Reactive Intermediates. Part XI.[1] The Generation and Some Reactions of Benzynequinone.[2]

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1-Amino-4,7-dimethoxybenzotriazole is prepared in six steps from 2,5-dimethoxybenzamide. Demethylation of the former with boron tribromide, followed by oxidation with silver oxide gives 1-aminobenzotriazole-4,7-quinone which, on treatment with lead tetra-acetate yields benzynequinone, isolated as 5,6,7,8-tetraphenyl-1,4-naphthoquinone from a reaction with tetracyclone. 1-Amino-5,6-dimethoxybenzotriazole is synthesised in four steps from 4-amino-5-nitroveratrole, but attempts to isolate 1-amino-5,6-dihydroxybenzotriazole from it by demethylation have so far proved unsuccessful.

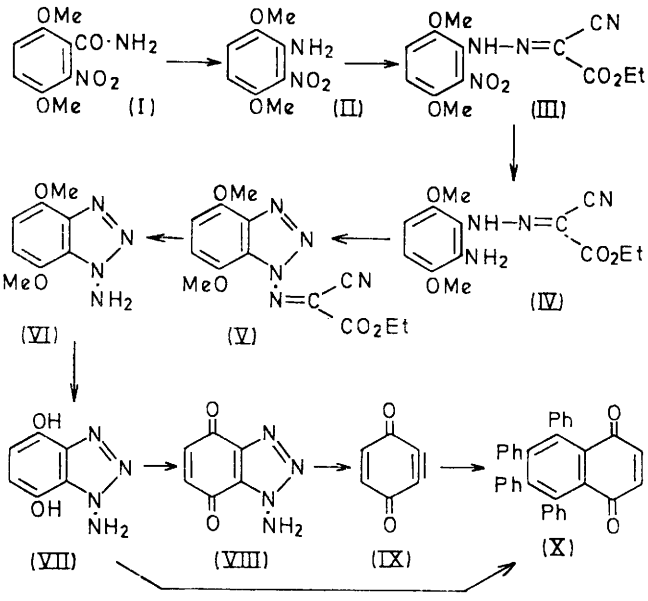
The generation of 3,6- and 4,5-dimethoxybenzyne is described.

A LARGE number of dehydro-aromatic species have now been reported,[3] but no analogous dehydro-quinones appear to have been described. The adjacent quinone carbonyl groups should modify the aryne orbitals, especially in view of the possibility of interaction with the filled lone pair orbitals on oxygen; the geometry of such an interaction would be similar, for example, to that in 1,8-dehydronaphthalene.[4]

These dehydro-quinone intermediates could also be of value in synthesis, *e.g.* of naturally occurring quinones like juglone. We report here the generation and trapping of the simplest dehydro-quinone, cyclohex-2-en-5-yne-1,4-dione (IX) or ' benzynequinone '.

1-Aminobenzotriazole was first prepared [5] in four steps from *o*-nitroaniline *via* *o*-nitrophenylhydrazine derivatives. We expected the key intermediate for the preparation of benzynequinone, 1-amino-4,7-dimethoxybenzotriazole (VI), to be obtainable similarly from the hitherto unreported 3,6-dimethoxy-2-nitroaniline (II). Several synthetic approaches to (II) were investigated. Nitration of 2,5-dimethoxyacetanilide had previously been shown [6] to yield only the 4-nitro-derivative, and attempted partial reduction of 2,3-dinitro-1,4-dimethoxybenzene with sodium sulphide had given [7] bis-(3,6-dimethoxy-2-nitrophenyl) sulphide. The following routes to (II) also proved inadequate: acid-catalysed rearrangement of 2,5-dimethoxy-*N*-nitroaniline, Schmidt rearrangement of 3,6-dimethoxy-2-nitroacetophenone, and Beckmann rearrangement of the oxime of 3,6-dimethoxy-2-nitroacetophenone. However Hofmann rearrangement of 3,6-dimethoxy-2-nitrobenzamide (I), obtained as the major product (together with the isomeric 2,5-dimethoxy-4-nitrobenzamide) on nitration of 2,5-dimethoxybenzamide with concentrated nitric acid at low temperature, gave the required 3,6-dimethoxy-2-nitroaniline (60%).

Coupling of diazotised (II) with ethyl cyanoacetate in an aqueous acetate buffer produced the hydrazone (III) in high yield. Catalytic hydrogenation of this over palladium–charcoal at atmospheric pressure was slow, but generally gave the corresponding amine (IV) in good yield. Diazotisation of the amine produced a high yield



of the triazole (V). Prolonged treatment of the triazole with hot concentrated hydrochloric acid then gave, after basification, 1-amino-4,7-dimethoxybenzotriazole (VI) in good yield.

Coupling of diazotised (II) with diethyl malonate also produced the corresponding hydrazone (XI; R = NO_2). However, catalytic hydrogenation of the hydrazone (XI; R = NO_2) gave ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (XII) as a by-product; yields of this quinoxaline derivative were higher (up to *ca.* 60%) when ethyl alcohol rather than ethyl acetate was the solvent.

The quinoxaline derivative (XII) has been shown to

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[1] Part X, D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, preceeding paper.

[2] Preliminary communication, C. W. Rees and D. E. West, *Chem. Comm.*, 1969, 647.

[3] R. W. Hoffmann, ' Dehydrobenzene and Cycloalkynes,' Academic Press, London, 1967.

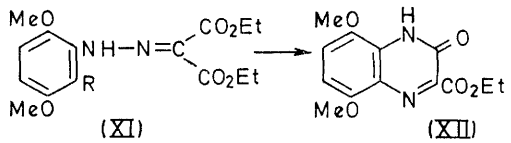
[4] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499; C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 765.

[5] R. Trave and G. Bianchetti, *Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1960, **28**, 652.

[6] A. Baessler, *Ber.*, 1884, **17**, 2121.

[7] S. Kawai and Y. Suzuki, *J. Chem. Soc. Japan*, 1959, **80**, 338.

arise in the following manner: the nitro-compound (XI; R = NO_2) is reduced to the amine (XI; R = NH_2) which is reductively cleaved to give 3,6-dimethoxy-*o*-phenylenediamine and the imine $HN{=}C(CO_2Et)_2$ which



(XI) (XII)

presumably is rapidly hydrolysed to give diethyl mesoxalate, $O{=}C(CO_2Et)_2$; reaction of 3,6-dimethoxy-*o*-phenylenediamine with diethyl mesoxalate then gives rise to ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (XII). Indeed, Sen and Madan [8] have prepared (XII) in this very way. Evidence for this intermolecular mechanism is as follows: (*a*) catalytic hydrogenation of the amine (XI; R = NH_2) also produced quinoxalone (XII); (*b*) hydrogenation of 2-nitrophenylazomalonate in the presence of 3,6-dimethoxy-*o*-phenylenediamine gave not only a small amount of the 'crossed' product, *i.e.* (XII), but also *o*-phenylenediamine itself. Hydrolysis of the quinoxalinecarboxylic acid ester, followed by thermal decarboxylation gave the hitherto unreported 2-hydroxy-5,8-dimethoxyquinoxaline.

1-Amino-4,7-dimethoxybenzotriazole (VI) was demethylated with boron tribromide [9] in methylene chloride to give a good yield of the corresponding quinol (VII) which crystallised from water with solvent of crystallisation.

Silver oxide in tetrahydrofuran containing anhydrous sodium sulphate oxidised a suspension of the quinol (VII) cleanly at room temperature to give, after filtration and rapid evaporation under reduced pressure, 1-aminobenzotriazole-4,7-quinone (VIII) as an unstable orange-brown oil. This decomposed too rapidly for full characterisation but its i.r. spectrum showed typical quinone absorption at 1680 and 1630 $cm.^{-1}$. Its crystalline isopropylidene derivative, formed by similar oxidation of (VII) but in acetone, was more stable and also absorbed at 1680 and 1630 $cm.^{-1}$.

When the oily benzotriazolequinone (VIII) was rapidly dissolved in methylene chloride containing tetraphenylcyclopentadienone (tetracyclone) (1 equiv.), and oxidised with lead tetra-acetate, 5,6,7,8-tetraphenyl-1,4-naphthoquinone (X) was obtained in 40% yield. The only simple explanation of this result is that benzynequinone is generated and undergoes cycloaddition with tetracyclone, the adduct suffering the expected spontaneous decarbonylation. Thus the scope of our oxidative fragmentation route to dehydro-intermediates [10] is extended in providing a means of generating dehydro-quinones.

Oxidation of the quinol (VII) with lead tetra-acetate in the presence of tetracyclone gave a higher yield (60%) of the naphthoquinone (X), but the intermediate here could well be 3,6-dihydroxybenzyne rather than benzynequinone. The fact that the quinol (VII) is so sparingly soluble in methylene chloride precluded the possibility of carrying through this oxidation in the presence of a deficiency of lead tetra-acetate in order to determine whether or not 1,4-dihydroxy-5,6,7,8-tetraphenylnaphthalene is initially formed in the reaction.

When benzyne and benzynequinone, generated from 1-aminobenzotriazole (1 mmole) and 1-aminobenzotriazole-4,7-quinone [from the quinol (VII) (1 mmole)] respectively, competed for tetracyclone (1 mmole), much more 1,2,3,4-tetraphenylnaphthalene (90%) than 5,6,7,8-tetraphenyl-1,4-naphthoquinone (8%) was obtained, possibly because benzynequinone is indeed less reactive than benzyne in this [2 + 4] cycloaddition. A similar experiment carried out in the presence of 2 equiv. of tetracyclone gave 1,2,3,4-tetraphenylnaphthalene (77%) and the naphthoquinone (X) (13%). It is not possible, however, to arrive at any precise conclusions from these experiments, since the rate of generation of benzyne by this oxidative fragmentation may differ markedly from that of benzynequinone.

Oxidation of 1-amino-4,7-dimethoxybenzotriazole (VI) with lead tetra-acetate in benzene and methylene chloride gave, after chromatography on silica gel, the hitherto unreported 1,4,5,8-tetramethoxybiphenylene (formed by dimerisation of 3,6-dimethoxybenzyne) in yields of up to 37%. Demethylation of 1,4,5,8-tetramethoxybiphenylene with boron tribromide in methylene chloride gave 1,4,5,8-tetrahydroxyphenylene [11] in low yield.

When 3,6-dimethoxybenzyne was generated in the presence of benzyne by oxidation of 1-amino-4,7-dimethoxybenzotriazole (2 mmoles) and 1-aminobenzotriazole (2 mmoles) with excess of lead tetra-acetate in acetonitrile, 1,4-dimethoxybiphenylene (18%), arising from a [2 + 2] cycloaddition of 3,6-dimethoxybenzyne to benzyne, was obtained, together with biphenylene (40%) and a trace of 1,4,5,8-tetramethoxybiphenylene.

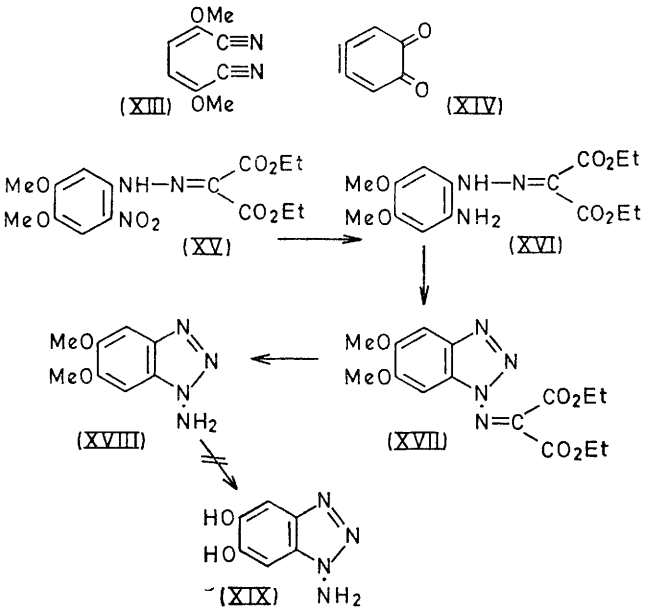
Oxidation of (VI) with lead tetra-acetate in furan gave 1,4-epoxy-1,4-dihydro-5,8-dimethoxynaphthalene (63%) as colourless prisms, m.p. 86—87°, after chromatography on silica gel.

cis,cis-Muconononitrile has been obtained [12] by the oxidation of *o*-phenylenediamine with lead tetra-acetate; 3,6-dimethoxy-*o*-phenylenediamine similarly gave the corresponding *cis,cis*-muconitrile (XIII) in 48% yield after chromatography on alumina. This di-enol ether was surprisingly resistant to acid hydrolysis, being recovered unchanged after treatment with warm concentrated hydrochloric acid in ethanol. Presumably protonation on nitrogen competes effectively with protonation on the deactivated double bonds.

[8] A. B. Sen and O. P. Madan, *J. Indian Chem. Soc.*, 1961, **38**, 225.
[9] J. F. W. McOmie, M. L. Watts, and D. E. West, *Tetrahedron*, 1968, **24**, 2289.
[10] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742, 748, 752; C. W. Rees and R. C. Storr, *ibid.*, pp. 756, 760.
[11] E. H. Gold and D. Ginsburg, *J. Chem. Soc.* (*C*), 1967, 15.
[12] K. Nakagawa and H. Onoue, *Chem. Comm.*, 1965, 396.

An interesting extension to this work would be to generate 'benzyne-*o*-quinone' (cyclohexa-3,4,5-triene-1,2-dione) (XIV), in which no formal triple bond can be written, by a similar oxidation of the 1-aminobenzotriazole-5,6-quinone.

Our approach to the synthesis of the key intermediate, 1-amino-5,6-dimethoxybenzotriazole (XVIII) was similar to that for the 4,7-dimethoxy-isomer. Frisch and



Bogert [13] had reported that hydrogenation of 4,5-dinitroveratrole in ethanol at 3 atmos. over palladium, gave 70—75% yields of 4-amino-5-nitroveratrole. We found that these conditions led to slow and variable uptake of hydrogen and irreproducible yields. It was better to carry out the hydrogenation at 1 atmos. and room temperature with glacial acetic acid as solvent and platinum oxide as catalyst. This gave 4-amino-5-nitroveratrole as a red crystalline solid, sufficiently pure for the next stage of the synthesis.

Coupling of this diazotised *o*-nitroaniline derivative with diethyl malonate in an aqueous carbonate buffer produced the hydrazone (XV) in *ca.* 65% overall yield from 4,5-dinitroveratrole. Catalytic hydrogenation of this hydrazone gave the corresponding amine (XVI) which was not generally isolated, but was diazotised to give the triazole (XVII) in yields of up to 57%. Hydrolysis of the triazole by heating with concentrated hydrochloric acid gave, after basification, a high yield of 1-amino-5,6-dimethoxybenzotriazole (XVIII).

However, all attempts to demethylate this compound to the dihydroxybenzotriazole (XIX) with boron tribromide, hydrobromic acid, or aluminium chloride led only to the formation of high-melting solids which did not liberate nitrogen on treatment with lead tetra-acetate.

[13] K. C. Frisch and M. T. Bogert, *J. Org. Chem.*, 1943, **8**, 333.

Oxidation of 1-amino-5,6-dimethoxybenzotriazole (XVIII) with lead tetra-acetate in the presence of tetracyclone gave 6,7-dimethoxy-1,2,3,4-tetraphenylnaphthalene (35%), thus demonstrating the intermediate formation of 4,5-dimethoxybenzyne. However, oxidation of this *N*-amino-compound (XVIII), in the absence of a trapping agent, gave no 2,3,6,7-tetramethoxybiphenylene.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. I.r. spectra of solids were taken for Nujol mulls, and of liquids for capillary films. ^{1}H N.m.r. spectra were taken for solutions in deuteriochloroform with tetramethylsilane as internal reference, except where indicated. Lead tetra-acetate was freed from acetic acid by pressing between filter papers, and keeping over concentrated sulphuric acid at atmospheric pressure.

Methylation of 2,5-Dihydroxybenzoic Acid.—Dimethyl sulphate (250 ml.) and concentrated aqueous potassium hydroxide (50%; 250 ml.) were added alternately in small portions, with stirring, to a solution of 2,5-dihydroxybenzoic acid (50·0 g.) in ethanol (100 ml.) and aqueous potassium hydroxide (50%; 50 ml.). The solution warmed to 50—60° as reaction took place. When the addition was complete, the mixture was heated to 90—95° in order to hydrolyse excess of dimethyl sulphate.

The cooled solution was extracted with ether; the organic extract was then extracted with 2N-sodium hydroxide, and the ethereal layer was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to give methyl 2,5-dimethoxybenzoate [14] (41·1 g., 65%) as a colourless, mobile liquid.

The basic extract was acidified with hydrochloric acid to give 2,5-dimethoxybenzoic acid (14·1 g., 24%) as prisms, m.p. 73—75° (lit.,[15] 76°), after filtration and drying.

Methyl 2,5-Dimethoxybenzoate.—A solution of 2,5-dimethoxybenzoic acid (25·9 g.) in methanol (50 ml.) containing concentrated sulphuric acid (2 ml.) was refluxed for 5·5 hr. Excess of methanol was distilled off, the residual oil was poured into water, and the mixture was extracted with ether. The organic layer was washed with 2N-aqueous sodium hydrogen carbonate and then with water. The ether extract was dried ($MgSO_4$) and evaporated under reduced pressure to give methyl 2,5-dimethoxybenzoate (24·6 g., 88%) as a pale yellow, mobile liquid.

2,5-Dimethoxybenzamide.—A suspension of methyl 2,5-dimethoxybenzoate (42·0 g.) in concentrated aqueous ammonia (200 ml.) was stirred at room temperature in a loosely stoppered flask for 15 hr. The white solid which separated was filtered off, washed with water, and recrystallised from hot water to yield 2,5-dimethoxybenzamide (35·5 g., 92%) as blades, m.p. 141—142° (lit.,[16] 140°).

Nitration of 2,5-Dimethoxybenzamide.—2,5-Dimethoxybenzamide (1·00 g.) was added in portions during 25 min. to stirred nitric acid (*d* 1·42; 10 ml.) at −10 to −5°. The temperature was allowed to rise to 0—5° and the mixture was stirred for a further 20 min. and then poured into ice–

[14] H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1961, 5239.
[15] F. Tiemann and W. H. M. Müller, *Ber.*, 1881, **14**, 1993.
[16] H. Kauffmann, *Annalen*, 1906, **344**, 70.

water (*ca.* 150 ml.). The precipitated pale yellow solid was filtered off, washed well with water, and dried (1·10 g.).

The solid was dissolved as completely as possible in warm chloroform (*ca.* 30 ml.) and applied to a silica gel column (31 × 3·5 cm.). Elution with chloroform gave (*a*) 2,5-*dimethoxy*-4-*nitrobenzamide* (0·10 g., 8%) as pale yellow blades, m.p. 224—224·5° (from benzene) (Found: C, 47·9; H, 4·2; N, 12·3. $C_9H_{10}N_2O_5$ requires C, 47·8; H, 4·45; N, 12·4%), $\nu_{max.}$ 3420m, 3150m, 1682s, 1520s, 1348s, and 890s cm.$^{-1}$; (*b*) 3,6-*dimethoxy*-2-*nitrobenzamide* (I) (0·61 g.) 49%) as pale yellow needles, m.p. 225—226° (from methanol) (Found: C, 48·0; H, 4·2; N, 12·5%), $\nu_{max.}$ 3380m, 3160m, 1655s, 1560s, 1365m, and 798s cm.$^{-1}$.

The experiment was repeated with 2,5-dimethoxybenzamide (28·1 g.) and nitric acid (*d* 1·42; 180 ml.). The precipitated yellow solid was dried and extracted twice with boiling benzene (500 and 250 ml., respectively). The residue was crystallised from acetone to yield (*a*) 3,6-dimethoxy-2-nitrobenzamide (19·7 g., 57%) as pale yellow leaflets, and (*b*) a mixture (1·0 g., 3%) of the two isomeric nitroamides. A mixture (7·95 g., 23%) of the two nitroamides was also obtained on concentration and cooling of the combined benzene extracts.

3,6-*Dimethoxy*-2-*nitroaniline* (II).—A suspension of 3,6-dimethoxy-2-nitrobenzamide (27·0 g.) in aqueous sodium hydroxide (15%; 450 ml.) was treated at room temperature with a suspension of bromine (19·2 g., 6·2 ml.) in water (300 ml.) with stirring. The mixture was slowly warmed to *ca.* 80° and maintained at this temperature for 1 hr. during which time the yellow amide dissolved and a red oil separated. It was then cooled; the oil solidified to give an orange-red product which was filtered off, washed well with water and dried. Crystallisation from light petroleum (b.p. 60—80°)–benzene gave 3,6-*dimethoxy*-2-*nitroaniline* (II) (14·2 g., 60%), or orange-red prisms, m.p. 76—77° (Found: C, 48·7; H, 5·2; N, 14·3. $C_8H_{10}N_2O_4$ requires C, 48·5; H, 5·1; N, 14·1%), $\nu_{max.}$ 3445m, 3330m, 1515s, 1335s, 785s cm.$^{-1}$, τ 3·26 (1H, d, *J* 9·0 c./sec.), 3·84 (1H, d, *J* 9·0 c./sec.), 4·70 (2H), 6·21 (3H), and 6·24 (3H).

Ethyl 2-*Cyano*-2-(3,6-*dimethoxy*-2-*nitrophenyl*)*azoacetate* (III).—3,6-Dimethoxy-2-nitroaniline (9·9 g., 0·05 mole) was made into a paste with concentrated hydrochloric acid (15 ml.), and water (50 ml.) was added to produce a fine suspension; sodium nitrite (4·0 g.) in water (15 ml.) was added at *ca.* 5°. The resulting suspension was added in portions to a well stirred emulsion of ethyl cyanoacetate (6·3 g., 6·0 ml.) in water (30 ml.) at 5—10°; anhydrous sodium acetate (15 g.) was added during the course of the reaction. The mixture was then allowed to warm to *ca.* 20° with stirring. The resultant yellow solid was filtered off and washed well with water to give the *azo-derivative* (13·3 g., 82%) as yellow prisms, m.p. 187—188° (from ethanol–acetone) (Found: C, 48·5; H, 4·5; N, 17·4. $C_{13}H_{14}N_4O_6$ requires C, 48·4; H, 4·4; N, 17·4%), $\nu_{max.}$ 3150w, 3110w, 2230s, 1698s, 1555s, 1320m, and 810s cm.$^{-1}$, τ 3·15 (1H), 3·02 (1H, d, *J* 8·5 c./sec.), 3·28 (1H, d, *J* 8·5 c./sec.), 5·63 (2H, q, *J* 7·5 c./sec.), 6·07 (3H), 6·17 (3H), and 8·61 (3H, t, *J* 7·5 c./sec.).

Ethyl 2-(2-*Amino*-3,6-*dimethoxyphenyl*)*azo*-2-*cyanoacetate* (IV).—A suspension of finely powdered ethyl 2-cyano-2-(3,6-dimethoxy-2-nitrophenyl)azoacetate (5·0 g.) in ethyl acetate (100 ml.) was hydrogenated at 25° and 1 atmos. over 10% palladium–charcoal (0·2 g.). After 60 hr., the theoretical amount (*ca.* 1200 ml.) of hydrogen had been consumed. The solution was warmed and filtered and the filtrate was evaporated under reduced pressure. The residue gave the *amino-azo-derivative* (3·3 g., 74%) as orange prisms, m.p. 138—139° (from ethanol) (Found: C, 53·5; H, 5·5; N, 19·3. $C_{13}H_{16}N_4O_4$ requires C, 53·4; H, 5·5; N, 19·2%), $\nu_{max.}$ 3480m, 3365m, 3090w,br, 2225s, 1683s, and 778m cm.$^{-1}$, τ −3·78 (1H), 3·43 (1H, d, *J* 8·5 c./sec.), 3·85 (1H, d, *J* 8·5 c./sec.), 4·53 (2H), 5·63 (2H, q, *J* 7·5 c./sec.), 6·14 (3H), 6·17 (3H), and 8·63 (3H, t, *J* 7·5 c./sec.).

Ethyl 2-*Cyano*-2-(4,7-*dimethoxybenzotriazol*-1-*yl*)*iminoacetate* (V).—A warm solution of ethyl 2-(2-amino-3,6-dimethoxyphenyl)azo-2-cyanoacetate (6·20 g.) in ethanol (*ca.* 200 ml.) was added to sodium nitrite (1·5 g.) in water (30 ml.). This mixture was then added in portions with stirring to a mixture of concentrated hydrochloric acid (15 ml.) and water (15 ml.) at 0—7°. The mixture was then allowed to warm to *ca.* 15° with stirring. The product was filtered off and washed with water to give the *benzotriazole* (5·72 g., 89%) as deep red needles, m.p. 185—186° (from ethanol–acetone) (Found: C, 51·7; H, 4·4; N, 23·2. $C_{13}H_{13}N_5O_4$ requires C, 51·5; H, 4·3; N, 23·1%), $\nu_{max.}$ 2215w, 1755s, 1730s, and 820s cm.$^{-1}$, τ 2·96 (1H, d, *J* 8·5 c./sec.), 3·24 (1H, d, *J* 8·5 c./sec.), 5·47 (2H, q, *J* 7·5 c./sec.), 5·91 (3H), 6·04 (3H), and 8·55 (3H, t, *J* 7·5 c./sec.).

1-*Amino*-4,7-*dimethoxybenzotriazole* (VI).—Ethyl 2-cyano-2-(4,7-dimethoxybenzotriazol-1-yl)iminoacetate (2·53 g.) was heated on a steam-bath with concentrated hydrochloric acid (30 ml.) for 3 hr. The cooled solution was basified with concentrated aqueous sodium hydroxide; 1-*amino*-4,7-*dimethoxybenzotriazole* (1·10 g., 68%) separated. Recrystallisation from water gave prisms, m.p. 118—119° (Found: C, 47·3; H, 5·0; N, 27·3. $C_8H_{10}N_4O_2$,0·5H_2O requires C, 47·3; H, 5·5; N, 27·6%), $\nu_{max.}$ 3610w, 3355m, 3320m, 3180m, 1600m, and 812s cm.$^{-1}$, τ(D_2O) 3·18—3·28 (2H), 5·97 (3H), and 6·03 (3H).

1-*Benzylideneamino*-4,7-*dimethoxybenzotriazole*.—A mixture of 1-amino-4,7-dimethoxybenzotriazole (0·194 g.) and redistilled benzaldehyde (0·5 ml.) in ethanol (10 ml.) was heated on a steam-bath for 15 min. It was then cooled and diluted with water; an oil separated and slowly solidified. This was washed with water and gave the *benzylidene derivative* (0·204 g., 72%) as lemon needles, m.p. 119—120° [from light petroleum (b.p. 60—80°)] (Found: C, 63·8; H, 5·0; N, 19·85. $C_{15}H_{14}N_4O_2$ requires C, 63·8; H, 5·0; N, 19·85%), $\nu_{max.}$ 1540s and 7955s cm.$^{-1}$, τ 0·51 (1H), 1·93—2·65 (5H, m), 3·20 (1H, d, *J* 8·5 c./sec.), 3·47 (1H, d, *J* 8·5 c./sec.), 5·97 (3H), and 6·04 (3H).

1-*Amino*-4,7-*dihydroxybenzotriazole* (VII).—Boron tribromide (6·1 g., 2·3 ml.) in dry methylene chloride (21 ml.) was added to a suspension of 1-amino-4,7-dimethoxybenzotriazole (0·776 g.) in dry methylene chloride (25 ml.). The mixture was stirred at room temperature for 16 hr. and was then cautiously hydrolysed with water. The *dihydroxy-derivative* (0·440 g., 66%) was obtained as an off-white solid after filtration, washing with water, and drying, and gave the hemi-hydrate as off-white blades, m.p. >300° (from water) (Found: C, 41·6; H, 3·6; N, 31·7. $C_6H_6N_4O_2$,0·5H_2O requires C, 41·2; H, 4·0; N, 32·0%), $\nu_{max.}$ 3300m, 3190m, 2700m,br, 1535s, and 815s cm.$^{-1}$.

Oxidation of 1-*Amino*-4,7-*dihydroxybenzotriazole with Lead Tetra-acetate in the Presence of Tetracyclone*.—A suspension of 1-amino-4,7-dihydroxybenzotriazole (0·085 g., 0·0005 mole) in dry methylene chloride (15 ml.) was added in portions to a well-stirred solution of tetracyclone (0·19 g., 0·0005 mole), and lead tetra-acetate (0·665 g., 0·0015 mole)

in dry methylene chloride (10 ml.). Nitrogen was slowly evolved; the mixture was stirred at room temperature for 21 hr. and filtered, and the residue was washed with warm methylene chloride. The combined filtrate and washings were reduced in volume under reduced pressure and applied to a column (20 × 2·5 cm.) of silica gel. Elution with benzene gave tetracyclone (0·052 g., 27% recovery); elution with benzene–chloroform gave 5,6,7,8-*tetraphenyl*-1,4-*naphthoquinone* (X) (0·128 g., 54%), which yielded orange microprisms, m.p. 302—303° [from light petroleum (b.p. 60—80°)–benzene–methylene chloride] (Found: C, 88·7; N, 4·65. $C_{34}H_{22}O_2$ requires C, 88·3; H, 4·8%), $\nu_{max.}$ 1675s, 865s, 785s, and 700s cm.$^{-1}$, τ 2·66—3·27.

Generation and Trapping of Benzyne-p-*quinone* (IX).—Anhydrous sodium sulphate (0·10 g.) and silver oxide (0·20 g.) were added to a stirred suspension of 1-amino-4,7-dihydroxybenzotriazole (0·10 g.) in dry tetrahydrofuran (10 ml.). The mixture was stirred at room temperature for 1·5 hr. and then filtered to give an orange-yellow solution. This was evaporated to dryness under reduced pressure (water-bath at 23°) to leave an orange-brown oil ($\nu_{max.}$ 3320m, 3250m, 1680s, 1630m, and 740s cm.$^{-1}$) together with a brown solid (probably polymeric). The oil was dissolved in dry methylene chloride (5 ml.) together with tetracyclone (0·232 g., 1 equiv.) and treated with excess of lead tetra-acetate (0·28 g.). When evolution of nitrogen had ceased, the mixture was applied to a column of silica gel (28 × 2·5 cm.). Elution with benzene gave tetracyclone (0·133 g., 57% recovery); elution with benzene–chloroform gave 5,6,7,8-tetraphenyl-1,4-naphthoquinone (0·108 g., 39%) as an orange-yellow crystalline solid, m.p. 300—302° [from light petroleum (b.p. 60—80°)–benzene].

1-*Isopropylideneaminobenzotriazole*-4,7-*dione*.—Anhydrous sodium sulphate (0·10 g.) and then silver oxide (0·2 g.) were added to a stirred suspension of 1-amino-4,7-dihydroxybenzotriazole (0·10 g.) in acetone (10 ml.). The mixture was stirred at room temperature for 1 hr. and then filtered; the filtrate was evaporated under reduced pressure and the residue gave 1-*isopropylideneaminobenzotriazole*-4,7-*dione* (VIII) as colourless prisms (0·063 g., 51%), m.p. 140—143° [from light petroleum (b.p. 60—80°)–benzene], $\nu_{max.}$ 1680s, 1630s, 1585m, and 860s cm.$^{-1}$, τ 3·13 (2H), 7·57 (3H), and 7·97 (3H).

Generation of Benzyne-p-*quinone and Benzyne in the Presence of Tetracyclone*.—Anhydrous sodium sulphate (0·17 g.) and silver oxide (0·33 g.) were added to a suspension of 1-amino-4,7-dihydroxybenzotriazole (0·166 g., 0·001 mole) in dry tetrahydrofuran (16 ml.). The mixture was stirred at room temperature for 1 hr. and then filtered; the filtrate was evaporated to dryness under reduced pressure to leave an orange-brown oil together with a little polymeric material.

Finely powdered 1-aminobenzotriazole (0·134 g., 0·001 mole) and tetracyclone (0·384 g., 0·001 mole) were added to the oil and the whole was dissolved in dry methylene chloride (15 ml.); excess (*ca.* 2·0 g.) of lead tetra-acetate was added in portions to the stirred solution; nitrogen was evolved and the colour of the solution gradually changed from purple to deep green.

When the addition was complete and gas evolution had ceased, the mixture was applied to a silica gel column (27·5 × 2·5 cm.). Elution with benzene gave 1,2,3,4-tetraphenylnaphthalene [17] (0·388 g., 90%) as a white crystalline solid identical (i.r. spectrum) with an authentic sample; elution with benzene–chloroform gave 5,6,7,8-tetraphenyl-1,4-naphthoquinone (0·037 g., 8%) as an orange crystalline solid.

Diethyl (3,6-*Dimethoxy*-2-*nitrophenyl*)*azomalonate* (XI; R = NO_2).—3,6-Dimethoxy-2-nitroaniline (9·9 g., 0·05 mole) was made into a paste with concentrated hydrochloric acid (15 ml.) and water (33 ml.) was added to produce a suspension; sodium nitrite (3·8 g.) in water (9 ml.) was added at *ca.* 5°. The solution was added dropwise during 15 min. to a well stirred emulsion of diethyl malonate (8·0 g., 7·6 ml.) in water (33 ml.) at 5—10°; anhydrous sodium acetate (16·6 g.) was added during the reaction. The mixture was then allowed to warm to *ca.* 20° with stirring. The orange product was filtered off and washed with water to yield the *azo-derivative* (12·65 g., 68%) as orange yellow prisms, m.p. 116—117° [from ethanol (charcoal)] (Found: C, 49·0; H, 5·3; N, 11·4. $C_{15}H_{19}N_3O_8$ requires C, 48·8; H, 5·2; N, 11·4%), $\nu_{max.}$ 3155m, 1716s, 1708s, 1667s, 1548s, 1310s, and 802s cm.$^{-1}$, τ 3·10 (1H, d, *J* 8·5 c./sec.), 3·41 (1H, d, *J* 8·5 c./sec.), 5·66 (2H, q, *J* 7·0 c./sec.), 5·73 (2H, q, *J* 7·0 c./sec.), 6·12 (3H), 6·21 (3H), 8·61 (3H, t, *J* 7·0 c./sec.), and 8·64 (3H, t, *J* 7·0 c./sec.).

Diethyl (2-*Amino*-3,6-*dimethoxyphenyl*)*azomalonate* (XI; R = NH_2).—Diethyl (3,6-dimethoxy-2-nitrophenyl)azomalonate (5·0 g.) was suspended in ethyl acetate (50 ml.) and hydrogenated at 1 atmos. and room temperature over 10% palladium–charcoal (0·2 g.). Approximately the theoretical amount of hydrogen was consumed during *ca.* 80 hr. The solution was then filtered through Kieselguhr and the latter was washed with warm acetone; the combined filtrate and washings were evaporated under reduced pressure. The residue was fractionally crystallised from ethanol to give (*a*) diethyl (2-amino-3,6-dimethoxyphenyl)-azomalonate (3·36 g., 73%) as orange-yellow prisms, m.p. 97—99°; and (*b*) ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (0·14 g., 4%) as an orange-yellow crystalline solid, m.p. 254—255°.

A sample of the *azomalonate* (IX; R = NH_2) was obtained as orange orthorhombic prisms, m.p. 103—104° (from ethanol) (Found: C, 53·1; H, 6·4; N, 12·4. $C_{15}H_{21}N_3O_6$ requires C, 53·1; H, 6·2; N, 12·4%), $\nu_{max.}$ 3475m, 3335m, 3110w, 1700s, 1644s, and 768s cm.$^{-1}$, τ 3·55 (1H, d, *J* 8·5 c./sec.), 3·92 (1H, d, *J* 8·5 c./sec.), 4·20 (2H), 5·64 (2H, q, *J* 7·0 c./sec.), 5·76 (2H, q, *J* 7·0 c./sec.), 6·18 (3H), 6·24, (3H), 8·63 (3H, t, *J* 7·0 c./sec.), and 8·68 (3H, t, *J* 7·0 c./sec.).

Ethyl 3-*Hydroxy*-5,8-*dimethoxyquinoxaline*-2-*carboxylate* (XII).—Pure diethyl (3,6-dimethoxy-2-nitrophenyl)azomalonate (5·0 g.) was suspended in ethanol (70 ml.) and hydrogenated at 1 atmos. and room temperature over 10% palladium–charcoal (0·2 g.). Hydrogen ceased to be consumed after *ca.* 75 hr. The solution was warmed and filtered; the residue was extracted with boiling ethanol–acetone and the extract was filtered and cooled to give ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (0·48 g., 13%) as yellow prisms, m.p. 258—259°; the filtrate was evaporated to dryness under reduced pressure and the residue was dissolved in the minimum of chloroform and applied to a silica gel column (27 × 3·5 cm.). Elution with benzene–chloroform and chloroform removed traces of coloured oils; elution with chloroform–ethyl acetate gave ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (1·92 g., 51%) as yellow plates, m.p. 259—260° (from ethanol–acetone) (lit.,[8] 242°) (Found: C, 55·8; H, 5·2;

[17] G. Wittig and E. Knauss, *Chem. Ber.*, 1958, **91**, 895.

N, 10·2. Calc. for $C_{13}H_{14}N_2O_5$: C, 56·1; H, 5·1; N, 10·1%), $\nu_{max.}$ 3140w, 3105w, 1750s, 1660s, and 792s cm.$^{-1}$, τ 3·02 (1H, d, J 9·5 c./sec.), 3·39 (1H, d, J 9·5 c./sec.), 5·54 (2H, q, J 7·5 c./sec.), 6·05 (3H), 6·08 (3H), and 8·60 (3H, t, J 7·5 c./sec.).

2-Hydroxy-5,8-dimethoxyquinoxaline.— Ethyl-3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (1·43 g.) was treated with aqueous 2N-sodium hydroxide (30 ml.) at room temperature; the resultant solution was filtered and the filtrate was acidified with 2N-hydrochloric acid to precipitate a red solid. The product was collected, washed with water, then with methanol, and finally dried to give 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylic acid (1·11 g., 86%) as a red crystalline solid, m.p. *ca.* 215° (decomp.) (lit.,[8] 213°), $\nu_{max.}$ 3070m, 2630w,br, 1758s, and 810s cm.$^{-1}$.

3-Hydroxy-5,8-dimethoxyquinoxaline-2-carboxylic acid (0·34 g.) was sublimed at *ca.* 215—220°/0·2 mm. The sublimate was dissolved in a minimum of chloroform and applied to a silica gel column (15 × 2·5 cm.). Elution with chloroform gave *2-hydroxy-5,8-dimethoxyquinoxaline* (0·15 g., 53%) as pale yellow needles, m.p. 228—228·5° (from benzene) (Found: C, 58·2; H, 4·9; N, 13·7. $C_{10}H_{10}N_2O_3$ requires C, 58·2; H, 4·9; N, 13·6%), $\nu_{max.}$ 3100w, 1735s, and 800s cm.$^{-1}$, τ 1·74 (1H), 3·07 (1H, d, J 9·0 c./sec.), 3·40 (1H, d, J 9·0 c./sec.), 6·05 (3H), and 6·08 (3H).

Hydrogenation of Diethyl (2-Amino-3,6-dimethoxyphenyl)-azomalonate (XI; R = NH_2).—A suspension of the azomalonate (0·35 g.) in ethanol (15 ml.) was hydrogenated at room temperature and 1 atmos. over 10% palladium–charcoal (0·05 g.). After 68 hr. the uptake of hydrogen was 80 ml. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in the minimum of chloroform and applied to silica gel (16 × 2·5 cm.). Elution with benzene–chloroform gave an unidentified orange-red oil (0·06 g.); elution with chloroform gave ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (0·087 g., 30%) as yellow prisms, m.p. 252—253° [from light petroleum ether (b.p. 60—80°)–chloroform].

Hydrogenation of Diethyl (2-Nitrophenyl)azomalonate in the Presence of 3,6-Dimethoxy-o-phenylenediamine.—A suspension of 1,4-dimethoxy-2,3-dinitrobenzene (2·28 g., 0·01 mole) in ethanol (25 ml.) was hydrogenated at room temperature and 1 atmos. over 10% palladium–charcoal (0·1 g.). The theoretical amount of hydrogen was consumed in 15 hr. Diethyl (2-nitrophenyl)azomalonate (3·09 g., 0·01 mole), 10% palladium–charcoal (0·1 g.), and ethanol (35 ml.) were then added to the mixture which was further hydrogenated at room temperature and 1 atmos. In 5 days a total of 1370 ml. of hydrogen was consumed.

The solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residual oil was dissolved in the minimum of chloroform and applied to silica gel (26 × 3·5 cm.). Elution with benzene–chloroform removed an unidentified yellow-brown oil (1·41 g.); elution with chloroform gave *o*-phenylenediamine (0·18 g., 16%) as colourless plates, m.p. 100—101° [from light petroleum (b.p. 60—80°)], mixed m.p. 102°. Elution with chloroform–ethyl acetate gave a solid which was extracted with boiling ethanol; ethyl 3-hydroxy-5,8-dimethoxyquinoxaline-2-carboxylate (0·06 g., 2%) separated as orange-yellow prisms, m.p. 254—255°, from the cooled, concentrated solution.

1,4,5,8-Tetramethoxybiphenylene.—A solution of 1-amino-4,7-dimethoxybenzotriazole (0·11 g.) in dry benzene (20 ml.) and dry methylene chloride (5 ml.) was added in portions to a suspension of lead tetra-acetate (0·4 g., *ca.* 1·5 equiv.) in dry benzene (15 ml.) at *ca.* 40°. When gas evolution ceased the mixture was applied to silica gel (20 × 2·5 cm.). Elution with benzene gave *1,4,5,8-tetramethoxybiphenylene* (0·028 g., 37%) which formed yellow needles, m.p. 138—139° [from light petroleum (b.p. 60—80°)] (Found: C, 70·6; H, 5·8. $C_{16}H_{16}O_4$ requires C, 70·55; H, 5·9%), $\nu_{max.}$ 1590s, 785s, and 770s cm.$^{-1}$.

1,4,5,8-Tetrahydroxybiphenylene.—A solution of 1,4,5,8-tetramethoxybiphenylene (0·075 g.) in dry methylene chloride (3 ml.) was treated with excess of boron tribromide (1·3 g.) in dry methylene chloride (4·5 ml.); dry benzene (10 ml.) was added to the solution, which was gently refluxed for 16·5 hr. while protected with a calcium chloride tube. The cooled mixture was hydrolysed carefully with water; the product was filtered off, washed well with water, and dried to give 1,4,5,8-tetrahydroxybiphenylene (0·016 g., 27%) as an off-white crystalline solid, m.p. *ca.* 250° (decomp.) [lit.,[11] 255—257° (decomp.)], $\nu_{max.}$ 3290s, 1630m, and 795s cm.$^{-1}$.

Generation of 3,6-Dimethoxybenzyne in the Presence of Benzyne.—A solution of 1-aminobenzotriazole (0·268 g., 2 mmoles) and 1-amino-4,7-dimethoxybenzotriazole (0·388 g., 2 mmoles) in warm, dry acetonitrile (25 ml.) was added dropwise to a stirred suspension of lead tetra-acetate (2·0 g., 4·5 mmoles) in dry acetonitrile (10 ml.). When gas (N_2) ceased to be evolved, the mixture was filtered and the residue was washed with methylene chloride. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in the minimum of warm light petroleum (b.p. 60—80°) and applied to silica gel (19 × 2·5 cm.). Elution with light petroleum (b.p. 40—60°)–light petroleum (b.p. 60—80°) gave biphenylene (0·062 g., 40%) as a very pale yellow crystalline solid, identical (i.r. spectrum) with an authentic specimen; elution with light petroleum (b.p. 60—80°)–benzene (*ca.* 8 : 1) gave 1,4-dimethoxybiphenylene (0·076 g., 18%) as a pale yellow crystalline solid, m.p. 78—79° (lit.,[18] 81—82°), $\nu_{max.}$ 1660m, 1603s, 805s, and 730s cm.$^{-1}$; elution with light petroleum (b.p. 60—80°)–benzene (*ca.* 1 : 1) gave an oily solid (0·036 g.) containing 1,4,5,8-tetramethoxybiphenylene (t.l.c.) and carbonyl compounds.

Generation of 3,6-Dimethoxybenzyne in Furan.—A suspension of 1-amino-4,7-dimethoxybenzotriazole (0·388 g., 0·002 mole) in furan (25 ml.) (freshly distilled from calcium hydride) was added in portions to a suspension of lead tetra-acetate (1·32 g., 0·003 mole) in dry furan (5 ml.) at room temperature. When gas (N_2) ceased to be evolved, the mixture was filtered and the residue was washed with methylene chloride. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in the minimum of light petroleum (b.p. 60—80°)–methylene chloride and applied to silica gel (14 × 2·5 cm.). Elution with benzene–methylene chloride gave *1,4-epoxy-1,4-dihydro-5,8-dimethoxynaphthalene* (0·259 g., 63%) as prisms, m.p. 86—87° [from light petroleum (b.p. 40—60°)] (Found: C, 71·1; H, 5·95. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%), $\nu_{max.}$ 1610m, 1260s, and 798s cm.$^{-1}$, τ(CCl_4) 3·08 (2H), 3·65 (2H), 4·29 (2H), and 6·33 (6H).

Oxidation of 2,3-Diamino-1,4-dimethoxybenzene with Lead

[18] J. W. Barton, unpublished results.

Tetra-acetate.—A mixture of 2,3-diamino-1,4-dimethoxybenzene [19] (0·20 g., 1·2 mmole), lead tetra-acetate (1·38 g., 3·1 mmoles) and dry ether (25 ml.) was stirred at room temperature under nitrogen for 3·25 hr. The inorganic precipitate was filtered off and the filtrate was concentrated by evaporation, diluted with the minimum of chloroform and applied to alumina (27 × 2·5 cm.) made up with light petroleum (b.p. 60—80°). Elution with light petroleum (b.p. 60—80°) gave cis,cis-2,5-*dimethoxymuconononitrile* (XIII) (0·094 g., 48%) as needles, m.p. 130—131° [from light petroleum (b.p. 60—80°)] (Found: C, 58·7; H, 5·0; N, 16·9. $C_6H_8N_2O_2$ requires C, 58·55; H, 4·9; N, 17·1%), $\nu_{max.}$ 2250s, 1595s, 867s, and 823s cm.$^{-1}$.

Attempted Hydrolysis of cis,cis-2,5-*Dimethoxymuconononitrile*.—(*a*) A solution of the muconononitrile (0·0267 g.) in ethanol (5 ml.) and hydrochloric acid (2N; 5 ml.) was warmed on a water-bath for 20 min.; concentrated hydrochloric acid (*ca.* 10 drops) was then added to the solution, which was heated on a water-bath for a further 5 min. Starting material (0·019 g., 74%) separated from the cooled solution as a crystalline solid identical (i.r. spectrum) with an authentic sample of *cis,cis*-2,5-dimethoxymuconononitrile.

(*b*) The muconononitrile (0·0142 g.) was treated with concentrated hydrochloric acid (3 ml.) and ethanol (4 ml.) and the mixture was heated on a water-bath for *ca.* 15 min. and allowed to cool. Starting material (0·0067 g., 47%) separated as a white crystalline solid, m.p. 129—130°.

Diethyl (4,5-*Dimethoxy*-2-*nitrophenyl*)*azomalonate* (XV) (with K. P. Parry).—A solution of 4,5-dinitroveratrole [20] (40·0 g.) in glacial acetic acid (300 ml.) was hydrogenated at room temperature and 1 atmos. over platinum oxide (0·05 g.). The theoretical amount (13 l.) of hydrogen (for the reduction of one nitro-group) was absorbed during 2 days. The catalyst was filtered off and the acetic acid was removed under reduced pressure to leave 4-amino-5-nitroveratrole as a red crystalline solid, sufficiently pure for the next stage. It was immediately dissolved in ice-cold hydrochloric acid (5N; 200 ml.) and the stirred solution was treated with sodium nitrite (14·0 g.) in water (20 ml.) at 0° (frothing!) to yield a dark-coloured solution. This was stirred for 30 min. and then poured into a well stirred suspension of diethyl malonate (25 ml.) in sufficient sodium carbonate solution to render the total mixture basic when addition was complete. The yellow product was filtered off and crystallised from dioxan to yield the *azomalonate* (XV) (42·1 g., 65% overall) as orange-yellow microneedles, m.p. 219—220° (Found: C, 48·9; H, 5·0; N, 11·6. $C_{15}H_{19}N_3O_8$ requires C, 48·8; H, 5·2; N, 11·4%), $\nu_{max.}$ 3160w, 1725s, 1670w, 1580m, and 1510 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 222, 317, and 414 nm.

With smaller quantities of 4,5-dinitroveratrole the hydrogenation could be effected in 4—5 hr. and the overall yield of azomalonate rose to *ca.* 80%.

Diethyl (5,6-*Dimethoxybenzotriazol*-1-*yl*)*iminomalonate* (XVII) (with K. P. Parry).—A suspension of diethyl (4,5-dimethoxy-2-nitrophenyl)azomalonate (12·0 g.) in ethyl acetate (200 ml.) was hydrogenated at *ca.* 27° and 1 atmos. over 10% palladium–charcoal (2·0 g.). After 2 days the theoretical amount (2340 ml.) of hydrogen had been absorbed. The solution was filtered and evaporated to dryness under reduced pressure to leave diethyl (2-amino-4,5-dimethoxyphenyl)azomalonate as a red solid, sufficiently pure for the next stage.

The product was dissolved in ice-cold 3N-hydrochloric acid (100 ml.) and the solution was treated with sodium nitrite (2·0 g.) in water at 0°. The mixture was stirred at this temperature for 30 min. and then at room temperature for 2 hr. The precipitate was filtered off and washed with water to give the *iminomalonate* (6·5 g., 57%) as pale yellow prisms, m.p. 147—148° (from ethanol) (Found: N, 15·8. $C_{15}H_{18}N_4O_6$ requires N, 16·0%), $\nu_{max.}$ 1750s, 1730s, 1620s, 1508s, and 1200s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 280 and 331 nm., τ 2·65 (1H), 2·79 (1H), 5·43 (2H, q, *J* 7 c./sec.), 5·53 (2H, q, *J* 7 c./sec.), 5·97 (3H), 6·03 (3H), and 8·58 (6H, t, *J* 7 c./sec.).

1-*Amino*-5,6-*dimethoxybenzotriazole* (XVIII).—Diethyl (5,6-dimethoxybenzotriazol-1-yl)iminomalonate (0·82 g.) was heated on a water-bath with concentrated hydrochloric acid (10 ml.) for 1 hr.; the cooled mixture was diluted with water (10 ml.) and filtered. The acid filtrate was extracted with ether (3 × 20 ml.) and the aqueous acid layer was basified with sodium hydroxide pellets; 1-*amino*-5,6-*dimethoxybenzotriazole* (0·42 g., 93%) separated. Recrystallisation from water gave prisms, m.p. 187·5—188·5° (Found: C, 49·1; H, 5·2; N, 28·45. $C_8H_{10}N_4O_2$ requires C, 49·5; H, 5·2; N, 28·85%), $\nu_{max.}$ 3320m, 3270w, 3150w, 1650w, 1620w, 1230s, and 810s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 275sh and 295 nm., τ(D_2O) 2·80 (1H), 3·00 (1H), 6·35 (3H), and 6·40 (3H).

1-*Benzylideneamino*-5,6-*dimethoxybenzotriazole* (with P. J. Ennis).—A mixture of 1-amino-5,6-dimethoxybenzotriazole (0·194 g.) and redistilled benzaldehyde (0·5 ml.) in ethanol (10 ml.) was heated on a steam-bath for 15 min. Water was added to the cooled mixture, and an off-white solid slowly separated. The product was filtered off and washed with water to give the *benzylidene derivative* (0·218 g., 79%) as light buff crystalline plates, m.p. 165° [from light petroleum (b.p. 60—80°)] (Found: C, 63·4; H, 4·8; N, 19·4. $C_{15}H_{14}N_4O_2$ requires C, 63·8; H, 4·95; N, 19·8%), $\nu_{max.}$ 1630w, 1595w, 1570w, 1000s, 800s, 750s, and 680s cm.$^{-1}$.

Generation of 4,5-*Dimethoxybenzyne in the Presence of Tetracyclone*.—Lead tetra-acetate (0·66 g., 0·0015 mole) was added in portions to a well stirred suspension of 1-amino-5,6-dimethoxybenzotriazole (0·194 g., 0·001 mole) and tetracyclone (0·45 g., 0·0012 mole) in dry methylene chloride (11 ml.). When gas (N_2) ceased to be evolved, the mixture was added to the minimum of warm light petroleum (b.p. 60—80°)–benzene (1 : 1) and applied to silica gel (27 × 2·5 cm.). Elution with light petroleum (b.p. 60—80°)–benzene (1 : 1) gave unchanged tetracyclone (0·222 g., 49% recovery) and 6,7-*dimethoxy*-1,2,3,4-*tetraphenylnaphthalene* (0·171 g., 35%) as prisms, m.p. 328—329° [from light petroleum (b.p. 60—80°)–methylene chloride] (Found: C, 87·8; H, 5·7. $C_{36}H_{28}O_2$ requires C, 87·8; H, 5·7%), $\nu_{max.}$ 3150w, 3120w, 1620w, 1600w, 1130s, 855s, 733s, 705s, and 697 cm.$^{-1}$.

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