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BIPHENYLENES—XXXI[1]

CONDENSATION OF BENZOCYCLOBUTENE-1,2-DIONE WITH ALIPHATIC AND HETEROCYCLIC 1,2-DIAMINES AND THE SYNTHESIS OF *cis*-2-CYANO-3-(2′-CYANOVINYL)-1,4-DIAZABIPHENYLENE

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Abstract—As possible routes to 1,4-diazabiphenylene and its 2,3-disubstituted derivatives we have studied the condensation of benzocyclobutene-1,2-dione (BBD) with various 1,2-diamines. Instead of giving the 1,4-diazabiphenylene ring system, BBD reacted with ethylenediamine, diaminomaleonitrile, 4,5-diaminopyrimidine, 2-aminopyridine, also 2,3- and 3,4-diaminopyridine to give, respectively, 2-*o*-carboxyphenylimidazolidinium acetate **4**, 3,4-dicyano-2,5-dihydro[2,5]benzodiazocine-1,6-dione **10**, 4-amino-5a,9b-dihydro-5-,9b-dihydroxybenzo [3′,4′]cyclobuta[1′,2′-4,5]imidazo[1,2-*c*]pyrimidine **14**, 5a,9b-dihydro-5a,9b-dihydroxybenzo[3′,4′]cyclobuta[1′,2′-4,5] imidazo[1,2-*a*]pyridine **17**, the 4-amino derivative **16** of the latter, and the zwitter ion **18** of 4-amino-3(2-carboxybenzylideneamino)-pyridine. However, BBD reacted with 4,5-diaminobenzotriazole to give the expected 1,2,3,6,11-penta-aza-1-H-indeno [4,5-*b*]biphenylene **20**, which, on amination followed by oxidation, gave a very low yield of *cis*-2-cyano-3-(2′-cyanovinyl)-1,4-diazabiphenylene **3**. In model experiments, 7,8-diphenylfurazano [3,4-*f*]quinoxaline **28** was reduced to 2,3-diamino-5,6-diphenyl quinoxaline **29**, which on oxidation, gave a mixture of *cis*- and *trans*-2-cyano-3-(2′-cyanovinyl)5,6-diphenylpyrazine, **30** and **31**. The pentacyclic compounds, 1,3,6,11-tetra-aza-2-oxa-2H-indeno [4,5-*b*]biphenylene **23** and 1,3,5,10-tetra-aza-1-H-indeno[5,6-*b*] biphenylene **25**, were formed from BBD and the appropriate 1,2-diamines but the 5-membered heterocyclic rings could not be cleaved by reduction and hydrolysis respectively) to give tetracyclic diamines which might have undergone oxidation to give derivatives of 1,4-diazabiphenylene. Compounds **14**, **16**, **20**, **23**, **25** and **28** are derivatives of new heterocyclic systems.

The previous paper in this series[1] described our attempts to degrade some benzo-substituted 5,10-diazabenzo[*b*]biphenylenes to 2,3-disubstituted 1,4-diazabiphenylenes with the ultimate intention of preparing 1,4-diazabiphenylene itself. As part of a similar approach we have studied the condensation of benzocyclobutene—1,2-dione (BBD) with some aliphatic and heterocyclic 1,2-diamines. Although these reactions did not lead to the desired ring system they gave a variety of products including derivatives of six new fused heterocyclic systems. Further work, involving the cleavage of a benzene ring of a 5,10 - diazabenzo[*b*]biphenylene (see previous paper[1]), has led to the synthesis of *cis* - 2 - cyano - 3(2′ - cyanovinyl) - 1,4 - diazabiphenylene **3**, but attempts to degrade this to the parent compound **1** have been discontinued because of the low yields at the final stages and because compound **1** has recently been synthesised by an alternative route.[2]

Condensation with ethylenediamine. 1,2-Diones are known to condense with ethylenediamine to give dihydropyrazines which readily aromatise by loss of hydrogen either spontaneously or on heating. However, the reaction of BBD with ethylenediamine did not give 2,3 - dihydro - 1,4 - diazabiphenylene nor the parent compounds **1**. When the reaction was carried out in pyridine containing acetic acid it gave 2 - *o* - carboxyphenylimidazolidinium acetate **4**. The reaction does not proceed via hydrolysis of the dione to phthalaldehydic acid since condensation of the latter with ethylenediamine under the same conditions gave the "open-chain" compound **5**. The latter exists in the zwitterion form **5** as shown by its IR and NMR spectra and by its sparing solubility in organic solvents. The mass spectra of compounds **4** and **5** are almost identical and can be rationalised if it is assumed that when the compounds are volatilised they are both converted into a mixture of imidazolidine **6** and phthalide **7** each of which undergoes fragmentation in the mass spectrometer. Thus one set of *m/e* values, after dehydration, (M^+ 192→174, 173, 145, 117, 90) is the same as that given by an authentic specimen of the isoindolone **9** (M^+ 174) made by refluxing phthalaldehydic acid with ethylenediamine in methanol for 17 hr.[3] The other set [M^+ 192→133 (M^+ –$NHCH_2CH_2NH_2$)→105→77] is similar to that of 3-ethoxyphthalide **8** [M^+ 178→133 (M^+ –OEt)→105→77].

Condensation with diaminomaleonitrile. Reaction of the nitrile with BBD at room temperature gave the diazocine **10** instead of the expected diazabiphenylene **2**. The overall reaction involves loss of two atoms of hydrogen but the reaction mechanism is unknown. The IR spectrum of **10** in Nujol showed bands at 3220(NH), 2206(CN), 1700, 1668 and 1645(CO) cm^{-1} similar to those of the diazocine **11**, i.e. 3180 and 1647br (3180 and

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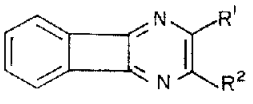
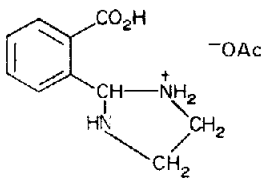


1: $R^1 = R^2 = H$
2: $R^1 = R^2 = CN$
3: $R^1 = CN$, $R^2 = cis\ CH_a:CH_bCN$



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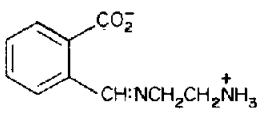

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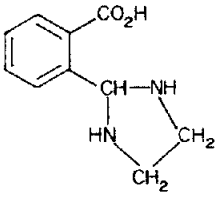

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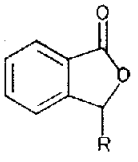
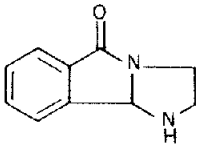


7: $R = NHCH_2CH_2NH_2$
8: $R = OEt$



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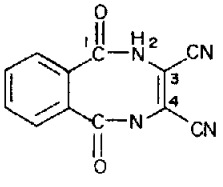

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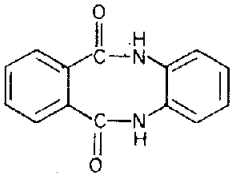

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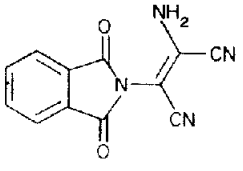

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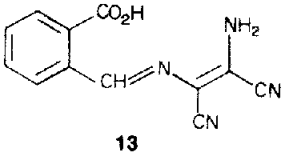

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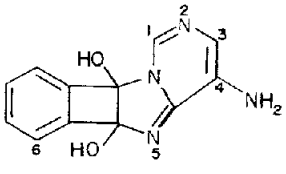

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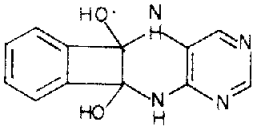

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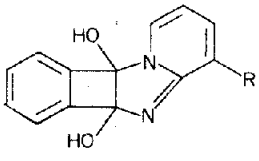
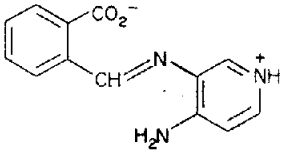


16: $R = NH_2$
17: $R = H$



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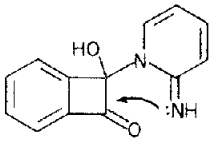

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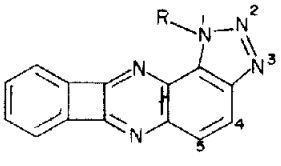
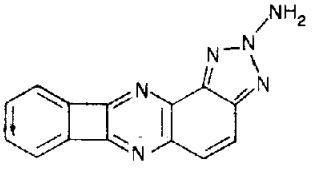


20: $R = H$
21: $R = NH_2$



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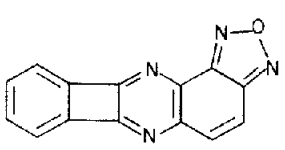

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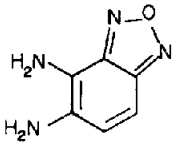

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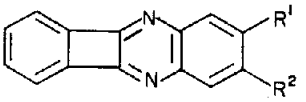
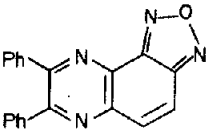


25: R^1R^2 = NH·CH:N
26: R^1R^2 = NAc·CH:N
27: R^1 = R^2 = NH_2



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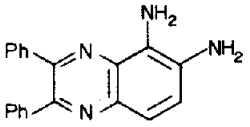

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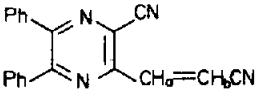
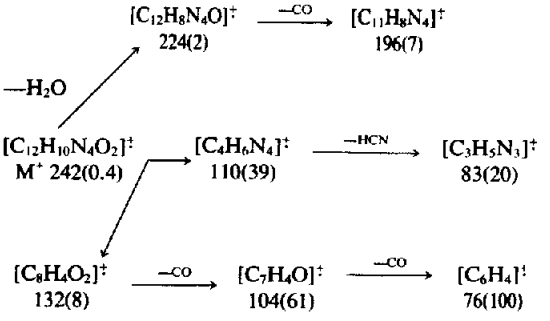


30: *Cis*-isomer
31: *Trans*-isomer

1695 cm^{-1} in KBr disc[4]). The NMR spectrum of **10** in d_6 DMSO showed only a symmetrical AA'BB' multiplet at τ 2.40 (aromatic H) and a very broad absorption at *ca.* −0.4 (NH) (addition of D_2O caused precipitation): the corresponding values for the diazocine **11** are τ 2.72 and −0.06.[1] When attempts were made to recrystallise compound **10** it underwent isomerisation to give the known compound, 2 - amino - 3 - phthalimidomaleonitrile **12**.[5] The mass spectra of **10** and **12** are almost identical except for slight differences in the relative intensities of the fragment ions, suggesting that both compounds dehydrate to give the same compound (and hence the same fragmentation pattern) in the mass spectrometer, thus for compounds **10** and **12** the main ions (%) are respectively, M^+ 238 (20 and 40%) $-H_2O \rightarrow$ 220 (27 and 30%) $-CN \rightarrow$ 194 (100 and 100%) $-C_4N_3 \rightarrow$ 104 (77 and 64%) $-CO \rightarrow$ 76 (80 and 67%). Diaminomaleonitrile is a weak base and it evidently reacts with BBD as such since condensation of the nitrile with phthalaldehydic acid gave the Schiff base **13**. Attempts to prepare the diazocine **10** by heating the nitrile with diethyl phthalate (see Ref. 4) were unsuccessful.

Condensation with amino-pyrimidines and -pyridines. The pyrimidine ring of pteridine (pyrimido[4,5-*b*]pyrazine) is readily cleaved by acids and bases to give 2 - amino - 3 - formylpyrazine. We therefore studied the condensation of BBD with 4,5 - diaminopyrimidine (pK_a 6.04[6]) in the hope of obtaining benzocyclobutenopteridine and thence, by hydrolysis, a derivative of 1,4-diazabiphenylene. However, this reaction gave a colourless compound **A**, $C_{12}H_{10}N_4O_2$, which was insoluble in all common organic solvents. Its IR spectrum showed absorptions above 3000 cm^{-1} characteristic of both amino and of hydroxy groups, but no absorptions in the carbonyl region. The compound was stable to prolonged heating at 110° and 0.01 Torr but attempted sublimation at 190° and 0.1 Torr gave a sublimate consisting of a mixture of the original dione and diamine. Similarly, treatment with 0.5 M sulphuric acid regenerated BBD. More vigorous treatment with concentrated hydrochloric acid in ethanol gave 3-ethoxyphthalide **8**. Attempts to gain other evidence by chemical reactions were unsuccessful.

The NMR spectrum of compound **A** could not be measured: the compound was insoluble in deuteriochloroform, and in dimethyl sulphoxide dissociation occurred and the spectrum corresponded to a 1:1 mixture of BBD and diaminopyrimidine. The mass spectrum of compound **A** showed that only one molecule of water was lost on electron impact and the main fragmentation pathway involved the dissociation of the compound into its two precursors. The mass spectrum, *m/e* (%) is shown diagramatically below.



Thus the evidence discussed so far indicates that the C–O skeleton of BBD is still present in compound **A** and is compatible with structures **14** and **15**. Structure **15** would be expected to undergo dehydration very easily whereas structure **14** could not undergo dehydration unless a molecular rearrangement took place. Further support for structure **14** comes from studies of the reaction of BBD with 2,3- and 3,4-diamino-pyridine. Clearly the 2,3-diamine could yield a product **16** with a structure analogous to that of **14** whereas the 3,4-diamine could not. In fact, condensation of BBD with 2,3-diaminopyridine (pK_a 6.88[6]) gave a very sparingly soluble compound **B** whose IR and mass spectra were very similar to those of compound **A**. In particular the mass spectrum showed that the main fragmentation products were ions derived from BBD and 2,3-diaminopyridine. In contrast, reaction of BBD with 3,4-diaminopyridine (pK_a 9.14[6]) gave compound **C** whose properties were quite different from those of compounds **A** and **B**. The structure of **C** is discussed below.

In order to obtain more information about compounds **A** and **B** we attempted to condense BBD with 2 - amino - 4,6 - dimethylpyrimidine (pK_a 4.85[6]) and 4-aminopyridimidine (pK_a 5.71[6]) but there was no reaction even after 48 hr at room temperature. However, BBD reacted with the stronger base, 2-aminopyridine (pK_a 6.86[6]) to give a product **D** which probably has structure **17**. The IR spectrum of compound **D** shows the presence of

hydroxyl and absence of carbonyl groups, and hydrolysis of **D** regenerated BBD. A sample of compound **D** was silylated and the mass spectrum of the resulting monosilyl derivative gave a base peak at $M^+ - 89$ (loss of Me_3SiO) and a strong peak at *m/e* 78 (Me_2SiOH^+) confirming that **D** contains at least one hydroxyl group. We conclude that compounds **A**, **B** and **D** have structures **14**, **16** and **17** respectively.

As mentioned above, condensation of BBD with 3,4-diamino-pyridine gave a compound **C** whose properties are very different from those of compounds **A**, **B** and **D**. Compound **C** was formed in 28% yield after 72 hr at room temperature whereas when phthalaldehydic acid was used in place of BBD compound **C** was formed in 92% yield after 1 hr. We assign structure **18** to compound **C** by analogy with the reaction of benzaldehyde with 4,5-diamino-2-methylpyrimidine which gives 4-amino-5-benzylideneamino-2-methylpyrimidine[7] and since the 3- is much more basic than the 4-amino group in pyridines.[6b] Moreover the anil **18** would be expected to be more stabilised by resonance than the isomeric anil formed by condensation at the 4-amino group just as the conjugate acid of 4-aminopyridine is more stabilised than that of 3-aminopyridine.[6b] The other alternative structure, namely a pyridoimidazoline, is considered less likely because benzimidazolines (if formed) normally undergo dehydrogenation to give benzimidazoles during the reaction of aldehydes with *o*-phenylenediamines. Unfortunately compound **C** was too sparingly soluble otherwise its NMR spectrum might have distinguished between **18** and a pyridoimidazoline structure.

DISCUSSION OF RESULTS

The reactivity of the amino-pyridines and -pyrimidines with BBD can be rationalised if it is assumed that (a) the reaction is initiated by attack of the most basic N atom, i.e. the ring nitrogen, on one of the carbonyl groups, followed by prototropic rearrangement to give an intermediate, for example **19**, which could easily cyclise to compound **17**; and (b) that the order of nucleophilicity of the ring nitrogens in this closely related series of heterocyclic amines parallels their basicity (i.e. pK_a values) and that a pK_a value of about 6 or more is needed for any reaction to occur. With 4,5-diaminopyridine an intermediate similar to **19** (but with the imino group γ instead of α to the ring nitrogen) might be formed but it could not cyclise. Instead, the diamine could effect a slow hydrolysis of BBD to phthalaldehydic acid which then condenses to give the observed product **18**. We have found that BBD is unchanged when a solution of it in 95% ethanol is kept at room temperature (*ca.* 23°) for 80 hr whereas an equimolar solution of BBD and N,N,N',N'-tetramethylethylene-diamine in undried absolute ethanol was at least 42% hydrolysed to phthalaldehydic acid under the same conditions even though the solvent contained much less water. The tetramethyldiamine was chosen for this study because it has almost the same pK_a (9.14)[6] as 3,4-diaminopyridine (9.08) but it could not condense with BBD.

We note that the nucleophilicity of the amino groups of *o*-phenylenediamine (1st pK_a 4.47) is clearly greater than that of the amino groups of the diaminoheterocyclic compounds studied here as shown by the ready condensation of a wide variety of *o*-phenylenediamines with BBD to give 5,10-diazabenzo[*b*]biphenylenes (see Ref. 1 and following section).

cis-2-Cyano-3-(2'-cyanovinyl)-1,4-diazabiphenylene, **3**. The observation of Campbell and Rees that oxidation of 2-aminobenzotriazole results in loss of one molecule of nitrogen accompanied by cleavage of the benzene ring to give *cis-cis*-mucononitrile[8] suggested a possible route to a derivative of 1,4-diazabiphenylene. Condensation of BBD with 4,5-diaminobenzotriazole[9] gave the pentacyclic triazole **20** or a tautomeric form thereof. Amination of this triazole with O-(2,4-dinitrophenyl)hydroxylamine gave an inseparable mixture of the 2-amino-compound **22** and the 1-amino-compound **21** or the isomeric 3-amino-compound. Oxidation of the mixture of N-aminotriazoles gave very low yields of *cis*-2-cyano-3-(2'-cyanovinyl)-1,4-diazabiphenylene **3** and 1- or 2-acetoxy-5,10-diazabenzo[*b*]biphenylene, the former coming from the 2-aminotriazole **22** and the latter from either the 1- or the 3-aminotriazole via a benzyne intermediate which reacted with acetic acid.

The structure of compound **3** follows from its method of preparation and its spectra. In particular the NMR spectrum shows that the side-chain double bond is *cis*-disubstituted. No attempts were made to degrade compound **3** to **1** because of the very low yields (*ca.* 7% overall from the triazole **21**) and because the parent compound **1** had been made by an alternative route[2] during the course of our work.

Some alternative routes to compound **3** via 1,2-diamino-5,10-diazabenzo[*b*]biphenylene or the corresponding 1,2-dinitrene were explored. Attempts to prepare the 1,2-diamine by condensation of BBD with 1,2,3,4-tetra-aminobenzene or by reduction of the furazanobiphenylene **23** (made from BBD and the benzofurazan **24**) with REDAL were unsuccessful (*cf* below). It is known that benzimidazole can be cleaved by acetic anhydride and water to give 1,2-diacetamidobenzene.[10] In our case the desired 4,5-diaminobenzimidazole was not easily obtainable so we tried a model experiment with the 5,6-diamino isomer. This, with BBD, gave 1,3,5,10-tetra-aza-1-H-indeno[5,6-*b*]biphenylene **25** (characterised as its N-acetyl derivative **26**) but attempts to hydrolyse it selectively to give the 2,3-diamine **27** failed.

In other model experiments benzil was condensed with the diaminofurazan **24** to give the furazanoquinoxaline **28**, but this was not deoxygenated by zinc dust in quinoline for 24 hr or by refluxing it in triethyl phosphite for 5 days, otherwise the expected dinitrene most probably would have undergone ring cleavage to give the dicyano compound **30**. However, reduction of the furazan **28** with REDAL gave the diamine **29** which could be oxidised by air in presence of copper (I) chloride (method of Kajimoto *et al.*[11]) or by lead tetra-acetate to give, in low yield, a *ca.* 1:4 mixture of *cis*- and *trans*-2-cyano-3-(2'-cyanovinyl)-5,6-diphenylpyrazine (**30** and **31**). Presumably the *cis* compound **30** is formed first and then undergoes extensive isomerisation during isolation and purification.

EXPERIMENTAL

IR and UV spectra were measured in Nujol mulls and in 95% ethanol respectively. NMR spectra were measured in $CDCl_3$ at 100 MHz unless otherwise stated. The mass spectra were recorded on an MS902 instrument at 70 eV with an EI source at *ca.* 150°. Petroleum refers to light petroleum (b.p. 60–80°). Merck Kieselgel HF (Type 60 nach Stahl) was used for TLC.

Condensation of BBD with ethylenediamine. Ethylenediamine

(232 mg) was added to a soln of benzocyclobutenedione (500 mg) in pyridine (8 ml) containing AcOH (0.5 ml). The yellow colour of the soln gradually faded and a white solid soon began to separate. More AcOH (*ca.* 0.5 ml) was added and the mixture was kept for 24 hr. The solid was collected and recrystallised from C_2H_5OH–hexane to give 2 - (2' - ***carboxyphenylimidazolidinium acetate*** **4** as needles (0.5 g, 69%), m.p. 153–155°. It was not possible to get a satisfactory elemental analysis. The mass spectrum showed that acetic acid was eliminated when the sample was volatilised (Found: M^+ 192.0892. $C_{10}H_{12}N_2O_2$ requires: M 192.0899), IR 3100–2500, 1680 (CO_2H), 1620 (NH_2^+), 1543 and 1410 (OAc^-), cm^{-1}, NMR (d_6-DMSO), τ 2.49 (4 ArH, m), 4.21 (CH, s), 6.47 (CH_2, t), 7.15 (CH_2, t) and 8.29 (OAc^-, s). Note ammonium acetate has τ (d_6-DMSO) 8.24 (OAc^-).

Condensation of phthalaldehydic acid with ethylenediamine. A mixture of ethylenediamine (400 mg) and phthalaldehydic acid (500 mg) in pyridine (8 ml) containing AcOH (0.7 ml) was kept overnight. The oily solid which was deposited was collected by filtration and was then shaken with EtOH (100 ml) to remove the oily material. The solid (170 mg, 27%) consisted of 2-*carboxybenzylidene ethylenediamine* **5**, m.p. 179–181°. An analytical sample m.p. 181–182°, was prepared by boiling the solid with EtOH, in which it is almost insoluble (Found: C, 62.6; H, 6.4; N, 14.7. $C_{10}H_{12}N_2O_2$ requires: C, 62.5; H, 6.3; N, 14.6%), IR 3070 (NH_3^+), 1669 (C=N), 1648 and 1548 (NH), 1584 (CO_2^-) cm^{-1}, NMR (CD_3OD) τ 1.54 (CH=N, br s), 2.35 (2 ArH, m), 2.64 (2 ArH, m) and 6.55 (CH_2CH_2, br s), NMR (CF_3CO_2H) τ 1.53 (CH=N, br d), 2.10 (4 ArH, m), 2.45 (3 H, v. br exchangeable with D_2O), 5.33 (CH_2, br t) and 6.04 (CH_2, br m).

The same product was obtained when ethanol was used in place of pyridine and acetic acid as solvent.

1,2,3,9b - *Tetrahydro* - 5H - *imidazo*[2,1 - a]*isoindol* - 5 - *one* **9**.[3] NMR τ ($CDCl_3$) 2.15–2.55 (4 ArH, m), 4.67 (ArCH), *ca.* 6.2–6.8 (CH_2–CH_2, m) and 8.27 (NH, br s).

Condensation of BBD with diaminomaleonitrile. A soln of BBD (264 mg) and diaminomaleonitrile (216 mg) in EtOH (10 ml) containing a trace of AcOH was kept at room temp. for 2 hr. The mixture was cooled and the product was collected, washed with EtOH, and dried at room temp. to give the *diazocine* **10** (228 mg, 48%) as plates which darken at *ca.* 225° and melt at 260–262° (dec). (Found: M^+ 238; C, 60.3; H, 3.0; N, 23.5. $C_{12}H_6N_4O_2$ requires: M 238; C, 60.5; H, 2.5; N, 23.6%). When the compound was recrystallised from hot EtOH it gave **12**, m.p. 275–277°(dec) (lit.[5] m.p. 275° dec), IR 3353, 3300, 3180, 2223, 1780, 1720, 1650 and 1602 cm^{-1}, NMR (d_6 DMSO) τ 1.66 (NH_2, s) and 2.03 (4 ArH, s). The IR spectrum was identical with that of a specimen made by heating phthalic anhydride with diaminomaleonitrile[5]

Condensation of phthaldehydic acid with diaminomaleonitrile. The acid (540 mg) and the nitrile (600 mg) were heated in EtOH (9 ml) for 1 hr. After being cooled to 0° the soln deposited 2 - *amino* - 3 - (2' - *carboxybenzylideneamino*) - *maleonitrile* **13** as yellow crystals (300 mg), m.p. 216–217°. (Found: M^+ 240.065; C, 59.7; H, 3.4; N, 23.0. $C_{12}H_8N_4O_2$ requires: M 240.065; C, 60.0; H, 3.3; N, 23.3%), IR 3480 and 3450 (NH_2), 3320 (CO_2H), 2250 and 2220 (CN), 1675 (CO_2H), 1625 cm^{-1}, NMR (d_6 DMSO) τ 0.96 (CH=N, s), 1.57 (ArH, m) 2.10 (ArH, m), 2.40 (2 ArH, m) and 1.99 (NH_2, s: exchanges with D_2O), mass spectrum, *m/e* 240, 221, 194, 133, 122, 119, 105, 77, 76.

Condensation of BBD with 4,5 - *diaminopyrimidine.* A soln of BBD (500 mg) and 4,5 - diaminopyrimidine (416 mg) in EtOH (15 ml) containing a few drops of AcOH was kept at room temp. for 24 hr. The ppt was collected, washed well with MeOH, and dried at room temp. to give 4 -*amino* - 5a,9b - *dihydro* - 5a,9b - *dihydroxybenzo*[3,4']*cyclobuta*[1',2' - 4,5]*imidazo*[1,2 - c]*pyrimidine* **14** (760 mg, 83%) as an amorphous solid, m.p. 167–168° (dec) (Found: M^+ 242.077; N, 23.2. $C_{12}H_{10}N_4O_2$ requires: M 242.080; N, 23.1%), IR 3273s, 3218 br, 3193 br, 1593 m, 1508 s, 1310 m, 1110 s and 1095 cm^{-1}.

Attempted sublimation of compounds **14** at 190°/0.1 Torr gave a yellow sublimate identified by IR and UV as a mixture of BBD and 4,5 - diaminopyrimidine.

Acid hydrolysis of compound **14**. (a) The compound **14** (150 mg) rapidly dissolved in 1 N H_2SO_4 (2 ml) to give a pale yellow soln. After the mixture had been warmed on a water-bath for 10 min the pH was adjusted to 6 and the precipitated BBD (55 mg, 67%) was collected. (b) A soln of **14** (150 mg) in the minimum volume of EtOH containing a few drops of conc HCl was warmed on a water bath for 1 hr. On cooling, the mixture deposited a small amount of **8**, m.p. 65–67° (lit.[12] 66°) identified by its IR and mass spectra.

Condensation of BBD with 2,3-*diaminopyridine.* AcOH (2 drops) was added to a soln of BBD (132 mg) and 2,3-diaminopyridine (109 mg) in EtOH (2 ml). The soln immediately turned orange and a ppt began to form. After 2 hr the ppt was collected and well washed with MeOH to give 4 - *amino* - 5a,9b - *dihydro* - 5a,9b - *dihydroxybenzo*[3',4']*cyclobuta*[1',2' - 4,5]*imidazo*[1,2 - a]*pyridine* **16** (106 mg, 44%) as needles m.p. 117–118° (dec). It was very sparingly soluble and could not be recrystallised. (Found: M^+ 241.038; C, 64.3; H, 4.0; N, 17.0. $C_{13}H_{11}N_3O_2$ requires: M 241.037; C, 64.7; H, 4.6; N, 17.4%), IR 3237 m, 3140 br, 3100 br, 1601 w, 1317 m, 1228 m, 1114 s and 1106 s cm^{-1}, mass spectrum, *m/e* (%) 241 (0.7), 223 (0.5), 195 (4), 132 (10), 109 (100), 104 (57), 82 (31) and 76 (69).

Condensation of BBD with 3,4 - *diaminopyridine.* A soln of the diamine (109 mg) and BBD (132 mg) in EtOH (3 ml) was kept at room temp. for 72 hr. The very sparingly soluble ppt was collected and washed well with MeOH to give 4 - *amino* - 3 - (2 - *carboxybenzylideneamino*)*pyridine* as its zwitter ion **18** (68 mg, 28%) as very pale yellow needles, m.p. 210–212° (dec) which could not be purified by recrystallisation (Found: M^+ 241.086. $C_{13}H_{11}N_3O_2$ requires: M 241.085), IR 3450, 3260 br, 3100 br, 1640 br (CO_2^-), 1575 and 1350 br (CO_2^-) cm^{-1}.

Condensation of phthaldehydic acid with 3,4 - *diaminopyridine.* AcOH (5 drops) was added to a soln of phthaldehydic acid (636 mg) and the diamine (418 mg) in EtOH (10 ml). After 1 hr the product (854 mg, 92%) was collected. It was identical with compound **18** obtained in the preceding experiment.

Condensation of BBD with 2 - *aminopyridine.* A soln of BBD (50 mg) and 2-aminopyridine (44 mg) in EtOH (7 ml) was stirred for 3 hr. The solvent was removed and the residue was recrystallised twice from EtOH giving the *imidazo*[1,2 - a]*pyridine* **17** as crystals, m.p. 136–137°. (Found: C, 68.8; H, 4.6; N, 12.1. $C_{13}H_{10}N_2O_2$ requires: C, 69.0; H, 4.5; N, 12.4%), IR 3360 m, 1700 s, 1590 s, 1574 s, 1302 s, 1106 m cm^{-1}. A sample treated with bistrimethylsilyltrifluoroacetamide gave a monosilylated product which was shown to be homogeneous by GC–MS, *m/e* (%) 298 (51), 283 (52), 269 (38), 209 (100) and 78 (92). Hydrolysis of **17** with 1 N H_2SO_4 under the same conditions as for **14** gave BBD which was identified by tlc and m.p.

Stability of BBD in ethanol. (a) A soln of BBD (264 mg) in 95% EtOH (10 ml) was kept in the dark at room temp. (*ca.* 23°) for 80 hr. No colour change occurred and preparative tlc in CH_2Cl_2 gave BBD (260 mg) which was identified by m.p. 129–130°, mixed m.p. 130–131° and IR spectrum. (b) A soln of BBD (264 mg, 2 mmol) and N,N,N',N' - tetramethylethylenediamine (132 mg, 2 mmol) in undried absolute EtOH (10 ml) was kept in the dark at room temp. for 80 hr. The mixture was evaporated to dryness under vacuum below 35° and separated by tlc using benzene as eluent. The first fraction (with highest R_f value) (8 mg) was an unidentified gum; the second fraction (70 mg) was an oil which contained ethyl 2-formylbenzoate, identified by IR and mass spectra;[12] the third fraction (125 mg) was identified as phthalaldehydic acid by m.p. and mixed m.p. 95–96°, IR and mass spectra. Attempts to follow the rate of ring cleavage of BBD by UV spectroscopy failed because a mixture of products was formed and their spectra were too similar to that of BBD to allow accurate measurements to be made

1,2,3,6.11 - *Penta* - *aza* - 1 - H - *indeno*[4,5 - b]*biphenylene* **20**. A suspension of BBD (264 mg), 4,5 - diaminobenzotriazole dihydrochloride[9] (444 mg) and NaOAc (328 mg) in EtOH–water (3:1, 20 ml) was warmed on a water-bath for 30 min. The product, which separated on cooling, was recrystallised from $HCONMe_2$ and gave the *biphenylene* **20** as yellow needles (392 mg, 80%) which did not melt up to 360°. (Found: C, 68.3: H, 3.1; N. 28.9. $C_{14}H_7N_5$ requires: C, 68.6; H, 2.9; N, 28.6%), IR 1650 w cm^{-1}.

N-Amination of biphenylene **20**. The biphenylene **20** (400 mg), anhyd Na_2CO_3 (85 mg), and dry $HCONMe_2$ (15 ml) were stirred and heated to boiling. When the solids had dissolved the soln was cooled to 20° and 0 - (2,4 - dinitrophenyl)hydroxylamine (325 mg) was added during 1 hr. The mixture was stirred for 4 hr then filtered to remove the sodium salt of biphenylene **20** (25 mg). The filtrate was poured into ice-water (100 ml) and the yellow ppt was collected and washed with water. This solid (288 mg, 68%), m.p. 235–240°, showed two overlapping spots on tlc in CH_2Cl_2 but the mixture of isomers could not be separated. (Found: M^+ 260.082. Calc. for $C_{14}H_8N_6$: M 260.081, IR 3600–3100 w v br, 1670 m and 750 m cm^{-1}.

N-amination with 0-mesitylenesulphonyl hydroxylamine gave a mixture (64%) similar to that above.

Oxidation of the N-amino derivatives of biphenylene **20**. Lead tetra-acetate (500 mg) was added to a suspension of the mixture of N-amino derivatives obtained in the previous experiment (300 mg) in dry CH_2Cl_2 (20 ml). The mixture was stirred for 15 min, after which time evolution of N_2 had ceased. The mixture was filtered and the filtrate was evaporated to dryness. The residue was immediately purified by preparative tlc on silica gel plates. After one elution with CH_2Cl_2, the plate was dried and then eluted again with the same solvent.

Two bands were scraped off and extracted with CH_2Cl_2. (a) The slowest running band, which was colourless but which fluoresced under UV, gave an oil which slowly solidified. This compound is thought to be 1- or 2 - acetoxy - 5,10 - diazabenzo[*b*]biphenylene (*ca.* 1% yield). It had m.p. 184–188° and *m/e* (%) 262 (15), 234 (6), 220 (100) and 192 (10). (b) The fastest running band, which was yellow, gave a solid which was sublimed twice at 150–160°/0.03 Torr and gave *cis* - 2 - *cyano* - 3 - (2' - *cyanovinyl*) - 1,4 - *diazabiphenylene* **3** (7 mg, 2.5% overall from **20**) as yellow crystals, m.p. 202–204°. (Found: M' 230.059; C, 72.8: H, 2.9; N, 24.6. $C_{14}H_6N_4$ requires: M 230.059; C, 73.0; H, 2.6; N, 24.3%), IR 2210 br, 1660 m and 752 cm $^{-1}$, UV λ_{max} 267, 380 and 393 nm (log ϵ 4.58, 3.93 and 3.95), NMR τ 2.61 (H-5, H-6, H-7, H-8, m), 2.70 (Ha, d) and 4.20 (Hb, d), J_{ab} 11.9 Hz, mass spectrum, *m/e* (%) 230 (39), 178 (13), 128 (100) and 102 (12).

When phenyliodoso acetate was used in place of lead tetraacetate the yield of diazabiphenylene **3** was *ca.* 1 mg.

4,5-*Furazanobenzofurazan*. (Note, use of triethyl phosphite in place of the trimethyl ester avoids the necessity of using a sealed tube). A soln of 4,5-furoxanobenzofuroxan[13] in freshly distilled, deoxygenated triethyl phosphite (15 ml) was refluxed under N_2 for 1 hr then the volatile products were removed by distillation under reduced pressure. The residue was dissolved in CH_2Cl_2 and chromatographed on a column of silica gel eluting first with petroleum then with CH_2Cl_2/petroleum (1:1). The yellow band yielded 4,5-furazanobenzofurazan (1.25 g, 51%) as white crystals (from EtOH) m.p. 60–61° (lit.[13] 60–61°).

4,5-*Diaminobenzofurazan* **24**. This was made by catalytic reduction of 4,5-furazanobenzofurazan in MeOH in presence of Pd/C at atmospheric pressure. The diamine was chromatographed on a dry alumina column using EtOAc as eluent. The diamine (78%) formed orange brown crystals (from toluene), m.p. 149–150 (lit.[14] 151°).

1,3,6,11 - *Tetra* - *aza* - 2 - *oxa* - 2H - *indeno*[4,5 - b]*biphenylene* **23**. BBD (80 mg), 4,5-diaminobenzofurazan **24** (100 mg), EtOH (7 ml), and AcOH (2 drops) were warmed together on a water-bath for 1 hr. The orange crystals were collected, dried, and sublimed at 290°/1 Torr and gave the *biphenylene* **23** (59 mg, 34%) as a yellow-orange power, m.p. 305–307°. (Found: M^+ 264; C, 67.8; H, 2.4; N, 22.3. $C_{14}H_6N_4O$ requires: M 264; C, 68.3; H, 2.5; N, 22.8%), IR 1650 w br, 1560 w br, 1310 m and 740 cm $^{-1}$, UV λ_{max} 283, 300 sh, 363 sh, 375 and 394 nm (log ϵ 4.54, 4.24, 4.09 4.23 and 4.24), FT NMR τ 1.95 (1 H, d), 2.23 (1 H, d) and 2.36–2.52 (4 H, m), J 9.5 Hz.

1,3,5,10 - *Tetra* - *aza* - 1 - H - *indeno*[5,6 - b]*biphenylene* **25**. A soln of BBD (264 mg) and 5,6 - diaminobenzimidazole[15] (300 mg in EtOH (15 ml) and AcOH (5 drops) was kept at 50° for 1 hr then cooled to −5° and the crystals were collected. The *biphenylene* **25** (349 mg, 60%) formed yellow plates (from EtOH), m.p. 343–345° (dec). The compound contained EtOH of crystallisation and a satisfactory microanalysis could not be obtained. (Found: M^+ 244.074. $C_{15}H_8N_4$ requires: M, 244.075), IR 3080 m br, 1660 w br, 1270 s and 760 s cm^{-1}, UV λ_{max} 261 sh, 280, 301, 366, 385 and 405 (log ϵ 4.42, 4.57, 4.28, 4.04, 4.23 and 4.20), NMR (d_6 DMSO) τ − 2.7 (NH, Br s, disappears in D_2O), 1.60 (N–CH=N, s), 2.16 (2 H, s) and 2.36–2.61 (4 H, m), mass spectrum, *m/e* (%) 244 (100), 217 (8) and 116 (40).

When the biphenylene 25 was boiled with Ac_2O for 1 hr it gave the 1-*acetyl derivative* **26** (78%), as yellow crystals (from toluene), m.p. 291–292°. (Found: C, 71.7; H, 3.8. $C_{17}H_{12}N_4O$ requires: C, 71.3; H, 3.5%), IR 1720 s br, 1610 m and 750 s cm^{-1}, UV λ_{max} 265, 284, 306, 371, 389 and 409 nm (log ϵ 4.49, 4.62, 4.36, 4.10, 4.28 and 4.26), NMR τ (d_6 DMSO) 1.00 (1 H, s), 1.67 (1 H, s), 2.07 (1 H, s) and 2.32–2.56 (4 H, m), mass spectrum, *m/e* (%) 286 (50), 244 (100), 217 (10) and 116 (65).

7,8 - *Diphenylfurazano*[3,4 - f]*quinoxaline* **28**. Benzil (70 mg) and 4,5 - diaminobenzofurazan (50 mg) in EtOH (3 ml) and AcOH (1 drop) were warmed on a water-bath for 1 hr then the mixture was cooled and the ppt collected. The quinoxaline **28** (84 mg, 78%) formed white crystals (from EtOH), m.p. 181–182°. (Found: C, 73.9; H, 3.8. $C_{20}H_{12}N_4O$ requires: C, 74.1; H, 3.7%), IR 1560 w, 1240 w and 650 s cm^{-1}, UV λ_{max} 230, 289 and 348 nm (log ϵ 4.38, 4.33 and 4.14), NMR τ 2.12 (2 H, s), 2.44–2.56 (5 H, m) and 2.64–2.78 (5 H, m).

2,3 - *Diamino* - 5,6 - *diphenylquinoxaline* **29**. REDAL (600 mg of a 70% soln in toluene) was added to a soln of **28** (108 mg) in toluene (5 ml) and the mixture was refluxed for 1 hr. The mixture was cooled and water (10 ml) and toluene (10 ml) were added and the whole was stirred for 10 min to decompose any unused REDAL. The mixture was filtered and the toluene layer was set aside. The aqueous layer was extracted with toluene (2 × 10 ml) and the united toluene layers were concentrated. The residue gave the diamine **29** (67 mg, 64%) as orange-red crystals (from toluene/petroleum) m.p. 196–198° (lit.[16] 199–200°).

Oxidation of 2,3 - *diamino* - 5,6 - *diphenylquinoxaline* **29**. (a) Air was bubbled through a stirred mixture of copper (I) chloride (200 mg) and pyridine (10 ml) for 10 min then a soln of the diamine **29** (312 mg) in pyridine (4 ml) was added. The mixture was aerated and stirred for 1 hr then evaporated to dryness and the residue extracted with CH_2Cl_2. The extract was concentrated and chromatographed on a column of silica gel with CH_2Cl_2 as eluent. The first fraction was evaporated to dryness, sublimed (120°/1 Torr), then recrystallised from EtOH thereby giving a mixture of *cis*- and *trans* - 2 - cyano - 3 - (2' - cyanovinyl)5,6 - diphenylpyrazine (*ca.* 1:4; 25 mg, 8%). Further crystallisation from EtOH gave the pure *trans-diphenylpyrazine* **31**, m.p. 204–205° (Found: C, 77.7; H, 3.9; N, 17.9. $C_{20}H_{12}N_4$ requires: C, 77.9; H, 3.9; N, 18.1%), IR 2210 m br, 1600 w, 1375 s, 950 m, 765 s and 690 s cm^{-1}, FT NMR τ 2.16 (Ha, d), 2.44–2.68 (10 H, m) and 3.06 (Hb, d), J_{ab} 16 Hz, mass spectrum, *m/e* (%) 308 (99), 307 (100), 103 (89) and 76 (26). Although **30** was not obtained pure its NMR spectrum was obtained from that of the mixture of the *cis*- and *trans*-isomers: τ 2.28 (Ha, d), 2.40–2.70 (10 H, m), 4.02 (Hb, d), J_{ab} 12 Hz. (b) Oxidation of the diamine **29** with lead tetra-acetate in CH_2Cl_2 gave a mixture (*ca.* 4:1) (9% yield) of the *cis*- and *trans*-isomers **30** and **31**, m.p. 194–197°.

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