Reactions of 5,6,7,8-Tetrahalogeno-1,4-dihydronaphthalen-1,4-imines with Dimethyl Acetylenedicarboxylate

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Isomeric 1 : 1 adducts obtained from tetrachlorobenzyne and *N*-t-butylpyrrole are a naphthalen-1,4-imine and a benzo[3,4]cyclobuta[1,2-*b*]pyrrole derivative. The former (5) decomposes thermally by a retro-Diels–Alder reaction to give an isoindole (17), which forms another naphthalen-1,4-imine (6) by addition of dimethyl acetylenedicarboxylate. 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-methyliminonaphthalene (1) reacts with the acetylene ester to give two simple naphthalene derivatives, a benz[*g*]indole (18) and a benzo[*de*]quinoline (26). Adducts are obtained from 5,6,7,8-tetrachloro-1,4-dihydro-1,4-methyliminonaphthalene (2) with benzyne, dibenzoylacetylene, and dimethyl acetylenedicarboxylate. Unusually large long-range H–F and C–F nuclear spin interactions are observed for two fluorinated benz[*g*]indole derivatives (18) and (22).

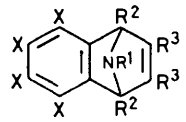
TETRACHLOROBENZYNE adds to *N*-methyl- or 1,2,5-trimethyl-pyrrole to give the 1,4-dihydronaphthalen-1,4-imine derivatives (2) [1] and (3),[2] respectively [however, details of the preparation and characterisation of the adduct (2) are still lacking]. The corresponding adducts of benzyne and *N*-alkylpyrroles are in many cases unstable, undergoing spontaneous rearrangement to naphthylamines or reacting further with benzyne to give rearranged 2 : 1 adducts.[3-6] Rearrangement of the tetrafluorobenzyne adduct (1) in solution to isomers (9) [7] and (10) [8,9] and decomposition of (1) to form other products [9] at higher temperatures in the gas phase have been reported. We describe the preparation of some new adducts [10] from tetrachlorobenzyne and *N*-substituted pyrroles, their thermal decomposition, addition of benzyne to compound (2), and reactions of (1), (2), and (5) with dimethyl acetylenedicarboxylate.

RESULTS AND DISCUSSION

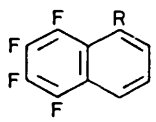
Tetrachlorobenzyne was generated from hexachlorobenzene and n-butyl-lithium and trapped *in situ* by *N*-benzyl- or *N*-t-butyl-pyrrole to give the adducts (4) and (5), respectively. The symmetrical structures

[1] G. W. Gribble, N. R. Easton, jun., and J. T. Eaton, *Tetrahedron Letters*, 1970, 1075.
[2] J. M. Vernon, M. Ahmed, and J. M. Moran, *J.C.S. Perkin I*, 1977, 1084.
[3] G. Wittig and W. Behnisch, *Chem. Ber.*, 1958, **91**, 2358; G. Wittig and B. Reichl, *ibid.*, 1963, **96**, 2851.
[4] E. Wolthuis and A. De Boer, *J. Org. Chem.*, 1965, **30**, 3255.
[5] E. Wolthuis, D. V. Jagt, S. Mels, and A. De Boer, *J. Org. Chem.*, 1965, **30**, 190; E. Wolthuis, W. Cady, R. Roon, and B. Weidenaar, *ibid.*, 1966, **31**, 2009.
[6] *Cf.* L. J. Kricka and J. M. Vernon, *Adv. Heterocyclic Chem.*, 1974, **16**, 87.
[7] D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedron*, 1969, **25**, 25.
[8] H. Heaney and S. V. Ley, *J.C.S. Perkin I*, 1974, 2698.
[9] P. L. Coe and A. J. Uff, *Tetrahedron*, 1971, **27**, 4065.
[10] Preliminary publication, M. Ahmed and J. M. Vernon, *J.C.S. Chem. Comm.*, 1976, 462.

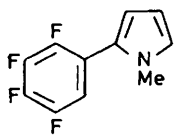
proposed are in accord with the evidence of ^{1}H n.m.r. spectra and with the mass-spectral fragmentation of



(1) X = F, R^1 = Me, R^2 = R^3 = H
(2) X = Cl, R^1 = Me, R^2 = R^3 = H
(3) X = Cl, R^1 = R^2 = Me, R^3 = H
(4) X = Cl, R^1 = CH_2Ph, R^2 = R^3 = H
(5) X = Cl, R^1 = Bu^t, R^2 = R^3 = H
(6) X = Cl, R^1 = Bu^t, R^2 = H, R^3 = CO_2Me
(7) X = H, R^1 = Bu^t, R^2 = R^3 = H

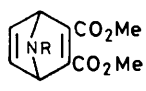


(8) R = H
(9) R = NHMe



(10)

these compounds with loss of acetylene.[2] The appearance of triplet n.m.r. signals for the vinylic and bridgehead hydrogens in (4) and (5) is as observed for the related 7-azabicyclo[2.2.1]heptadiene derivatives (11).[11] A minor product of the reaction leading to (5) was an isomeric adduct, for which structure (12) is assigned on the evidence of its ^{1}H n.m.r. spectrum: τ($CDCl_3$) 3.22 (1 H, dd, 2-H), 3.59 (1 H, dd, 3-H), 6.57 (1 H, d,



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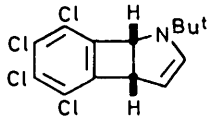

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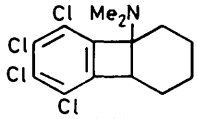

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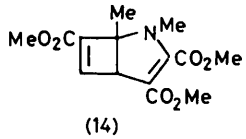

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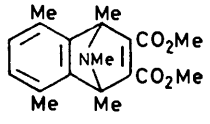

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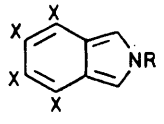


(16) X = F, R = Me
(17) X = Cl, R = Bu^t

7b-H), 7.31 (1 H, 8 lines, 3a-H), and 8.93 (9 H, s, Bu^t); $J_{2,3}$ 10, $J_{2,3a}$ 1, $J_{3,3a}$ 4, and $J_{3a,7b}$ 6 Hz. This is apparently the first example of the benzo[3,4]cyclobuta-[1,2-*b*]pyrrole ring system, although 1,2-cycloaddition of tetrachlorobenzyne to *NN*-dimethylcyclohex-1-enylamine gives the adduct (13) [12] and other precedents involving cyclobutene ring formation from benzyne and enamines or indol-1-yl-lithium are known.[12,13]

Attempts to isomerise compound (12) to a benz[*c*]azepine derivative, based on a reaction of the cyclobuta[*b*]pyrrole triester (14),[14] were unsuccessful.

When the adduct (5) was heated with dimethyl acetylenedicarboxylate (DMAC) a new compound was obtained. Analysis gave a formula $C_{18}H_{17}Cl_4NO_4$, and the structure contained two identical methyl ester groups (i.r. and ^{1}H n.m.r. spectra). Structure (6) is established by this evidence and by appropriate mass-spectral fragmentations (see Experimental section) including loss of DMAC from the molecular ion, as observed for (15) and related compounds.[15] Formation of (6) stepwise from (5) by loss of acetylene followed by addition of DMAC was proved by heating (5) alone to 220 °C. Acetylene was removed in a stream of nitrogen, and the residue afforded 4,5,6,7-tetrachloro-2-t-butylisoindole (17).

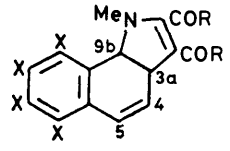
This retro-Diels–Alder reaction of compound (5) matches a characteristic mass-spectral fragmentation pathway of 1,4-dihydronaphthalen-1,4-imines.[2,15] It is the first recorded preparation of an isoindole by this route, although the 2,3-dihydro-derivative of the adduct (1) decomposes thermally to ethylene and the isoindole (16).[16] The adduct (1) itself decomposes above 300 °C in the gas phase to a number of products [9] including acetylene and tetrafluoro-*N*-methylphthalimide; the latter could well be formed by autoxidation of the isoindole (16). Acetylene was also evolved when the adduct (4) was heated, although the corresponding isoindole was not identified in this case.

The adducts (1) and (2) of tetrahalogenobenzynes and *N*-methylpyrrole reacted with DMAC in less vigorous conditions and by different pathways. The products obtained from the reaction of compound (1) in refluxing dioxan were 1,2,3,4-tetrafluoronaphthalene (8) and two isomeric 1 : 1 adducts of (1) and DMAC. The major isomer, m.p. 131—132 °C, is assigned the structure (18) analogous to that of the 1 : 2 adduct (21) obtained from *N*-ethylisoindole and the acetylene ester.[15] A relatively intense peak at *m/e* 200 in the mass spectrum of (18) corresponds to the molecular ion of tetrafluoronaphthalene (8), which is a likely fragment from structure (18). The ^{19}F n.m.r. spectrum confirmed the presence of four fluorine atoms in adjacent positions of an aromatic ring. The ^{1}H n.m.r. spectrum showed two independent AB systems, one for the *cis*-CH=CH grouping, the other for the bridgehead hydrogen atoms. Dehydrogenation of the adduct (18) with palladium afforded the benz[*g*]indole derivative (22); its ^{1}H n.m.r. spectrum showed only the AB system of two vinylic hydrogens and, as expected, a downfield shift of the *N*-methyl resonance compared with the spectrum of (18).

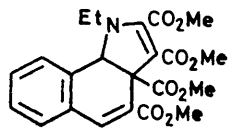
The most interesting feature of the n.m.r. spectra of compounds (18) and (22) is the appearance of doublet signals for the *N*-methyl group ($|J|$ 3 and 12 Hz, re-

[11] R. Kitzing, R. Fuchs, M. Joyeux, and H. Prinzbach, *Helv. Chim. Acta*, 1968, **51**, 888.
[12] H. Heaney and S. V. Ley, *J.C.S. Perkin I*, 1974, 2693.
[13] M. E. Kuehne, *J. Amer. Chem. Soc.*, 1962, **84**, 837; M. E. Kuehne and T. Kitagawa, *J. Org. Chem.*, 1964, **29**, 1270.
[14] R. F. Childs and A. W. Johnson, *Chem. Comm.*, 1965, 95.
[15] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1972, 904.
[16] H. Heaney, S. V. Ley, A. P. Price, and R. P. Sharma, *Tetrahedron Letters*, 1972, 3067.

spectively), which we ascribe to coupling with the fluorine atom at the 9-position. For compound (22) we confirmed that the separation of the component lines of the *N*-methyl doublet remains the same while its position is shifted upfield or downfield of the *O*-methyl absorptions by changing the solvent from [$^2H_6$]benzene to [^{2}H]chloroform. The value of J_{HF} for (22) is very large for an interaction through six intervening bonds (*cf.* values of $^6J_{HF}$ reported previously [17-19]), and it emphasises that a 'through-space mechanism' is primarily responsible, as other workers have also concluded. In the proton-decoupled ^{13}C n.m.r. spectra of compounds (18) and (22) the *N*-methyl carbon resonance is also a doublet ($|^5J_{CF}|$ 4 and 30 Hz, respectively) due to unusually large long-range coupling to fluorine. Dreiding models confirm that the *N*-methyl group is close to fluorine at the 9-position in (18) and that this crowding is significantly greater in the fully aromatic structure (22).



(18) X = F, R = OMe
(19) X = Cl, R = OMe
(20) X = Cl, R = Ph



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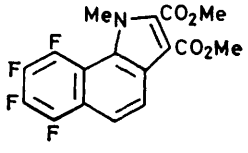

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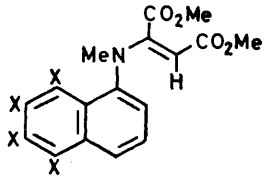
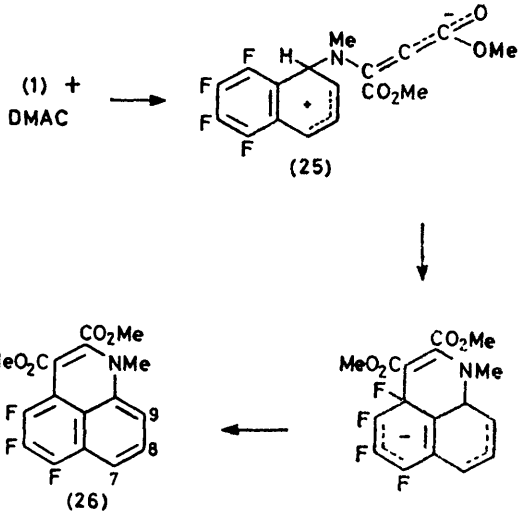


(23) X = F
(24) X = H

For the constitution of the isomeric adduct, m.p. 117—118 °C, we considered possible formulations that could arise *via* thermal isomerisation of (1) to (10) and reaction of the latter with DMAC. However, the structure (23) is supported by compelling similarities of the u.v. and ^{1}H n.m.r. spectra of the adduct to those of the model compound (24) (see Experimental section), which we obtained by addition of *N*-methyl-1-naphthylamine to DMAC. The Michael adducts of other secondary amines and DMAC are known [20] to be aminomaleate derivatives as in structures (23) and (24), and the single vinylic hydrogen resonance [τ 5.53 in (23) and (24)] is characteristically at higher field than in the spectra of aminofumarate derivatives obtained from primary amines and DMAC.

A fourth product obtained in low yield from the reaction of (1) with DMAC in different conditions (see Experimental section) was a yellow compound, m.p. 150—151 °C. Elemental analysis and its mass spectrum gave a formula $C_{17}H_{12}F_3NO_4$. The ^{19}F n.m.r. spectrum also showed the presence of only three fluorine atoms, and the ^{1}H n.m.r. spectrum included a pattern for three aromatic hydrogen atoms similar to that of compound (23). The benzo[*de*]quinoline structure (26) for the yellow product is consistent with these data, with the u.v.–visible absorption spectrum, and with a probable pathway for its formation (Scheme).



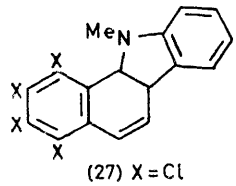
SCHEME

The same intermediate zwitterion (25) by an alternative cyclisation to the naphthalene 2-position or by a prototropic shift from the 1-position also accounts convincingly for the formation of the adducts (18) and (23), respectively. Tetrafluoronaphthalene (8) may be formed *via* (25) or by a different route.[6]

We noted previously [21] the formation of 1,2,3,4-tetrachloronaphthalene in the reaction of (2) with DMAC, and there are other examples of the aromatisation of 1,4-dihydronaphthalen-1,4-imines, including (15), by extrusion of a bridging NMe group.[22] Like (1), compound (2) gave a 1 : 1 adduct with DMAC, which is the tetrachlorobenz[*g*]indole diester (19) with ^{1}H n.m.r. spectrum like that of (18). Similar adducts (20) and (27) were obtained from compound (2) with dibenzoylacetylene and with benzyne, although no reaction was found with diphenylacetylene. The structure (27) is consistent with ^{1}H n.m.r. and mass spectra (see Experimental section) and with the analogy of stepwise formation of the 2 : 1 adduct (28) from benzyne and *N*-methylpyrrole.[3]

[17] P. A. Lehmann F., *Org. Magnetic Resonance*, 1970, **2**, 467; P. A. Lehmann F. and L. F. Johnson, *ibid.*, 1973, **5**, 61.
[18] G. W. Gribble and J. R. Douglas, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 5764; F. R. Jerome and K. L. Servis, *ibid.*, 1971, **93**, 1535; 1972, **94**, 5896.
[19] W. Adcock, D. G. Matthews, and S. Q. A. Rizvi, *Austral. J. Chem.*, 1971, **24**, 1829; H. Fritz and T. Winkler, *Helv. Chim. Acta*, 1974, **57**, 836; other refs. cited by R. Grinter in Chem. Soc. Specialist Periodical Report, 'Nuclear Magnetic Resonance,' vol. 5, ch. 2, 1976, and previous volumes in this series.
[20] E. Winterfeldt and H. Preuss, *Chem. Ber.*, 1966, **99**, 450; R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *ibid.*, p. 2526.
[21] L. J. Kricka and J. M. Vernon, *Chem. Comm.*, 1971, 942.
[22] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1973, 766.

The observation that the *N*-t-butyl compound (5) reacts with DMAC by a different pathway (see above) is understandable in view of the severely unfavourable steric interaction which would be expected in an adduct



(27) X = Cl
(28) X = H

of structure analogous to (18), but containing the larger *N*-t-butyl group and chlorine instead of fluorine at the 9-position. In order to test an intermediate case, we prepared the adduct (7) from benzyne and *N*-t-butylpyrrole, but we were unable to characterise any products of its reaction with DMAC.

EXPERIMENTAL

U.v. spectra were recorded in methanol. I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene; absorptions are quoted only for the range 1 600—1 800 cm^{-1}. ^1H N.m.r. spectra were recorded at 60, 90, or 100 MHz in carbon tetrachloride or [^2H]chloroform with tetramethylsilane as internal standard. ^{19}F N.m.r. spectra were recorded at 84.6 MHz in [^2H]chloroform; ^{19}F chemical shifts are upfield from trichlorofluoromethane as external standard. Mass spectra were obtained at 70 eV. Alumina for chromatography was deactivated by mixing thoroughly with 10% of its weight of aqueous acetic acid (5%). Light petroleum had b.p. 60—80 °C.

Tetrachlorobenzyne Adducts.—n-Butyl-lithium (2.56 g) in n-hexane was added dropwise to a stirred suspension of hexachlorobenzene (11.4 g) in dry ether (400 ml) which was cooled at −65 °C under dry nitrogen. After 1 h redistilled *N*-benzylpyrrole [23] (9.4 g) was added, and stirring was maintained as the mixture was allowed to warm to room temperature. It was left overnight before addition of water. The ether layer was separated and extracted twice with aqueous hydrochloric acid (4N) at 0 °C. The combined acid extracts were basified with sodium hydroxide and re-extracted with ether. The ether was dried (K_2CO_3) and evaporated leaving a gum, from which a yellow solid sublimed at 170 °C (bath) and 0.5 mmHg. Recrystallisation of this solid from carbon tetrachloride–methanol afforded *5,6,7,8-tetrachloro-1,4-dihydro-1,4-benzyliminonaphthalene* (4) (2.2 g, 15%), m.p. 101—103 °C (Found: C, 55.1; H, 3.1; N, 3.7. $C_{17}H_{11}Cl_4N$ requires C, 55.0; H, 3.0; N, 3.8%), τ 2.82 (5 H, s, ArH), 3.12 (2 H, t, 2- and 3-H), 5.26 (2 H, t, 1- and 4-H), and 6.59 (2 H, s, CH_2), *m/e* 369/371/373 (M^+, 9/11/5%), 343/345/347 ([M − C_2H_2]$^+$, 6/8/4), 278/280/282 ([M − CH_2Ph]$^+$, 10/13/6), and 91 (100).

n-Butyl-lithium in n-hexane was added as before to hexachlorobenzene in ether at −70 °C under nitrogen. Redistilled *N*-t-butylpyrrole [23] was added to the mixture at −35 °C, which was then allowed to reach room temperature and next day was worked up as before. The crude acid-soluble product obtained after evaporation was recrystallised directly from ethyl acetate giving a mixture of prisms and needles. These were separated mechanically and further recrystallised to afford *1-t-butyl-4,5,6,7-tetrachloro-3a,7b-dihydrobenzo*[3,4]*cyclobuta*[1,2-b]*pyrrole* (12) (2%), needles, m.p. 142—144 °C (Found: C, 49.85; H, 3.85; N, 4.1. $C_{14}H_{13}Cl_4N$ requires C, 49.9; H, 3.9; N, 4.15%), *m/e* 335/337/339 (M^+, 20/27/14%), 279/281/283 (66/86/43), 264/266/268 (17/23/11), 252/254/256 (9/12/6), 251/253/255 (15/25/15), 217/219/221 (28/26/8), 196 (12), 194 (18), 92 (12), 58 (17), 57 ([C_4H_9]$^+$, 100), and 41 (92); and *5,6,7,8-tetrachloro-1,4-dihydro-1,4-t-butyliminonaphthalene* (5) (50%), prisms, m.p. 96—98 °C (Found: C, 49.9; H, 4.0; N, 4.1%), τ 2.96 (2 H, t, 2- and 3-H), 4.89 (2 H, t, 1- and 4-H), and 9.08 (9 H, s, CH_3), *m/e* 335/337/339 (M^+, 14/18/9%), 320/322/324 ([M − Me]$^+$, 70/90/45), 309/311/313 ([M − C_2H_2]$^+$, 5/6/3), 285/287/289 (18/23/11), 270/272/274 (15/13/4), 264/266/268 (24/33/16), 253/255/257 (38/43/19), 217/219/221 (13/13/5), 196 (17), 194 (11), 149 (25), 113 (14), 99 (43), 73 (30), 57 (90), 56 (30), 55 (25), 42 (16), and 41 (100).

Thermal Decomposition of 5,6,7,8-Tetrachloro-1,4-dihydronaphthalen-1,4-imines.—The adduct (4) (0.52 g) was heated at 200 °C in a slow stream of nitrogen for 1.5 h. The exit gases when passed through aqueous ammoniacal copper(I) chloride gave a red precipitate showing the formation of acetylene. The residue was then heated *in vacuo* at 180 °C (bath) and 0.5 mmHg and a sublimate collected; the latter was fractionally recrystallised from carbon tetrachloride–methanol to give 1,2,3,4-tetrachloronaphthalene (30 mg), m.p. 194—197 °C, mixed m.p. with an authentic sample undepressed, and starting material (4) (52 mg), m.p. and mixed m.p. 99—101 °C.

The adduct (5) (0.4 g) was heated in the same way at 220 °C until no more acetylene was produced. Sublimation of the residue at 200 °C (bath) and 0.4 mmHg and recrystallisation of the sublimate from methanol afforded *2-t-butyl-4,5,6,7-tetrachloroisoindole* (17) (0.1 g, 27%), m.p. 156 °C (Found: C, 46.3; H, 3.55; N, 4.5. $C_{12}H_{11}Cl_4N$ requires C, 46.3; H, 3.6; N, 4.5%), τ 2.76 (2 H, s, 1- and 3-H) and 8.33 (9 H, s, CH_3), *m/e* 309/311/313 (M^+, 14/18/9%), 256 (10), 253/255/257 (80/100/49), 218/220/222 (12/12/4), 191/193/195 (7/7/2), 92 (15), 91 (10), 58 (8), 57 (56), 56 (6), 55 (6), and 41 (39).

The adduct (5) (0.3 g) and DMAC (0.23 g) were heated at 200 °C for 1.5 h. After cooling, the dark brown oil was dissolved in the minimum of carbon tetrachloride and chromatographed on a column of silica gel, which was eluted first with light petroleum and with benzene to remove DMAC. Then benzene–ether eluted a yellow solid which was recrystallised from methanol to afford the *adduct* (6) (0.1 g, 25%), m.p. 163—165 °C (Found: C, 47.5; H, 3.7; N, 3.05. $C_{18}H_{17}Cl_4NO_4$ requires C, 47.7; H, 3.8; N, 3.1%), $\nu_{max.}$ 1 748 cm^{-1} (C=O), τ 4.58 (2 H, s, CH), 6.18 (6 H, s, OCH_3), and 8.99 (9 H, s, CH_3), *m/e* 451/453/455 (M^+, 9/11/6%), 436/438/440 ([M − Me]$^+$, 32/41/21), 420/422/424 ([M − OMe]$^+$, 4/6/3), 404/406/408 (32/42/21), 392/394/396 ([M − CO_2Me]$^+$, 10/13/7), 377/379/381 (8/10/5), 363/365/367 (9/13/7), 366 (11), 364 (15), 349/351/353 (12/14/7), 336/338/340 (12/15/7), 309/311/313 ([M − DMAC]$^+$, 37/44/22), 274 (16), 253/255/257 (72/89/43), 243 (16), 197 (31), 165 (11), 111 (54), 105 (22), 77 (15), 59 (24), 58 (9), 57 ([C_4H_9]$^+$, 100), and 56 (34).

Reaction of 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-methyliminonaphthalene (1) *with DMAC.*—Resublimed adduct (1) [7] (3.44 g) and DMAC (5.0 g) in dioxan (25 ml) were heated under reflux for 20 h. The solvent was evaporated off *in vacuo*; the residual oil was redissolved in ether and

[23] C. F. Candy, R. A. Jones, and P. H. Wright, *J. Chem. Soc.* (*C*), 1970, 2563.

extracted with aqueous sulphuric acid (4N) to remove (1). The ether layer was washed with aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). The residue was redissolved in methanol, which slowly deposited *dimethyl* 6,7,8,9-*tetrafluoro*-3a,9b-*dihydro*-1-*methylbenz*[g]-*indole*-2,3-*dicarboxylate* (18) (1.05 g, 19% isolated, *ca.* 50% total yield including what was incompletely separated from later fractions), needles, m.p. 128—130 °C raised to 131—132 °C after further recrystallisation (Found: C, 55.1; H, 3.3; N, 3.8. $C_{17}H_{13}F_4NO_4$ requires C, 55.0; H, 3.5; N, 3.8%), $\lambda_{max.}$ 261 and 294 nm, $\nu_{max.}(CCl_4)$ 1 755 and 1 701 cm^{-1} (C=O), τ 3.33br and 4.05br (each 1 H, d, J 10 Hz, 4- and 5-H), 5.18 and 6.09 (each 1 H, d, J 11 Hz, 9b- and 3a-H), 6.13 and 6.31 (each 3 H, s, OCH_3), and 7.43 (3 H, d, $|J_{HF}|$ 3 Hz, NCH_3), δ_F 148.0 (t, F_a), 150.9 (dd, F_d), 157.9 (t of d, F_c), and 160.6 (t, F_b) p.p.m. ($|J_{ab}| = |J_{bc}| = |J_{cd}| = 21$, $|J_{ac}|$ 3, and $|J_{ad}|$ 13 Hz), *m/e* 372 (17%), 371 (M^+, 100), 340 ($[M - OMe]^+$, 26), 312 ($[M - CO_2Me]^+$, 48), 311 (52), 280 (39), 253 (35), 252 (22), 238 (15), 212 (41), 211 (14), 200 (39), and 100 (22), *m** 262.4 (371→312).

All the mother liquors from recrystallisation of the adduct (17) were combined, and methanol was evaporated off *in vacuo*. The residue was chromatographed on silica gel, from which a sticky solid was eluted with light petroleum (b.p. 30—60 °C). Sublimation of this solid at 100 °C (bath) and 20 mmHg gave 1,2,3,4-tetrafluoronaphthalene (8) (0.2 g), m.p. 107—109 °C (lit.,[24] 110—111 °C), *m/e* 200 (M^+, 100%). Further elution of the column with light petroleum–benzene returned unchanged DMAC (1.5 g). Benzene eluted orange oils (3.5 g) which afforded some solid material (1.4 g), a mixture of the isomeric adducts (18) and (23) (^1H n.m.r. spectrum). Fractional recrystallisation from cyclohexane and from methanol separated *dimethyl* (5,6,7,8-*tetrafluoro*-N-*methyl*-1-*naphthylamino*)*maleate* (23) (0.4 g, 7%), m.p. 117—118 °C (Found: C, 54.9; H, 3.6; N, 3.8%), $\lambda_{max.}$ 276 and *ca.* 310sh nm (ε 2 070 and 780 m^2 mol^{-1}), $\nu_{max.}(CCl_4)$ 1 663w, 1 710, and 1 752 cm^{-1} (C=O), τ 2.3br (1 H, d) and 2.6—3.1 (2 H, m, ArH), 5.53br (1 H, s, =CH), and 6.56, 6.63, and 6.92 (each 3 H, s, OCH_3 and NCH_3), δ_F 150.1, 151.2, 158.5, and 159.4 p.p.m. (each 1 F, m), *m/e* 371 (M^+, 23%), 340 ($[M - OMe]^+$, 14), 313 (17), 312 ($[M - CO_2Me]^+$, 100), 271 (25), 253 (53), 243 (16), 238 (18), 229 (27), 208 (16), 199 (15), 187 (13), 100 (40), and 56 (42), *m** 262.4 (371→312).

In a separate experiment the adduct (1) (5.0 g) and DMAC (6.2 g) were mixed and placed in an oil-bath at 175 °C. The flask was withdrawn as soon as a vigorous exothermic reaction occurred, after which it was heated again at 175 °C for 15 min. The mixture was cooled and the resulting tar was dissolved in ether and chromatographed on alumina (100 g). Elution with pentane (0.6 l) and pentane–ether (0.4 l, 4 : 1 v/v) gave solid (0.8 g) and oil (0.2 g): the solid was twice recrystallised from pentane and sublimed *in vacuo*, but its m.p. remained diffuse [n.m.r. spectrum showed only aromatic hydrogens, like tetrafluoronaphthalene (8)]. Further elution with pentane–ether (1 l, 1 : 1 v/v) gave an orange oil (1.2 g), which was triturated with ether to give a yellow solid (0.1 g), m.p. 147—149.5 °C. Elution with pentane–ether–dichloromethane (0.4 l, 1 : 1 : 1 v/v) gave a dark brown tar (1.6 g), which was redissolved in methanol; the solution was boiled with charcoal, filtered, and cooled to afford more of the same yellow product (0.1 g). Further recrystallisation of this from methanol gave *dimethyl* 4,5,6-*trifluoro*-1-*methyl*-1H-*benzo*[de]*quinoline*-2,3-*dicarboxylate* (26) (2.5%), yellow needles, m.p. 150—151 °C (Found: C, 58.1; H, 3.4; N, 4.0. $C_{17}H_{12}F_3NO_4$ requires C, 58.1; H, 3.4; N, 4.0%), $\lambda_{max.}$ 234, 342, and 422 nm (ε 2 660, 1 800, and 170 m^2 mol^{-1}), $\nu_{max.}$ 1 644, 1 723, and 1 738 cm^{-1} (C=O), τ 2.8—3.1 (2 H, m, 8- and 9-H), 3.79 (1 H, dd, J 6 and 2.5 Hz, 7-H), 6.14 and 6.23 (each 3 H, s, OCH_3), and 6.99 (3 H, s, NCH_3), δ_F 147.6 (d, F_a), 152.3 (d, F_c), and 162.8 (t, F_b) p.p.m. ($|J_{ab}| = |J_{bc}| = 21$ Hz), *m/e* 352 (21%), 351 (M^+, 100), 336 (15), 320 ($[M - OMe]^+$, 16), 308 (29), 287 (23), 234 (23), 233 (22), 232 (12), 221 (14), 220 (15), 219 (16), 218 (18), 207 (11), 206 (18), and 205 (12), *m** 321.6 (351→336) and 282.3 (336→308).

Aromatisation of the Adduct (18).—*p*-Cymene (30 ml) containing the dihydrobenz[*g*]indole (18) (0.4 g) and Pd–C (10%, 3.0 g) were heated under reflux for 24 h. The mixture was cooled, diluted with chloroform, and filtered. The filtrate was dried ($MgSO_4$) and evaporated to a solid residue which afforded *dimethyl* 6,7,8,9-*tetrafluoro*-1-*methyl*-*benz*[g]*indole*-2,3-*dicarboxylate* (22) (0.18 g, 38%), m.p. 164—165 °C (from benzene) (Found: C, 55.3; H, 3.0; N, 3.8. $C_{17}H_{11}F_4NO_4$ requires C, 55.3; H, 3.0; N, 3.8%), $\nu_{max.}$ 1 725 and 1 710 cm^{-1} (C=O), $\tau(C_6D_6)$ 1.36 and 2.03br (each 1 H, d, J 9 Hz, 4- and 5-H), 6.15 and 6.21 (each 3 H, s, OCH_3), and 6.34 (3 H, d, $|J_{HF}|$ 12 Hz, NCH_3), *m/e* 369 (M^+, 53%), 338 ($[M - OMe]^+$, 31), 309 (50), 280 (38), 223 (15), 111 (75), 110 (38), 97 (30), 96 (50), 95 (31), 83 (37), 82 (100), and 81 (19).

Dimethyl N-*Methyl*-1-*naphthylaminomaleate* (24).—1-Naphthyl isocyanate (3.0 g) in dry ether (10 ml) was added dropwise to a stirred mixture of $LiAlH_4$ (0.75 g) and dry ether (40 ml). After addition was complete the mixture was heated under reflux for 0.5 h, and cooled. Aqueous sodium hydroxide (4N) was added, and the ether layer was separated and dried (K_2CO_3). To this solution of *N*-methyl-1-naphthylamine cooled in ice was added DMAC (2.5 g). The mixture was then allowed to reach room temperature, ether was evaporated off *in vacuo*, and the residual oil was redissolved in methanol and chilled to obtain *dimethyl* N-*methyl*-1-*naphthylaminomaleate* (24), m.p. 14—16 °C, glass-like at room temperature, which was further recrystallised from methanol below 0 °C (Found: C, 68.4; H, 5.9; N, 4.6. $C_{17}H_{17}NO_4$ requires C, 68.2; H, 5.7; N, 4.7%), $\lambda_{max.}$ 276 and 290sh nm (ε 1 800 and 1 640 m^2 mol^{-1}), $\nu_{max.}(CCl_4)$ 1 751 and 1 706 cm^{-1} (C=O), τ 2.1—2.9 (7 H, m, ArH), 5.54br (1 H, s, =CH), and 6.50, 6.55, and 6.83 (each 3 H, s, NCH_3 and OCH_3), *m/e* 299 (M^+, 55%), 268 ($[M - OMe]^+$, 14), 240 ($[M - CO_2Me]^+$, 100), 208 (68), 180 (74), 127 ($[C_{10}H_7]^+$, 53), 100 ($MeN^+{\equiv}CCO_2Me$, 84), and 57, *m** 193 (299→240).

Addition Reactions of 5,6,7,8-*Tetrachloro*-1,4-*dihydro*-1,4-*methyliminonaphthalene* (2).—The adduct (2) (1.5 g) and DMAC (2.0 g) in benzene were heated under reflux for 4 h. The solution was cooled and extracted with aqueous hydrochloric acid (4N). The benzene layer was separated, washed with aqueous sodium carbonate and with water, and dried (K_2CO_3). The benzene was evaporated off leaving a dark oil, which was chromatographed on alumina. Light petroleum (1 l) eluted 1,2,3,4-tetrachloronaphthalene (40 mg), m.p. alone or mixed with an authentic sample 197—198 °C (lit.,[25] 198 °C). Elution with benzene (0.2 l)

[24] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227.

[25] J. v. Braun, O. Braunsdorf, P. Engelbertz, E. Hahn, G. Hahn, O. Hainback, W. Kredel, and K. Larbig, *Ber.*, 1923, **56B**, 2332.

and benzene–ether (0.5 l, 9 : 1 v/v) gave material which was redissolved in methanol and boiled with charcoal. The solute was recovered by evaporation and recrystallised from chloroform–methanol to give *dimethyl* 6,7,8,9-*tetrachloro*-3a,9b-*dihydro*-1-*methylbenz*[g]*indole*-2,3-*dicarboxylate* (19) (0.4 g, 18%), m.p. 149—153 °C (Found: C, 46.75; H, 3.0; N, 3.3. $C_{17}H_{13}Cl_4NO_4$ requires C, 46.7; H, 3.0; N, 3.2%), $\nu_{max.}$ 1 748 (C=O), 1 687, and 1 606 cm^{-1}, τ 2.93 and 3.95 (each 1 H, dd, $CH_A{=}CH_B$, $J_{4,5}$ 10 and $J_{3a,5} = J_{3a,4}$ = 2 Hz, 5- and 4-H, respectively), 4.82 (1 H, d, $J_{3a,9b}$ 10 Hz, 9b-H), 6.02 and 6.20 (each 3 H, s, OCH_3 overlapping with 1 H, m, 3a-H), and 7.38 (3 H, s, NCH_3), *m/e* 435/437/439 (M^+, 48/60/32%), 404/406/408 (15/18/10), 376/378/380 ($[M - CO_2Me]^+$, 33/38/18), 375/377/379 (50/65/35), 344/346/348 (23/30/15), 317/319/321 (14/17/9), 316/318/320 (9/13/9), 275/277/279 (15/23/12), 264/266/268 (17/28/18), 243 (12), 241 (10), 196 (15), 194 (17), 159 (7), 101 (5), 100 ($Me\overset{+}{N}{\equiv}CCO_2Me$, 100), 72 (17), 59 (27), and 56 (77).

Compound (2) (1.0 g) was heated with dibenzoylacetylene (1.6 g) in benzene under reflux. Evaporation of benzene and trituration of the residue with hot ethanol afforded 2,3-*dibenzoyl*-6,7,8,9-*tetrachloro*-3a,9b-*dihydro*-1-*methylbenz*[g]*indole* (20) (0.15 g, 15% based on reacted naphthalen-1,4-imine), m.p. 234—235 °C (from benzene) (Found: C, 59.2; H, 3.4; N, 2.4. $C_{27}H_{17}Cl_4NO_4$ requires C, 61.3; H, 3.2; N, 2.6%), $\nu_{max.}$ 1 667 cm^{-1} (C=O), *m/e* 527/529/531 (M^+, all <1%), 105 ($[PhCO]^+$, 100), and 77 (Ph^+, 42). Unchanged (2) (0.5 g) was recovered by acid extraction of the crude reaction mixture, and chromatography of the remainder separated 1,2,3,4-tetrachloronaphthalene (15%) and unchanged dibenzoylacetylene (0.8 g).

Benzenediazonium-2-carboxylate [26] [from anthranilic acid (0.7 g), isopentyl nitrite (0.6 g), and trichloroacetic acid (50 mg) in tetrahydrofuran] was slurried in 1,2-dimethoxyethane and slowly and carefully added to the adduct (2) (0.71 g) in refluxing 1,2-dimethoxyethane. The mixture was then heated under reflux for a further 0.2 h, and left at room temperature overnight. The solvent was evaporated off *in vacuo*, and the residue was chromatographed on silica gel. The solute eluted in fractions with benzene and benzene–ether was combined and recrystallised from chloroform–methanol to give 1,2,3,4-*tetrachloro*-6a,11a-*dihydro*-11-*methylbenzo*[a]*carbazole* (27) (0.2 g, 22%), m.p. 194—196 °C (Found: C, 54.7; H, 3.1; N, 3.7. $C_{17}H_{11}Cl_4N$ requires C, 55.0; H, 3.0; N, 3.8%), τ 2.6—3.3 (4 H, m, ArH), 3.52 and 4.23 (each 1 H, d, $J_{5,6}$ 8 Hz, broadened by further unresolved coupling to 6a-H, 5-, and 6-H), 5.18 and 6.12br (each 1 H, d, $J_{6a,11a}$ 8 Hz, 11a- and 6a-H), and 7.40 (3 H, s, CH_3), *m/e* 369/371/373 (M^+, 83/100/48%), 368/370/372 ($[M - H]^+$, 43/65/43), 333/335/337 (23/23/8), 332/334/336 (11/20/14), 319/321/323 (17/16/5), 299/301/303 (28/18/3), 149.5 (20), and 117 (22).

1,4-*Dihydro*-1,4-*t-butyliminonaphthalene* (7).—Benzenediazonium-2-carboxylate [26] [from anthranilic acid (4.1 g), isopentyl nitrite (3.5 g), and trichloroacetic acid (35 mg) in tetrahydrofuran] was slurried in 1,2-dimethoxyethane and added carefully over 0.5 h to *N*-t-butylpyrrole [23] (3.7 g) in 1,2-dimethoxyethane (10 ml). The mixture was heated under reflux during this addition and for a further 0.5 h. The solvent was evaporated off *in vacuo* and the oily residue was redissolved in ether. The ether solution was extracted with ice-cold aqueous hydrochloric acid (4N); the acid extract was separated, basified at once with sodium hydroxide, and re-extracted with ether. The ether layer was dried ($MgSO_4$) and the ether evaporated off leaving the naphthalen-1,4-imine (7) as an oil, i.r. (film) ν(N–H) absent, τ 3.02—3.44 (6 H, m, =CH), 5.36 (2 H, m, 1- and 4-H), and 9.11 (9 H, s, CH_3), *m/e* 199 (M^+, 34%), 184 ($[M - Me]^+$, 90), 179 (11), 169 (10), 168 (10), 143 (19), 142 ($[M - Bu^t]^+$, 100), 141 (30), 128 (37), 127 (10), 117 (77), 116 (27), 115 (37), 90 (15), 89 (15), 57 (27), and 41 (22); its *picrate* had m.p. 155—157 °C (from dioxan–methanol) (Found: C, 56.1; H, 4.7; N, 13.1. $C_{20}H_{20}N_4O_7$ requires C, 56.1; H, 4.7; N, 13.1%).

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[26] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.