography of the combined mother liquors gave compound (6) (7·88 g), orange prisms (from chloroform–petroleum), m.p. 121—122°; a mixture of (6) and (3) (1·67 g); and compound (3) (1·0 g), prisms (from chloroform–petroleum), m.p. 139—143°.

Dimethyl 2,2-*Bis*-(1-*methylindol*-3-*yl*)*succinate* (8).—Dimethyl 2,2-di(indol-3-yl)succinate (0·38 g) in tetrahydrofuran (50 ml) was stirred while sodium hydride (0·075 g) was added. After 2 h stirring methyl iodide (0·5 g) was added and stirring was continued for a further 2 h. Water was added until hydrogen evolution ceased, and the solution was evaporated to *ca.* 10 ml. Water (50 ml) was added, the mixture was extracted with chloroform (3 × 30 ml), and the extracts were dried ($MgSO_4$) and evaporated. Recrystallisation (from methanol) gave the succinate (8) (0·16 g), m.p. and mixed m.p. 206—207°, u.v. and i.r. spectra as expected.[3]

Dimethyl Indol-3-*ylfumarate and Dimethyl Acetylenedicarboxylate.*—The fumarate (12·9 g) and dimethyl acetylenedicarboxylate (14·2 g) were warmed until the mixture was homogeneous, and left in the dark at room temperature for 170 days. Methanol (30 ml) was added and the mixture warmed to 40°. Trituration gave a yellow solid (A), the filtrate on cooling overnight deposited yellow solid (B), and the mother liquor was evaporated to give a red tar which yielded compounds (14) (0·09 g) and (16) (0·16 g).

Four recrystallisations of (A) (from methanol) gave the

[6] E. Leete and L. Marion, *Canad. J. Chem.*, 1953, **31**, 775.

carbazole (16) (1·2 g), m.p. 178—180°. The combined mother liquors on evaporation gave a solid which was extracted rapidly with boiling methanol. The residue gave *tetramethyl* 9-(cis-1,2-*bismethoxycarbonylvinyl*)-1,2-*dihydrocarbazole*-1,cis-2,3,4-*tetracarboxylate* (27), yellow rods (0·27 g) (from methanol), m.p. 167—168° (Found: C, 57·6; H, 4·8; N, 2·5. $C_{26}H_{25}NO_{12}$ requires C, 57·5; H, 4·6; N, 2·6%), $\nu_{max.}$ 1765s, 1740s, 1720s, and 1659m cm^{-1}. The methanolic extract yielded more (0·41g) of (16).

Recrystallisation of (B) from methanol–acetonitrile (4 : 1) gave the phenanthridone (14) (0·19 g). Concentration of the mother liquor and cooling gave more of (27) (0·08 g) and further concentration gave a tarry solid which crystallised from methanol to give (26), pale yellow prisms, m.p. 168—170°.

Dimethyl 1-*Methylindol*-3-*ylfumarate* (5) *and Methyl Propiolate*.—The fumarate (0·13 g) and methyl propiolate (0·1 g) were heated at 100° for 24 h. Petroleum (10 ml) was added and distilled off, and the procedure was repeated until the smell of methyl propiolate had disappeared. The residue on crystallisation from methanol gave dimethyl 5,6-dihydro-5-methyl-6-oxophenanthridine-7,9-dicarboxylate (0·16 g), needles, m.p. 180—180·5° (lit.,[7] 192—193°) (Found: C, 66·2; H, 4·8; N, 4·4. Calc. for $C_{18}H_{15}NO_5$: C, 66·5; H, 4·6; N, 4·3%), $\nu_{max.}$ 1742s, 1657s, 1618m, and 1600w cm^{-1}, $\lambda_{max.}$ 211infl (3·76), 241 (5·99), 260infl (2·46), 273infl (1·67), 315 (0·84), and 350 (0·93) nm.

Methylation of Dimethyl Indol-3-*ylfumarate* (4).—This indole (0·26 g) was dissolved in dimethyl sulphoxide (10 ml), sodium hydride (50 mg) and then methyl iodide (1 ml) were added, and stirring was continued for 30 min. Methanol (5 ml) was added slowly and the mixture was poured into ice–water (50 ml) and extracted with chloroform (3 × 10 ml). The dried ($MgSO_4$) extract was evaporated to a yellow oil which solidified and gave dimethyl 1-methylindol-3-ylfumarate (5) (0·07 g), yellow prisms, m.p. 83—85° (lit.,[3] 85·5°), with u.v. and i.r. spectra similar to those quoted.[3]

Dimerisation of Dimethyl Indol-3-*ylfumarate* (4).—This indole (0·6 g) was refluxed in methanol (4 ml) containing concentrated sulphuric acid (1 drop) for 18 h. The solvent was removed and the tarry solid residue on recrystallisation from methanol gave prisms of the dimer (10) (0·4 g), m.p. 263—265° (lit.,[4] 265°).

Dimethyl 1-*Methylindol*-3-*ylsuccinate*.—Dimethyl 1-methylindol-3-ylfumarate (0·9 g) in methanol (150 ml) was shaken with 5% palladium–charcoal (0·1 g) for 3 h under hydrogen (3 atm); the solution was filtered and the solvent removed. The residual solid, on recrystallisation from petroleum, gave dimethyl 1-methylindol-3-ylsuccinate (0·52 g), needles (from petroleum), m.p. 52—54° (Found: C, 65·8; H, 6·4; N, 4·9. $C_{15}H_{17}NO_4$ requires C, 65·4; H, 6·2; N, 5·1%), $\nu_{max.}$ 1737s and 1612w cm^{-1}, $\lambda_{max.}$ 224 (3·84) and 285 (0·55) nm.

Tetramethyl 9-*Methylcarbazole*-1,2,3,4-*tetracarboxylate* (17).—The carbazole (16) (2·0 g) was methylated as for the indole (4) and gave the 9-methylcarbazole (17) (0·4 g), prisms (from methanol), m.p. 123—125° (lit.,[2] 124—125°), with u.v. and i.r. spectra closely similar to those quoted.[2]

Trimethyl 9-*Methylcarbazole*-1,2,4-*tricarboxylate* (30).—The carbazole (29) (0·17 g) was methylated as for the indole (4) and gave the 9-methylcarbazole (30) (30 mg), pale yellow prisms (from methanol), m.p. 184—185° (lit.,[3] 192·5—193·5°), with u.v. and i.r. spectra closely similar to those quoted.[3]

Tetramethyl 6-*Bromo*-9-(cis-1,2-*bismethoxycarbonylvinyl*)-*carbazole*-1,2,3,4-*tetracarboxylate* (21).—The dihydrocarbazole (26) (1·0 g) in methanol (50 ml) was refluxed while bromine (1·0 g) was added during 1 h. After 24 h refluxing all but *ca.* 10 ml of the solvent was removed. A yellow solid was deposited and recrystallisation gave the *carbazole* (21) (1·1 g), plates, m.p. 198—200° (Found: C, 50·4; H, 3·5; Br, 12·9; N, 2·3. $C_{26}H_{22}BrNO_{12}$ requires C, 50·6; H, 3·5; Br, 11·8; N, 2·0%), $\nu_{max.}$ 1740s, 1657m, and 1611w cm^{-1}.

The bromocarbazole (21) (0·7 g) was shaken with 5% palladium–charcoal (0·1 g) and magnesium oxide (0·1 g) in methanol (200 ml) for 3 h under hydrogen (3 atm). Filtration and evaporation gave tetramethyl 9-(*cis*-1,2-bismethoxycarbonylvinyl)carbazole-1,2,3,4-tetracarboxylate (18) (0·38 g), plates (from methanol), m.p. 161—162°.

Pyrolysis of Tetramethyl 1,2-*Dihydro*-9-*methylcarbazole*-trans-1,2,3,4-*tetracarboxylate* (25).—Compound (25) (0·1 g) was heated at 250° for 5 min, then cooled, and the resulting brown oil was triturated with methanol to give tetramethyl 9-methylcarbazole-1,2,3,4-tetracarboxylate (7), off-white microcrystals (from methanol), m.p. 118—123° (lit.,[2] 124—125°).

The mother liquors were examined by t.l.c.; the two major spots (R_F 0·45 and 0·62 in ether) were extracted and the products identified as compounds (17) and (30), by comparison of their u.v. spectra and R_F values with those of authentic samples.

Isomerisation of Tetramethyl 9-(cis-1,2-*Bismethoxycarbonylvinyl*)-1,2-*dihydrocarbazole*-1,cis-2,3,4-*tetracarboxylate* (27).—Compound (27) (0·1 g) in benzene (10 ml) was stirred with alumina (2·0 g) for 24 h. The mixture was filtered and the alumina was washed with hot chloroform (20 ml). The combined filtrate and washings were evaporated and the residue recrystallised from methanol to give pale yellow prisms of the *trans*-isomer (26) (0·02 g), m.p. and mixed m.p. 168—169°.

Comparison by t.l.c. of the mother liquor with authentic samples of compounds (26) and (27) showed that isomerisation was complete. In a similar way compound (27) was shown to give compound (26) and some tar on rapid treatment in methanol with a trace of sodium methoxide.

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