Approaches to Heterocyclic Analogues of Biphenylene. Part I. The Reaction of 5,6-Diaryl-2,3-dihydropyrazines with Alcoholic Alkali

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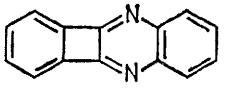
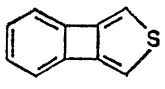
2,3-Dihydro-5,6-diphenylpyrazine reacts with alcoholic alkali to form 2,3-diphenylpyrazine and 5,5',6,6'-tetraphenyl-2,2'-bipyrazinyl, not 2,3,6,7-tetraphenyl-1,4,5,8-tetra-azabiphenylene. 2,3-Dihydro-5,6-bis-(*p*-methoxyphenyl)pyrazine undergoes an analogous reaction, but 2,3-dihydro-5,6-bis-(*p*-nitrophenyl)pyrazine yields only an apparently polymeric material. The reaction of *pp'*-dinitrobibenzoyl with ethylenediamine produces not only 2,3-dihydro-5,6-bis-(*p*-nitrophenyl)pyrazine, but also *NN'*-bis-(*p*-nitrobenzoyl)ethylenediamine.

ALTHOUGH biphenylene has been extensively studied, little has been published about its heterocyclic analogues. The benzodiazabiphenylene (1) has been prepared,[1] and the benzocyclobutathiophen (2) is the only reported [2] analogue without additional fused rings. The study of such compounds would be of particular interest in connection with the influence of the hetero-atoms on bond structure and the stability of the four-membered ring.



(1)



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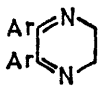
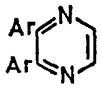
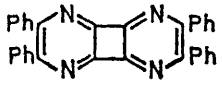


(3) Ar = Ph
(4) Ar = *p*-MeO·C_6H_4
(5) Ar = *p*-HO·C_6H_4
(6) Ar = *p*-O_2N·C_6H_4



(7) Ar = Ph
(8) Ar = *p*-MeO·C_6H_4
(9) Ar = *p*-O_2N·C_6H_4



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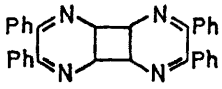

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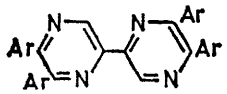


(12) Ar = Ph
(13) Ar = *p*-MeO·C_6H_4

The literature does, in fact, contain a reference to a compound to which a tetra-azabiphenylene structure was ascribed. Mason and Dryfoos found [3] that 2,3-dihydro-5,6-diphenylpyrazine (3) reacted with alcoholic potassium hydroxide to yield mainly 2,3-diphenylpyrazine (7) together with a compound (' tetraphenyldipiazine ') to which they ascribed the molecular formula $C_8N_4(C_6H_5)_4$, presumably representing the structure (10); no attempt was made to confirm the structure. ' Tetraphenyldipiazine ' was also obtained from the dihydropyrazine under other conditions, but few experimental details were given. More recently, Burata reported [4] the preparation of a compound identical with ' tetraphenyldipiazine ' from attempted Diels–Alder-type reactions between 2,3-dihydro-5,6-diphenylpyrazine and maleic anhydride or stilbene, and concluded that the u.v. spectrum of the product was consistent with the structure (10) rather than that of the tetrahydro-derivative (11). From a similar reaction with maleic anhydride, van Alphen reported [5] the isolation of an adduct $C_{16}H_{14}N_2,2C_4H_2O_3$.

If ' tetraphenyldipiazine ' does indeed have the structure (10), its formation, although in low yield, from the reaction of the readily prepared dihydrodiphenylpyrazine with alcoholic alkali represents an easy access to the 1,4,5,8-tetra-azabiphenylene series. In the present work, ' tetraphenyldipiazine ' was obtained, along with diphenylpyrazine, by treatment of dihydrodiphenylpyrazine with alcoholic alkali as described by Mason and Dryfoos,[3] but its preparation from the dihydropyrazine and maleic anhydride (*cf.* Burata [4]) could not be repeated.

The i.r. spectrum of ' tetraphenyldipiazine ' contains bands due to phenyl groups, but does not show absorption attributable to non-aromatic C=C or C=N bonds (dihydrodiphenylpyrazine has C=N stretch at 1560 cm^{-1}). As reported,[3] the compound is soluble in concentrated sulphuric acid, and is recovered unchanged on dilution with water. This behaviour is inconsistent with the presence of hydrogenated pyrazine rings, since such rings readily undergo hydrolytic cleavage under acidic conditions. Further, ' tetraphenyldipiazine ' is recovered unchanged after treatment with chloranil or tetrachloro-*o*-benzoquinone, whereas dihydrodiphenylpyrazine (3) is dehydrogenated almost quantitatively to compound (7) with chloranil; this method is superior to the thermal dehydrogenation previously used.[6] These findings suggest that the molecule does not contain non-aromatic heterocyclic rings. Attempts to remove the phenyl groups from the sparingly soluble ' tetraphenyldipiazine ' by oxidation and hence to prepare a more tractable product of lower molecular weight failed: the compound was unaffected by potassium permanganate, and converted to water-soluble products by chromic acid. The low solubility prevented the recording of the n.m.r. spectrum.

Mason and Dryfoos assigned the formula $C_8N_4(C_6H_5)_4$ to their product on the basis of elemental analysis and

[1] M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076.
[2] P. J. Garratt and K. P. C. Vollhardt, *Chem. Comm.*, 1970, 109.
[3] A. T. Mason and L. A. Dryfoos, *J. Chem. Soc.*, 1893, **63**, 1293.
[4] M. S. Burata, *Revista de la Real Academia de Ciencias de Madrid*, 1955, **49**, 23 (*Chem. Abs.*, 1956, **50**, 7112g).
[5] J. van Alphen, *Rec. Trav. chim.*, 1942, **61**, 895.
[6] A. T. Mason, *J. Chem. Soc.*, 1889, **55**, 97.

molecular weight determination. However, neither elemental analysis nor a molecular weight determination in solution would permit a conclusive distinction to be made between structures (10) (*M* 460) and (11) (*M* 464), or other possibilities differing in molecular formula by only a few hydrogen atoms. Mass spectrometric determination of the molecular weight gave a value of 462; this, together with the properties already described, suggests that ' tetraphenyldipiazine ' is, in fact, 5,5′,6,6′-tetraphenyl-2,2′-bipyrazinyl (12). This is thus the first substituted bipyrazinyl to be recognised; 2,2′-bipyrazinyl itself has been reported.[7]

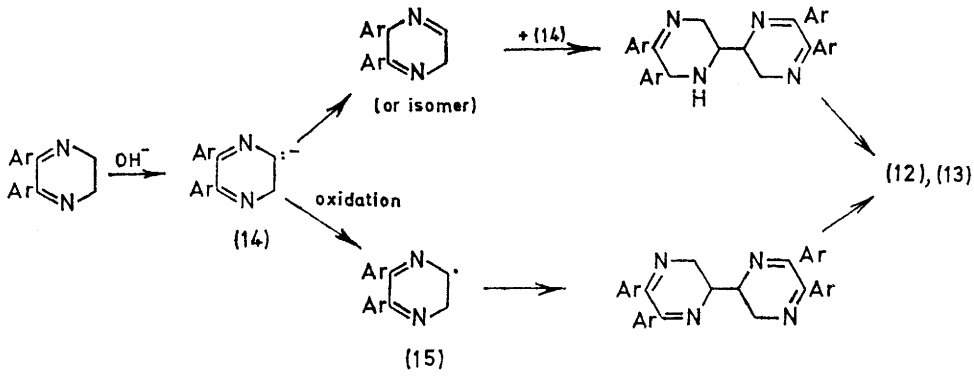
This preliminary investigation was extended in three ways: (*a*) by further examination of the unusual reaction of diaryldihydropyrazines with alkali to give products analogous to (7) and (12); (*b*) by rational synthesis of compound (12) (an unambiguous synthesis did, in fact, give a product identical with ' tetraphenyldipiazine '); and (*c*) by extension of such a synthesis to give 3,3′-disubstituted derivatives of (12) and investigation of their possible conversion into the heterobiphenylene (10) by routes analogous to those used for the preparation of biphenylene itself from 2,2′-disubstituted biphenyls.

We describe here some attempts to obtain information about the mode of formation of diarylpyrazines and tetra-arylbipyrazinyls from diaryldihydropyrazines; syntheses of bipyrazinyls will be described in a subsequent paper.

2,3-Diphenylpyrazine (7) is unaffected by boiling alcoholic potassium hydroxide. Further, the quantity of tetraphenylbipyrazinyl (12) obtained by treating a mixture of 2,3-dihydro-5,6-diphenylpyrazine (3) and 2,3-diphenylpyrazine with alkali is the same as that obtained from compound (3) alone; the amount of 2,3-diphenylpyrazine isolated is increased by the quantity added initially. These observations suggest that 2,3-diphenylpyrazine is not involved in the formation of the bipyrazinyl.

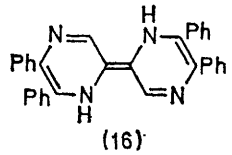
Scheme 1 indicates possible routes to the bipyrazinyl under basic conditions; both the carbanion (14) and the radical (15) should be stabilised by electron delocalisation. The formation of the pyrazine (7) (soluble in alcohol) and bipyrazinyl (12) (precipitated) must involve oxidation, but the yields were unchanged when the reaction was carried out under nitrogen. The aromatic products are not formed from compound (3) by disproportionation, since no polyhydrodiphenylpyrazine could be detected among the products.

The crude tetraphenylbipyrazinyl obtained in this way is red, but the colour is completely lost during recrystallisation. The i.r. spectrum of the crude red material is almost identical with that of pure colourless tetraphenylbipyrazinyl, indicating that the concentration of the coloured contaminant is low; nevertheless, the mass spectrum of the crude product reveals the presence of a compound of molecular weight 464. This suggests that a dihydrotetraphenylbipyrazinyl is first formed, and undergoes oxidation to the fully aromatic product. The red material could not be separated from the tetraphenylbipyrazinyl by t.l.c.



SCHEME 1

The crude red bipyrazinyl has a u.v. spectrum similar to that of the pure compound, but has an additional band in the visible region (see Table and Figure). Of the fifteen isomeric dihydro-5,5′,6,6′-tetraphenylbipyrazinyls only a few [*e.g.* (16)] seem likely to absorb at a sufficiently

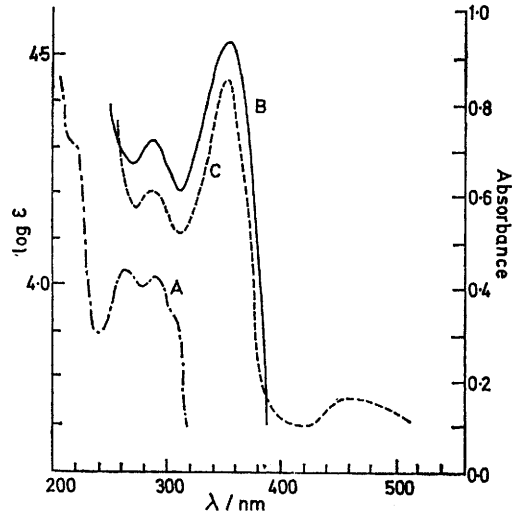


(16)

long wavelength. The tetraphenylbipyrazinyl is too insoluble in common spectroscopic solvents, except chloroform, to permit accurate extinction coefficient measurements, but is readily soluble in sulphuric acid, in which it forms a cherry-red solution. The intensity of the 298 nm band in the sulphuric acid solution of the crude red bipyrazinyl is higher than that of the 524 nm band, presumably because protonated dihydrotetraphenylbipyrazinyl also absorbs at *ca.* 298 nm. The Figure and Table also include data for diphenylpyrazine and dihydrodiphenylpyrazine, both of which dissolve in sulphuric acid to form golden yellow solutions.

[7] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1187.

If formation of carbanion (14) is involved as the first step in the reaction sequence, the yields of both (7) and (12) should vary according to whether substituents in the



U.v. spectra of, A 2,3-diphenylpyrazine, B 5,5′,6,6′-tetraphenyl-2,2′-bipyrazinyl, C crude red tetraphenylbipyrazinyl; A in MeOH, B and C in $CHCl_3$; A and B log ε *vs.* λ, C absorbance *vs.* λ

aryl groups stabilise or destabilise the anion. Mason and Dryfoos[3] treated 2,3-dihydro-5,6-bis-(*p*-methoxyphenyl)-pyrazine (4) with alkali and recorded that the yield of bis-(*p*-methoxyphenyl)pyrazine was ' good ', but that of

U.v. and visible spectra

Compound	$\lambda_{max.}$/nm (log ε) Neutral solution	H_2SO_4 solution
	$CHCl_3$:	
5,5′,6,6′-Tetraphenyl-2,2′-bipyrazinyl	289 (4·30) 353 (4·54)	233 (4·15) 295 (4·25) 385 (4·14) 529 (4·29)
	PrⁱOH * *ca.* 237infl.	
	$CHCl_3$:	
Crude red tetraphenylbipyrazinyl	290 350 474	298 382 524
	PrⁱOH: * 254	
	MeOH:	
2,3-Diphenylpyrazine	217sh (4·32) 265 (4·02) 290 (4·00) 307infl. (3·91)	261 (4·15) 268sh (3·91) 444 (3·92)
	MeOH:	
2,3-Dihydro-5,6-diphenylpyrazine	224 (4·15) 287 (3·73) 362 (2·69)	233 (4·02) 263infl. (3·55) 397 (3·93)

* Saturated solution; concentration unknown.

' tetramethoxyphenyldipiazine ' was ' very small '. We have confirmed that the yields of bipyrazinyl (13) and diarylpyrazine (8), and also the ratio of bipyrazinyl to diarylpyrazine, are lower in this reaction than in the case of dihydrodiphenylpyrazine. An attempt to prepare 2,3-dihydro-5,6-bis-(*p*-hydroxyphenyl)pyrazine (5), so that its reaction with alkali could be studied, failed; only tarry products were obtained from the reaction of *pp*′-dihydroxybibenzoyl with ethylenediamine. The dihydroxybibenzoyl was obtained by demethylation of *pp*′-dimethoxybibenzoyl, best with pyridinium chloride.

Since the presence of methoxy-groups in the diaryldihydropyrazine appears to reduce the yields of both products and the proportion of bipyrazinyl, it seemed worthwhile to investigate the effect of electron-attracting groups, and so the preparation of 2,3-dihydro-5,6-bis-(*p*-nitrophenyl)pyrazine (6) was attempted. The requisite *pp*′-dinitrobibenzoyl cannot be prepared *via* a benzoin condensation. Two routes to this compound are reported.[8,9] The first, nitration of 4,5-diphenylimidazol-2-one and subsequent cleavage to a (separable) mixture of *mm*′- and *pp*′-dinitrobibenzoyls,[8] could not be repeated; the nitration yielded no solid product (*cf.* ref. 8). The second, nitration of 2-methyl-4,5-diphenyloxazole followed by oxidative cleavage,[9] gave a high yield of *pp*′-dinitrobibenzoyl.

When the dinitrobibenzoyl was condensed with ethylenediamine in dimethylformamide, the expected dihydrobis-(*p*-nitrophenyl)pyrazine (6) was accompanied by a second product, the i.r. spectrum of which indicated the presence of amide linkages, and which yielded *p*-nitrobenzoic acid on hydrolysis; it was shown to be *NN*′-bis-(*p*-nitrobenzoyl)ethylenediamine (17), identical with material prepared from ethylenediamine and *p*-nitrobenzoyl chloride.

The dinitrobibenzoyl was recovered unchanged after being heated in dimethylformamide in the absence of ethylenediamine. The dihydrobis(nitrophenyl)pyrazine was also recovered unchanged after being heated in dimethylformamide; treatment with aqueous dimethylformamide produced only a small amount of the amide, consistent with slight hydrolysis to dinitrobibenzoyl and ethylenediamine followed by recombination to give dihydropyrazine and diamide. Hence, the two products appear to be formed by distinct reaction paths (Scheme 2). Ready cleavage of the central carbon–carbon bond in *pp*′-dinitrobibenzoyl is found in other reactions, and presumably involves the ability of a *p*-nitrophenyl group to stabilise a carbanion, as in the suggested intermediate (18). The conversion of such an intermediate into compound (17) would involve oxidation by air or nitro-groups.

2,3-Dihydro-5,6-bis-(*p*-nitrophenyl)pyrazine is dehydrogenated by chloranil to the bis-(*p*-nitrophenyl)-pyrazine (9). On boiling with ethanolic potassium hydroxide, the dihydropyrazine dissolved, but no insoluble product separated. Concentration of the solution, followed by dilution with water, produced a

[8] F. D. Chattaway and E. A. Coulson, *J. Chem. Soc.*, 1928, 1361.

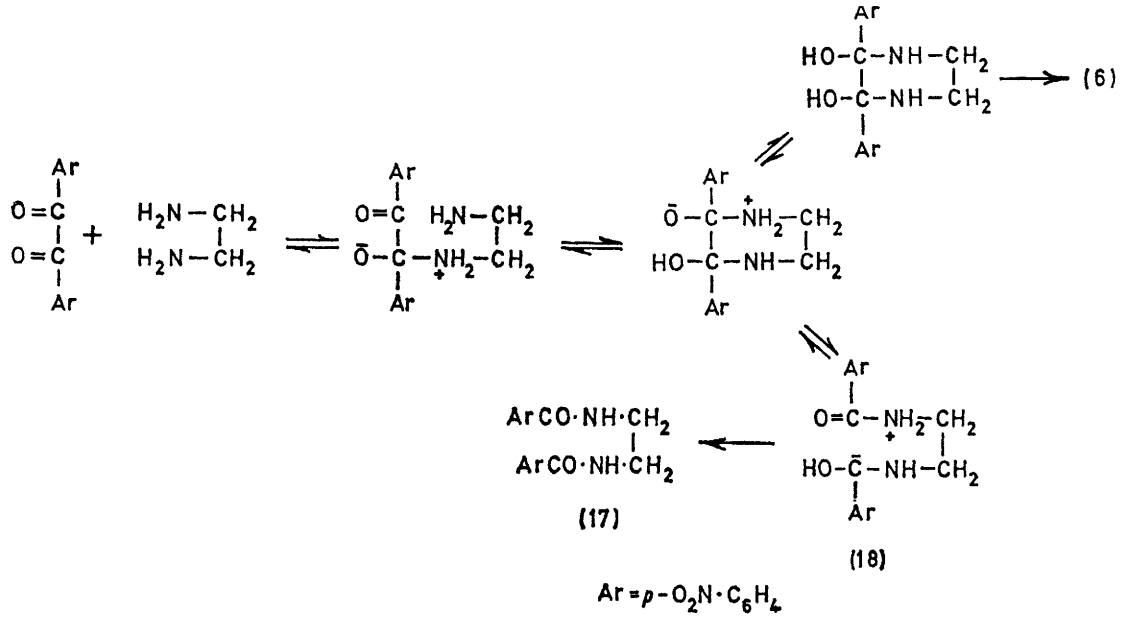
[9] T. van Es and O. G. Backeberg, *J. Chem. Soc.*, 1963, (*a*) 1363; (*b*) 1371.

brown, apparently polymeric, solid of m.p. 243—256°, from which no starting material or diarylpyrazine could be extracted, and which could not be further purified.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer Infracord model 137 or a Hilger–Watts Infrascan spectrophotometer, and u.v. and visible spectra with a Unicam SP 700 instrument.

2,3-*Dihydro*-5,6-*diphenylpyrazine*.—A solution of bibenzoyl (30·0 g) and ethylenediamine hydrate (11·4 ml) in ethanol (90 ml) was refluxed for 1·5 h, and then cooled to 0°. The solid deposited gave 2,3-dihydro-5,6-diphenylpyrazine (30·3 g, 91%), m.p. 163—164° (from ethanol) (lit.,[10] 162°).



SCHEME 2

2,3-*Diphenylpyrazine*.—A solution of 2,3-dihydro-5,6-diphenylpyrazine (5·8 g) and chloranil (6·15 g) in xylene (50 ml) was refluxed for 7 h, diluted with ether (100 ml), and extracted with sodium hydroxide solution to remove tetrachlorohydroquinone and then with concentrated hydrochloric acid (4 × 25 ml). Neutralisation of the acidic extracts gave 2,3-diphenylpyrazine (5·6 g, 97%), m.p. 120—121° (lit.,[6] 118—119°) (Found: C, 82·7; H, 5·2; N, 12·1. Calc. for $C_{16}H_{12}N_2$: C, 82·8; H, 5·2; N, 12·0%).

Reaction of 2,3-*Dihydro*-5,6-*diphenylpyrazine with Alcoholic Potassium Hydroxide*.—A solution of 2,3-dihydro-5,6-diphenylpyrazine (10·0 g) and potassium hydroxide (2·0 g) in ethanol (100 ml) was boiled for 5 h and then set aside at room temperature for 3—4 days. The red solid which separated was filtered off and extracted with ethanol (Soxhlet) to remove starting material and diphenylpyrazine. The residue (from xylene) yielded 5,5′,6,6′-*tetraphenyl*-2,2′-*bipyrazinyl* (0·32 g, 3·2%), m.p. 282—284° [Found: C, 82·9; H, 5·1; N, 12·1%; *M* (mass spectrometry), 462. $C_{32}H_{22}N_4$ requires C, 83·1; H, 4·8; N, 12·1%; *M*, 462].

The filtrate and extract were combined, concentrated to the point of crystallisation, and cooled to 0°, yielding a precipitate of 2,3-diphenylpyrazine (8·1 g, 81%), m.p. 120—121°. Evaporation of the mother liquor to dryness and extraction of the yellowish residue with petroleum (b.p. 40—60°) or chloroform gave, on evaporation of the solvent, only crude 2,3-diphenylpyrazine (1·0 g), m.p. 99—115°, identified by mixed m.p. and i.r. spectrum. The spectrum showed no absorption in the methylene C–H stretch region, indicating the absence of any significant amount of hydropyrazines.

Similar results were obtained when the reaction was conducted under nitrogen. When 2,3-diphenylpyrazine (5·0 g) was added to the reaction mixture and the reaction was carried out as before, tetraphenylbipyrazinyl (0·31 g) and diphenylpyrazine (12·9 g) were isolated.

pp′-*Dimethoxybibenzoyl*.—*p*-Methoxybenzaldehyde (68·0 g) [purified by shaking with saturated sodium hydrogen carbonate solution, drying ($MgSO_4$), and distilling (b.p. 92—94° at 0·1 mmHg)] and potassium cyanide (10·0 g) were dissolved in a mixture of water (75 ml) and ethanol (150 ml). The solution was boiled for 17 h, cooled, poured into water (600 ml), and extracted with ether. Evaporation of the extract gave impure anisoin (54·2 g), m.p. 90—105° (lit.,[11] 113°). The crude material was added to a boiling solution of hydrated copper sulphate (80·0 g) in a mixture of pyridine (120 ml) and water (40 ml), and refluxing was continued for 8 h. Dilution with water (600 ml) and extraction with ether yielded *pp*′-dimethoxybibenzoyl (18·7 g, 27%), m.p. 131—132° (lit.,[12] 132—133°).

The procedure of ref. 12 gave yields of 7—17% (*cf.* lit. yield 53%).

2,3-*Dihydro*-5,6-*bis*-(p-*methoxyphenyl*)*pyrazine*.—A solution of *pp*′-dimethoxybibenzoyl (10·0 g) and ethylenediamine hydrate (3·3 ml) in ethanol (140 ml) was refluxed for 20 h, concentrated to the point of crystallisation, and cooled, yielding the title compound (8·5 g, 78%), m.p. 118—122°

[10] H. I. X. Mager and W. Berends, *Rec. Trav. chim.*, 1965, **84**, 314.

[11] J. Dewar and J. Read, *J. Soc. Chem. Ind.*, 1936, **55**, 347.

[12] N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, 1949, **71**, 2997.

(from aqueous ethanol) (lit.,[3] 126—127°) (Found: C, 73·6; H, 6·0; N, 9·4. Calc. for $C_{18}H_{18}N_2O_2$: C, 73·5; H, 6·2; N, 9·5%).

2,3-*Bis*-(p-*methoxyphenyl*)*pyrazine*.—A solution of 2,3-dihydro-5,6-bis-(*p*-methoxyphenyl)pyrazine (3·0 g) and chloranil (2·5 g) in xylene (20 ml) was refluxed for 4 h. Work-up as for 2,3-diphenylpyrazine and recrystallisation from ethanol yielded 2,3-bis-(*p*-methoxyphenyl)pyrazine (2·5 g, 86%), m.p. 136—137° (lit.,[3] 134°) (Found: C, 74·2; H, 5·5; N, 9·5. Calc. for $C_{18}H_{16}N_2O_2$: C, 74·0; H, 5·5; N, 9·6%).

Reaction of 2,3-*Dihydro*-5,6-*bis*-(p-*methoxyphenyl*)*pyrazine with Alcoholic Potassium Hydroxide*.—The dihydrobis-(*p*-methoxyphenyl)pyrazine (2·3 g) was treated with potassium hydroxide (1·2 g) in ethanol (20 ml) and worked up as for dihydrodiphenylpyrazine, yielding 5,5′,6,6′-*tetrakis*-(p-*methoxyphenyl*)-2,2′-*bipyrazinyl* (0·03 g, 1·3%), m.p. 252—254° [Found: *M* (mass spectrometry), 582. $C_{36}H_{30}N_4O_4$ requires *M*, 582] and 2,3-bis-(*p*-methoxyphenyl)pyrazine (1·5 g, 66%), m.p. 136—137°.

pp′-*Dihydroxybibenzoyl*.—(*a*) Dimethoxybibenzoyl (20·2 g) was dissolved in glacial acetic acid (650 ml), and hydrobromic acid (48%; 650 ml) was added to the boiling solution. After refluxing for 21 h, the cold solution was poured into water, and the precipitated dihydroxybibenzoyl was recrystallised from ethanol (yield 15 g, 84%); m.p. 250—252° (lit.,[12] 244—246°).

No reaction was observed when the procedure of ref. 12 was used.

(*b*) An intimate mixture of pyridinium chloride (10·0 g) and dimethoxybibenzoyl (5·0 g) was heated at 195—200° for 2 h and allowed to cool. The syrupy residue was dissolved in sodium hydroxide solution, and the resulting solution was acidified to give pale yellow dihydroxybibenzoyl (4·4 g, 98%), m.p. 252—253°.

pp′-*Dinitrobibenzoyl*.—Benzoin acetate [13] (m.p. 81°) was converted into 2-methyl-4,5-diphenyloxazole [14] (yield 81%; b.p. 138° at 0·5 mmHg). Nitration [9a] yielded 2-methyl-4,5-bis-(*p*-nitrophenyl)oxazole (65%), m.p. 246—247° (lit., yield 98%; m.p. 241°) and cleavage with bromine in aqueous acetic acid [9b] gave *pp′*-dinitrobibenzoyl (92%), m.p. 213—214° (lit., 213—214°).

Reaction of pp′-*Dinitrobibenzoyl with Ethylenediamine*.—Ethylenediamine hydrate (1·4 ml) was added to a solution of the bibenzoyl (5·0 g) in *NN*-dimethylformamide (20 ml) at 100°, and, after being kept at this temperature for 15 min, the reaction mixture was cooled and poured into water (150 ml). The precipitated solid was filtered off and extracted several times with boiling ethanol. Concentration of the extract gave 2,3-*dihydro*-5,6-*bis*-(p-*nitrophenyl*)-*pyrazine* (3·1 g, 57%) as a brown solid, m.p. 233—235° (Found: C, 59·4; H, 3·8; N, 17·4. $C_{16}H_{12}N_4O_4$ requires C, 59·3; H, 3·7; N, 17·3%). The ethanol-insoluble residue (1·8 g, 30%), m.p. 239—245° was identical (mixed m.p. and i.r.) with *NN′*-bis-(*p*-nitrobenzoyl)ethylenediamine (see later). When this material (0·3 g) was refluxed with sulphuric acid (70%; 10 ml) for 5 min, diluted with water (50 ml), and extracted with chloroform (3 × 10 ml), *p*-nitrobenzoic acid (0·15 g) was obtained.

The ratio of *NN′*-bis-(*p*-nitrobenzoyl)ethylenediamine to dihydropyrazine was not altered by using anhydrous ethylenediamine in the condensation. When a solution of the dihydropyrazine (1·6 g) in dimethylformamide (5 ml) and water (1·0 ml) was kept at 100° for 15 min and then worked up as before, dihydropyrazine (1·3 g) and diamide (0·1 g) were recovered.

NN′-*Bis*-(p-*nitrobenzoyl*)*ethylenediamine*.—A solution of *p*-nitrobenzoyl chloride (2·8 g) and anhydrous ethylenediamine (0·5 ml) in dry pyridine (20 ml) was heated at 100° for 30 min and then cooled to 0°. The yellow-brown solid which separated was filtered off, washed with water, and recrystallised from acetic acid to give NN′-*bis*-(p-*nitrobenzoyl*)*ethylenediamine* (1·9 g, 70%) as a cream solid, m.p. 263—265°, $\nu_{max.}$ 3300 (NH), 3050 (ArH), 2950 and 2850 (CH_2), 1650 (amide CO), 1550, 1335, and 870 (NO_2), and 850 cm^{-1} (*p*-substituted benzene) (Found: C, 53·8; H, 4·2; N, 15·6. $C_{16}H_{14}N_4O_6$ requires C, 53·6; H, 3·9; N, 15·6%).

2,3-*Bis*-(p-*nitrophenyl*)*pyrazine*.—A solution of 2,3-dihydro-5,6-bis-(*p*-nitrophenyl)pyrazine (1·0 g) and chloranil (0·75 g) in xylene (10·0 ml) was boiled for 5 h, and the solid which precipitated on cooling (0·2 g) was filtered off and washed with sodium hydroxide solution. The xylene solution was extracted with sodium hydroxide solution, and then with concentrated hydrochloric acid. Neutralisation of the acid extract gave a solid which was combined with the precipitate and recrystallised from benzene, with charcoal treatment, to give 2,3-*bis*-(p-*nitrophenyl*)*pyrazine* (0·46 g, 46%), m.p. 247—249° (Found: C, 59·6; H, 3·1; N, 17·4. $C_{16}H_{10}N_4O_4$ requires C, 59·6; H, 3·1; N, 17·4%).

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[1/144 *Received*, *February* 11*th*, 1971]

[13] B. B. Corson and N. A. Saliani, *Org. Synth.*, 1942, Coll. Vol. 2, p. 69.

[14] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, 1937, 2, 328.