Deamination of Naphthalen-1,4-imines and Anthracen-9,10-imines by Reaction with Benzyne or Dimethyl Acetylenedicarboxylate

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Bridging *N*-methyl or *N*-ethyl groups are lost from 1,4,5,8-tetrasubstituted 1,4-dihydro-1,4-epiminonaphthalene-2,3-dicarboxylates by reaction with dimethyl acetylenedicarboxylate to give the corresponding naphthalene compounds. Some 9,10-dihydro-9,10-epiminoanthracene derivatives react similarly with benzyne or with the acetylenic ester to give the corresponding anthracene and/or its Diels–Alder adduct with the same dienophile.

NAPHTHALEN-1,4-IMINES, *e.g.* (1), with ester groups at the 2- and 3-positions are readily obtained by the Diels–Alder addition of acetylenes to isoindoles,[1-3] but some isoindoles give rearranged 1 : 2 adducts with dimethyl acetylenedicarboxylate (DMAC) instead of,[3] or as well as,[2] the imine, *e.g.* (1a) ⟶ (2). An alternative synthesis of the same ring system (1) involves addition of benzynes to pyrroles.[4-6] The usefulness of this second method is limited by spontaneous aromatisation of some naphthalen-1,4-imines to α- or β-naphthylamines, and by the possibility of further addition of benzyne, *e.g.* (3a) ⟶ (4). Anthracen-9,10-imines are similarly obtainable from benzyne and isoindoles,[1,7] although further attack of benzyne can lead to the formation of 9-anilinoanthracenes where the bridgehead 9-position of the intermediate imine is unsubstituted, *e.g.* (5) ⟶ (6).[7]

An unexplained feature of some of the reactions studied by Wittig *et al.*[4,7] was the formation of small

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[1] J. C. Emmett and W. Lwowski, *Tetrahedron*, 1966, **22**, 1011.

[2] C. O. Bender, R. Bonnett, and R. G. Smith, *J. Chem. Soc.* (*C*), 1970, 1251.

[3] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1972, 904.

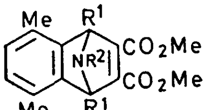
[4] (*a*) G. Wittig and W. Behnisch, *Chem. Ber.*, 1958, **91**, 2358; (*b*) G. Wittig and B. Reichel, *ibid.*, 1963, **96**, 2851.

[5] (*a*) E. Wolthuis, D. Vander Jagt, S. Mels, and A. DeBoer, *J. Org. Chem.*, 1965, **30**, 190; (*b*) E. Wolthuis and A. DeBoer, *ibid.*, 1965, **30**, 3225; (*c*) E. Wolthuis, W. Cady, R. Roon, and B. Weidenaar, *ibid.*, 1966, **31**, 2009; (*d*) L. A. Carpino and D. E. Barr, *ibid.*, p.764.

[6] (*a*) D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedron*, 1969, **25**, 25; (*b*) G. W. Gribble, N. R. Easton, jun., and J. T. Eaton, *Tetrahedron Letters*, 1970, 1075

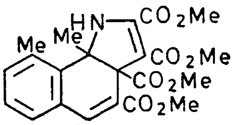
[7] G. Wittig, E. Knauss, and K. Niethammer, *Annalen*, 1960, **630**, 10.

amounts of deaminated products; naphthalene was obtained alongside the adducts (3a) and (4) of benzyne and *N*-methylpyrrole, and anthracene was found with the products (5a) and (6a) from the reaction of benzyne with *N*-phenylisoindole and alongside the adduct (6b) from benzyne and the imine (5b). An analogy is seen to the formation of dimethyl 3,4,5,6-tetraphenylphthalate from pentaphenylphosphole and DMAC at 150°, where neither the supposed intermediate (7) nor the complementary phosphorus-containing product was isolable.[8] We have established a number of related instances of deamination of naphthalen-1,4-imines and anthracen-9,10-imines, which occur in reactions of these compounds with DMAC and with benzyne.[9]

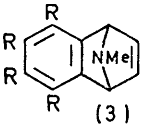


(1)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = Me, R^2 = $PhCH_2$
d; R^1 = Me, R^2 = Ph
e; R^1 = Ph, R^2 = Me
f; R^1 = Ph, R^2 = Et
g; R^1 = Ph, R^2 = $PhCH_2$
h; R^1 = R^2 = Ph

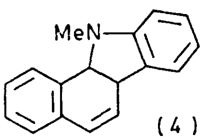


(2)



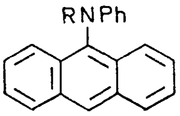
(3)

a; R = H
b; R = Cl



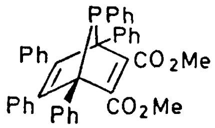
(4)

(5)

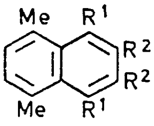


(6)

a; R = Ph b; R = Me



(7)



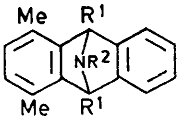
(8)

a; R^1 = Me, R^2 = CO_2Me
b; R^1 = Me, R^2 = CO_2H
c; R^1 = Me, R^2R^2 = CO·O·CO
d; R^1 = Me, R^2 = H
e; R^1 = Ph, R^2 = CO_2Me

The imine (1b) when heated with DMAC afforded in 33% yield the tetramethylnaphthalene diester (8a), the structure of which was proved by successive hydrolysis and decarboxylation to the known hydrocarbon (8d). The presence of two ester groups at adjacent ring positions in the product (8a) was confirmed by conversion of the intermediate dicarboxylic acid (8b) into the anhydride (8c). The naphthalene derivative (8e) was likewise obtained in 18 and 15% yields from the analogous reactions of the imines (1e and f) with DMAC at *ca.* 180°, respectively.

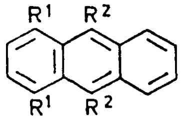
The unlikely possibility that the formation of the naphthalene (8a) involved the simple extrusion of '*N*-methyl' as a nitrene species from the precursor (1b) was discounted in view of the thermal stability of the latter compound in the absence of DMAC. Moreover, the *N*-phenylimines (1d and h) failed to react with DMAC under comparable conditions, although an easier extrusion of the more stable phenylnitrene would be anticipated.

In the anthracen-9,10-imine series, addition of DMAC in the sense of the reaction (1a) ⟶ (2) is impossible, and the aromatisation corresponding to the conversion (5) ⟶ (6) can be blocked by substituents at the 9- and 10-positions. We therefore prepared the imines (9a—c) by addition of benzyne to some polysubstituted isoindoles, which were already available from our previous work.[3] The reaction of the *N*-methylimine (9a) with DMAC at 180° provided another example of deamination, giving 1,4-dimethyl-9,10-diphenylanthracene (10a) together with its DMAC adduct, the 9,10-ethenoanthracene (11). Diels–Alder addition of other acetylenic dienophiles across the 9- and 10-positions of anthracene has been recorded previously.[10]



(9)

a; R^1 = Ph, R^2 = Me
b; R^1 = Ph, R^2 = $PhCH_2$
c; R^1 = R^2 = Ph
d; R^1 = Me, R^2 = $PhCH_2$



(10)

a; R^1 = Me, R^2 = Ph
b; R^1 = R^2 = Me
c; R^1 = H, R^2 = Ph

In contrast, the *N*-benzyl- and *N*-phenyl-imines (9b and c) were mostly recovered unchanged after heating with DMAC at 180°, although the blue fluorescence observed during work-up of the reaction of the first of these imines betrayed the presence of the anthracene (10a) in amounts too small to permit its isolation. The *N*-benzyl- and *N*-phenyl-imines (1c, d, g, and h) were similarly inert in presence of DMAC. The deamination reaction of compounds (1b, e, and f) possibly follows an initial step in which the electrophilic acetylene adds to the imine inducing ring-opening by C–N bond heterolysis to give a zwitterionic intermediate, a derivative of structure (12a); an *N*-benzyl or *N*-phenyl substituent reduces the nucleophilicity of the nitrogen

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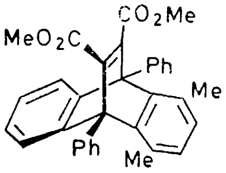
[8] E. H. Braye, W. Hübel, and I. Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

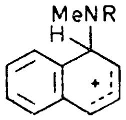
[9] Preliminary communication, L. J. Kricka and J. M. Vernon, *Chem. Comm.*, 1971, 942; presented in part at the Chemical Society Autumn Meeting, York, September, 1971.

[10] P. Baumgartner and G. Hugel, *Bull. Soc. chim. France*, 1954, **21**, 1005; C. G. Krespan and G. N. Sausen, U.S.P. 2,977,394/1961 (*Chem. Abs.*, 1962, **56**, 358e).

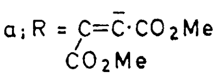
atom and the reactivity towards DMAC. The same intermediate, by cyclisation to the 2-position, accounts for the formation of adducts of the type (2).



(11)



(12)



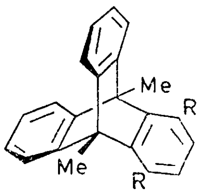
a; R = $C(CO_2Me)=\bar{C}\cdot CO_2Me$

b; R = $o\text{-}C_6H_4^-$

Attack of benzyne was also found to induce deamination of the imine (1b) to the same naphthalene (8a) as was obtained from the reaction with DMAC. The formation of *N*-methylcarbazole was detected in the reaction of benzyne with the imine (3b), although 1,2,3,4-tetrachloronaphthalene was not identified as a reaction product. (In a separate experiment tetrachloronaphthalene was shown not to survive under the conditions used for generation of benzyne, although its fate was not determined.) For the conversion (3a) ⟶ (4) a zwitterionic intermediate benzyne adduct (12b) is likely (*cf.* refs. 4*a* and 5*c*). This same intermediate could also account for the formation of naphthalene and *N*-methylcarbazole by reaction with a second molecule of benzyne or, more likely, with a benzyne precursor.

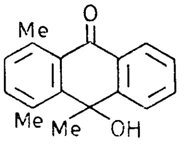
In the preparation of the anthracen-9,10-imines (9a—c) formation of deaminated by-products of further reactions with benzyne was not observed. On the other hand, addition of benzyne to 2-benzyl-1,3,4,7-tetramethylisoindole gave unexpectedly a hydrocarbon product, $C_{24}H_{22}$, instead of the adduct (9d). The product is formulated as the tetramethyltriptycene (13a) on the basis of its simple benzenoid u.v. absorption and other spectroscopic evidence. The n.m.r. spectrum shows, besides aromatic hydrogen atoms, the signals due to two pairs of magnetically equivalent methyl groups at τ 7·41 and 7·45. The known dimethyltriptycene (13b)[11] synthesised for comparison showed the corresponding absorption due to the methyl groups at τ 7·65. For an independent synthesis of the triptycene (13a) we required 1,4,9,10-tetramethylanthracene (10b), but all our attempts to prepare the latter compound *via* bis-Grignard or Wittig reactions on 1,4-dimethylanthraquinone were unsuccessful. The Grignard reactions with methylmagnesium iodide even under vigorous conditions gave only 10-hydroxy-1,4,10-trimethyl-9-anthrone (14), the product of monomethylation (*cf.* ref. 12).

In order to account for the formation of the triptycene (13a) we envisage benzyne-induced deamination of the intermediate anthracen-9,10-imine (9d) to form the anthracene (10b), which then adds another molecule of benzyne across the 9- and 10-positions. When the reaction of the same isoindole was repeated using a large excess of benzyne precursor, the formation of *N*-benzylcarbazole was detected. The mechanism of deamination presumably involves formation of a benzo-derivative of the intermediate (12b) and its further reaction with benzyne, and this also accounts for the formation of anthracene itself in those reactions[7] of the anthracen-9,10-imines (5a and b) with benzyne already cited.



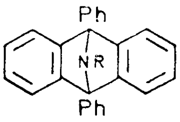
(13)

a; R = Me
b; R = H



(14)

Formally analogous to these deaminations, although probably dissimilar to them in mechanism, is a reaction described by Emmett and Lwowski.[1] 9,10-Diphenylanthracene (10c) was formed from the anthracen-9,10-imine (15) in cyclohexane at 215°, but whether or not



(15) R = CO_2Et

by extrusion of ethoxycarbonylnitrene could not be established, since the expected cyclohexyl urethane was not identified. Our tentative outline of a mechanism for the deaminations of naphthalen-1,4-imines and anthracen-9,10-imines by reaction with benzyne is based upon the evidence provided by our identification of carbazole derivatives as by-products in two instances. For the deaminations induced by DMAC it is precisely our failure so far to identify any nitrogen-containing product which inhibits discussion of a likely mechanism. Our search in this direction continues.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene. ^1H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Low resolution mass spectra were recorded with an A.E.I. MS 12 instrument operating at 70 eV, with a direct insertion probe and with facility for rapid scanning of g.l.c. peaks. High resolution mass spectra were obtained through the Physico-Chemical Measurements Unit, Aldermaston. G.l.c. analyses were performed on a column (1·6 m × 4 mm) containing silicone gum rubber SE 30 as stationary phase. Alumina for chromatography was Laporte type H, in some cases deactivated prior to use by being intimately mixed with

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[11] W. Theilacker, U. Berger-Brose, and K.-H. Beyer, *Chem. Ber.*, 1960, **93**, 1658; P. de Koe, A. J. van Bennekom, and J. Coops, *Rec. Trav. chim.*, 1963, **82**, 1051.

[12] M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Non-metallic Substances,' Constable, London, 1954, p. 529 ff.

10% w/w of 5% aqueous acetic acid. Light petroleum was the fraction b.p. 60—80°, unless otherwise stated.

The 1,4-dihydro-1,4-epiminonaphthalenes (1b—h) were obtained by reactions of the corresponding isoindoles with dimethyl acetylenedicarboxylate.[3]

Reaction of Naphthalen-1,4-*imines with Dimethyl Acetylenedicarboxylate*.—A mixture of the *N*-methylimine (1b) (10 g) and the acetylenic ester (18 g) was heated in an oil-bath at 110°; an exothermic reaction occurred, causing the acetylenic ester to distil from the flask. Heating at 110° was continued for 6 h, after which the resulting black tar was dissolved in the minimum quantity of benzene and chromatographed on deactivated alumina (350 g). The column was eluted with light petroleum–benzene (9 : 1 and 7 : 3 v/v) to yield *dimethyl* 1,4,5,8-*tetramethylnaphthalene*-2,3-*dicarboxylate* (8a) (2·3 g, 33%), m.p. 120° (from light petroleum–benzene) (Found: C, 71·9; H, 6·9. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7%), $\nu_{max.}$ 1740s and 1710s (C=O), 1240, 1205 (C–O), 1050, 845, and 835 cm^{-1}, τ 2·84 (2H, s, 6- and 7-ArH), 6·13 (6H, s, OCH_3), and 7·31 (12H, s, $ArCH_3$), *m/e* 301 (11%), 300 (M^+, 54), 270 (10), 269 (54), 268 (100), 254 (11), 253 (46), 225 (11), 211 (15), 210 (47), 209 (11), 197 (10), 182 (23), 181 (10), 167 (17), 166 (14), 165 (27), 153 (11), and 152 (13), m^* 239 ($300 \longrightarrow 268$), 215, and 158 ($210 \longrightarrow 182$). Further elution of the column with light petroleum–benzene mixtures gave only brown oils.

The *N*-benzylimine (1c) (0·7 g) was heated with the acetylenic ester (1·0 g) for 4·5 h at 100—110°. The mixture crystallised on cooling, and a portion of the solid was removed and dried; its m.p. (105°) and i.r. spectrum showed it to be unchanged (1c).

The *N*-phenylimine (1d) (6·0 g) and the acetylenic ester (6·0 g) in bis-(2-methoxyethyl) ether (15 ml) were heated at reflux temperature for 18 h. The mixture was evaporated to half bulk and the residue chromatographed on deactivated alumina (250 g). Elution with light petroleum–benzene mixtures gave unchanged (1d) (3·1 g, 52%), identified by m.p. and i.r. spectrum. Further elution gave brown oils which were not characterised.

The *N*-methylimine (1e) was recovered unchanged after being heated with the acetylenic ester under nitrogen at 110—120° for 5 h. A second batch of the imine (1e) and the acetylenic ester (6 ml) was heated under nitrogen at 170—180° for 4 h. The resulting tar was dissolved in chloroform (6 ml) and chromatographed on deactivated alumina (150 g). Elution with light petroleum–benzene mixtures afforded first an unidentified by-product (0·15 g), m.p. 93—94° (from light petroleum–benzene), and then *dimethyl* 5,8-*dimethyl*-1,4-*diphenylnaphthalene*-2,3-*dicarboxylate* (8e) (0·3 g, 18%), needles, m.p. 238—239·5° (from methanol) (Found: C, 79·1; H, 5·8. $C_{28}H_{24}O_4$ requires C, 79·2; H, 5·7%), $\nu_{max.}$ 1745 and 1723 (C=O), 1275br, 1160br (C–O), 830, 770, and 710 cm^{-1}, τ 2·4—2·6 (10H, m, ArH), 2·70 (2H, s, 6- and 7-ArH), 6·61 (6H, s, OCH_3), and 8·14 (6H, s, $ArCH_3$), *m/e* 425 (22%), 424 (M^+, 100), 393 (M – OMe, 22), 391 (18), 378 (13), 377 (43), 333 (15), 305 (15), 291 (16), 290 (20), 289 (35), 145 (28), 105 (41), and 77 (26), m^* 335 ($424 \longrightarrow 377$). Further elution of the column with benzene and benzene–ether gave yellow oils, which were combined and rechromatographed on alumina for isolation of a further small quantity of the diester (8e). The upfield shift of the n.m.r. signal for the methyl groups at the 5- and 8-positions in compound (8e) compared to its position in the related compound (8a) reflects *peri*-interactions: hydrogen atoms in these methyl groups are diamagnetically shielded by the phenyl substituents at the 1- and 4-positions in (8e), which are twisted out of the plane of the naphthalene ring system (*cf.* 5-methyl-1,2,3,4-tetraphenylnaphthalene [13]).

The *N*-ethylimine (1f) (0·8 g) and the acetylenic ester (3 ml) were heated under nitrogen at 180—200° for 2·5 h. The resulting brown oil in benzene (8 ml) was chromatographed on deactivated alumina (150 g). Elution with light petroleum–benzene mixtures gave initially unchanged starting material (1f) (0·32 g, 40%), identified by m.p. and i.r. spectrum, followed by the naphthalene diester (8e) (0·11 g, 15%), m.p. and mixed m.p. 232—233°. Elution with benzene and with benzene–ether gave yellow oils which were not characterised.

The *N*-benzylimine (1g) (1·2 g) and the acetylenic ester (3 ml) were heated under nitrogen at 185—200° for 2·5 h. After cooling, the tarry product was dissolved in benzene (15 ml) and chromatographed on deactivated alumina (150 g). Elution with light petroleum–benzene mixtures gave unchanged starting material (1g) (0·77 g, 64%), identified by mixed m.p. and i.r. spectrum. Further elution with benzene gave an unidentified ester (0·08 g) as plates, m.p. 116—118°, $\nu_{max.}$ 1740br (C=O), 1610br, and 1290br (C–O) cm^{-1}, τ 5·75, 6·05, 6·15, and 6·20 (four singlets of equal intensity, OCH_3?).

The *N*-phenylimine (1h) (1·0 g) and the acetylenic ester (3 ml) were heated together and the tarry product was worked up as described in the preceding paragraph. The starting material (1h) (57%), m.p. and mixed m.p. 216—217°, i.r. spectrum unchanged, and the same unidentified ester, m.p. 116—118°, were isolated by column chromatography.

Degradation of the Naphthalene Diester (8a).—A mixture of the diester (8a) (2·3 g) in methanol (40 ml) and potassium hydroxide (10 g) in water (10 ml) was heated under reflux for 3 days, then it was cooled and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed, and dried to give 1,4,5,8-tetramethylnaphthalene-2,3-dicarboxylic acid (8b) (1·7 g, 80%), m.p. 285°, $\nu_{max.}$ 3600br (O–H), 1685br (C=O), 1595, 1265br (C–O), 1160, 940br, 825s, and 720 cm^{-1}. A portion of the diacid (8b) was refluxed with acetic anhydride. The solid which separated on cooling was the *anhydride* (8c), m.p. 258° (from benzene) (Found: C, 75·4; H, 5·6. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%), $\nu_{max.}$ (O–H absent) 1840, 1800, and 1750 (anhydride), 1620, 1460, 1395, 1240, 1210 (C–O), 950s, 875s, and 770s cm^{-1}.

An intimate mixture of the diacid (8b) (1·6 g) and soda lime (18 g) was covered with an equal bulk of soda lime and heated with a free flame until a small quantity of red solid distilled from the flask. After cooling the flask, both its contents and the distillate were extracted with ether. These extracts were combined and evaporated, and the remaining solid was recrystallised (charcoal) to give 1,4,5,8-tetramethylnaphthalene (8d), m.p. 128° (from ethanol) (lit.,[14] 131°), which was converted into the picrate, m.p. 153° (from light petroleum) (lit.,[14] 154°).

Preparation of Anthracen-9,10-*imines* (9a—c).—Benzyne was generated in each case by reaction of *o*-bromofluorobenzene with magnesium in dry tetrahydrofuran in which was dissolved one of the appropriate isoindoles under

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[13] R. Harrison, H. Heaney, and P. Lees, *Tetrahedron*, 1968, **24**, 4589.

[14] J. Colonge and L. Pichat, *Compt. rend.*, 1948, **226**, 673.

nitrogen. The mixture was usually refluxed for 1—2 h, then worked up by pouring into aqueous ammonium chloride, separating the organic layer, drying it ($MgSO_4$), and evaporating off the tetrahydrofuran. A yellow oil obtained in this way using 2,4,7-trimethyl-1,3-diphenylisoindole[3] was chromatographed on alumina, from which light petroleum–benzene eluted first triphenylene, m.p. 198—199° (lit.,[15] 198°) and then 9,10-*dihydro*-1,4,11-*trimethyl*-9,10,*diphenyl*-9,10-*epiminoanthracene* (9a) (30%), obtained as prisms, m.p. 155—156° (from light petroleum) (Found: C, 90·0; H, 6·5; N, 3·6. $C_{29}H_{25}N$ requires C, 89·9; H, 6·5; N, 3·6%), $\nu_{max.}$ 1610w, 1500, 1310, 1140br, 820w, 750, and 715 cm^{-1}, τ 1·9—3·1 (14H, m, ArH), 3·43 (2H, s, 2- and 3-ArH), 8·24 (6H, s, $ArCH_3$), and 8·40 (3H, s, NCH_3), *m/e* 388 (15%), 387 (M^+, 65), 386 (100), 372 (M — Me, 9), 310 (6), 296 (6), 269 (10), 253 (10), 252 (12), 119 (13), 118 ($PhC\equiv\overset{+}{N}Me$, 95), 91 (13), 78 (10), and 77 (23), m^* 357 (387 $\longrightarrow$ 372).

The same procedure using 2-benzyl-4,7-dimethyl-1,3-diphenylisoindole[3] gave a yellow oil which was chromatographed on alumina. Elution with light petroleum–benzene gave triphenylene and 11-*benzyl*-9,10-*dihydro*-1,4-*dimethyl*-9,10-*diphenyl*-9,10-*epiminoanthracene* (9b) (73%), obtained as prisms, m.p. 152—153° (from light petroleum) (Found: C, 90·9; H, 6·0; N, 3·1. $C_{35}H_{29}N$ requires C, 90·7; H, 6·3; N, 3·0%), $\nu_{max.}$ 1600w, 1500, 1120, 1040, 810, 770, 730, and 710 cm^{-1}, τ 1·9—3·4 (19H, m, ArH), 3·45 (2H, s, 2- and 3-ArH), 6·74 (2H, s, NCH_2), and 8·29 (6H, s, $ArCH_3$), *m/e* 464 (18%), 463 (M^+, 59), 462 (56), 448 (M — Me, 5), 386 (M — Ph, 8), 373 (25), 372 (M — CH_2Ph, 55), 358 (M — NCH_2Ph, 9), 269 (36), 254 (14), 253 (24), 252 (23), 239 (15), 180 (12), 92 (12), 91 ($PhCH_2^+$, 100), and 77 (17), m^* 296 (463 $\longrightarrow$ 372).

The same procedure using 4,7-dimethyl-1,2,3-triphenylisoindole[3] gave a yellow oil which slowly crystallised after trituration with a little acetone. 9,10-*Dihydro*-1,4-*dimethyl*-9,10,11-*triphenyl*-9,10-*epiminoanthracene* (9c) was thereby obtained (77%), m.p. 215—217° (from light petroleum–benzene) (Found: C, 90·8; H, 6·3; N, 3·1. $C_{34}H_{27}N$ requires C, 90·8; H, 6·1; N, 3·1%), $\nu_{max.}$ 1600w, 1500, 1060br, 830w, 750, and 715 cm^{-1}, τ 2·0—3·0 (19H, m, ArH), 3·43 (2H, s, 2- and 3-ArH), and 8·26 (6H, s, $ArCH_3$), *m/e* 450 (31%), 449 (M^+, 100), 448 (86), 434 (M — Me, 7), 372 (M — Ph, 10), 181 (11), 180 ($PhC\equiv\overset{+}{N}Ph$, 74), and 77 (46), m^* 420 (449 $\longrightarrow$ 434) and 308 (449 $\longrightarrow$ 372).

Reaction of Anthracen-9,10-*imines with Dimethyl Acetylenedicarboxylate*.—The *N*-methylimine (9a) (0·9 g) and the acetylenic ester (3 ml) were heated together at 170—180° for 3·5 h. The tarry mixture was then dissolved in benzene–chloroform (10 ml; 3 : 1 v/v) and chromatographed on deactivated alumina (150 g). The eluate obtained with light petroleum exhibited an intense blue fluorescence and afforded on evaporation 1,4-dimethyl-9,10-diphenylanthracene (10a) (0·22 g, 26%) as pale yellow needles, m.p. 191—192° (lit.,[16] 189°), $\nu_{max.}$ 1600w, 1090, 1035, 835, 770, and 710 cm^{-1}, τ 2·3—2·8 (14H, m, ArH), 3·02 (2H, s, 2- and 3-ArH), and 8·09 (6H, s, $ArCH_3$), *m/e* 358 (M^+, 58%), 228 (55), and 210 (100). Further elution of the column with light petroleum–benzene (7 : 3 v/v) gave *dimethyl* 9,10-*dihydro*-1,4-*dimethyl*-9,10-*diphenyl*-9,10-*ethenoanthracene*-11,12-*dicarboxylate* (11) (0·16 g, 14%) as prisms, m.p. 218—219° [from light petroleum–benzene (1 : 2 v/v)] [Found: C, 81·1; H, 5·6%; M (mass spec.), 500·1979. $C_{34}H_{28}O_4$ requires C, 81·6; H, 5·6%; M, 500·1988], $\nu_{max.}$ 1720 (C=O), 1310, 1270 (C–O), 1090, 1040, 790, 740, and 710 cm^{-1}, τ 2·4—3·0 (14H, m, ArH), 3·60 (2H, s, 2- and 3-ArH), 6·36 (6H, s, OCH_3), and 8·68 (6H, s, $ArCH_3$), *m/e* 501 (25%), 500 (M^+, 71), 470 (24), 469 (M — OMe, 67), 441 (M — CO_2Me, 55), 440 (100), 437 (24), 436 (52), 424 (17), 407 (36), 406 (19), 381 (38), 380 (60), 379 (19), 365 (25), 364 (27), 363 (28), and 288 (30). Further elution of the column with light petroleum–benzene and benzene–chloroform mixtures gave brown oils from which nothing could be characterised.

The *N*-benzylimine (9b) (1·5 g) and the acetylenic ester (3 ml) were heated together at 170—180° for 1 h. The tarry product was dissolved in benzene (10 ml) and chromatographed on deactivated alumina (150 g). The first fractions eluted with light petroleum were blue-fluorescent, suggesting the presence of the anthracene (10a), but on evaporation there was obtained only the starting material (9b) (1·1 g, 73%), m.p. and mixed m.p. 152—154°. Elution with light petroleum–benzene mixtures gave oils which were not characterised.

The *N*-phenylimine (9c) was heated with the acetylenic ester at 170—180° for 1 h. The resulting tar dissolved in hot light petroleum–benzene (1 : 1 v/v); on cooling this solution the starting material (9c) (67%), m.p. and mixed m.p. 216—217°, was recovered.

Reaction of Naphthalen-1,4-*imines with Benzyne*.—Benzyne was generated from *o*-bromofluorobenzene (19·4 g) and magnesium (2·0 g) in dry tetrahydrofuran (30 ml) containing the *N*-methylimine (1b) (6·23 g). The usual work-up procedure gave a brown oil, which was shown to contain the naphthalene diester (8a) by g.l.c. comparison with an authentic sample. The crude product was chromatographed on deactivated alumina (400 g), from which light petroleum eluted triphenylene and later fractions eluted with light petroleum–benzene and benzene–ether mixtures contained the product (8a), still contaminated with other, unidentified material.

The *N*-methylimine (3b)[6b] (1·0 g) in dry tetrahydrofuran (20 ml) was treated with benzyne generated from *o*-bromofluorobenzene (2·0 g) and magnesium. The brown oil obtained after the usual work-up was shown to contain *N*-methylcarbazole by g.l.c. comparison with an authentic sample. The presence of the expected 1,2,3,4-tetrachloronaphthalene was not detected, and the only crystalline product isolated by subsequent chromatography of the oil on alumina (150 g) was triphenylene (0·1 g), m.p. 196—198° (lit.,[15] 198°).

Reaction of Benzyne with 2-*Benzyl*-1,3,4,7-*tetramethylisoindole*.—The isoindole[17] (15 g) in tetrahydrofuran was treated with benzyne generated *in situ* from *o*-bromofluorobenzene (10 g) and magnesium (1·5 g). After 2 h at reflux temperature the mixture was cooled, poured into aqueous ammonium chloride, and extracted with benzene. Evaporation of the dried ($MgSO_4$) benzene extract afforded 9,10-*dihydro*-1,4,9,10-*tetramethyl*-9,10-o-*benzenoanthracene* (13a) (3·35 g, 24%), m.p. 290—291° (from light petroleum–benzene) (Found: C, 92·8; H, 7·2. $C_{24}H_{22}$ requires C, 92·9; H, 7·1%), $\nu_{max.}$ 1035, 810, 790, 755, and 730 cm^{-1}, τ 2·5—3·1 (8H, m, ArH), 3·43 (2H, s. 2- and 3-ArH), and 7·41 and 7·45 (each 6H, s, $ArCH_3$), *m/e* 311 (14%), 310 (M^+, 57), 296 (23), 295 (M — Me, 100), 281 (18), 280

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[17] C. O. Bender and R. Bonnett, *J. Chem. Soc.* (*C*), 1968, 3036.

(71), 279 (20), 265 (17), and 140 (15), *m** 281 (310 ⟶ 295), 265 (295 ⟶ 280), and 251 (280 ⟶ 265). The mass spectrum of the crude product contained intense peaks attributable to the *N*-benzylimino-adduct (9d) [*m*/*e* 339 (M^+), 248 ($M - CH_2Ph$), and 91 ($PhCH_2^+$)], but this material was not isolable by chromatography on alumina.

The reaction was repeated with a five-fold excess of benzyne precursor. After work-up an oil was obtained in which g.l.c. analysis showed the presence of unchanged isoindole, its autoxidation product, *N*-benzyl-3,6-dimethylphthalimide,[18] and *N*-benzylcarbazole, all with retention times identical with those of authentic materials. Of these only the phthalimide, m.p. and mixed m.p. 125—126°, was separated by chromatography on alumina.

Attempted Preparation of 1,4,9,10-*Tetramethylanthracene*.—1,4-Dimethylanthraquinone [19] (23 g) in dry ether (300 ml) was added dropwise to a stirred ethereal solution of methylmagnesium iodide [from methyl iodide (28 g) and magnesium (6 g)]. The mixture was stirred at room temperature for 10 h, then poured into ice-cold aqueous sulphuric acid (2M; 150 ml). The ether layer was separated, washed with water, and dried (K_2CO_3). Evaporation left an orange oil which was triturated with a little ether to give 10-*hydroxy*-1,4,10-*trimethyl*-9-*anthrone* (14) (20 g, 80%), m.p. 90—92° (from ethanol) (Found: C, 80·9; H, 6·5. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·3), $\nu_{max.}$ 3500br (O–H), 1745br (C=O), 1600, 1505s, 1285, 1270, 1250 (C–O), 1125s, 1090s, 1040, 940, 925s, 835s, 765s, 740s, and 700 cm^{-1}, $\tau[(CD_3)_2CO]$ 1·9—2·6 (4H, m, ArH), 2·93 (2H, s, 2- and 3-ArH), and 7·78, 7·96, and 8·00 (three singlets, each 3H, CH_3), *m*/*e* 252 (M^+, 24%), 238 (17), 237 (M — Me, 100), 219 (6), 207 (38), 193 (13), 192 (16), 178 (15), 165 (15), 147 (24), 91 (16), and 77 (14), *m** 233 (252 ⟶ 237), 202 (237 ⟶ 219), and 170 (252 ⟶ 207). Several further attempts using excess of Grignard reagent, longer reaction times, or more vigorous conditions gave only the same product (14).

[2/1509 *Received*, 28*th June*, 1972]

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[19] J. von Braun and O. Bayer *Ber.*, 1926, **59**, 914.