Preparation and Reactions of Some Substituted Pyrazine Di-*N*-oxides

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2,5-Dichloro-3,6-dimethylpyrazine is readily oxidised by trifluoroperacetic acid to the di-*N*-oxide, in which only one chlorine atom is easily hydrolysed by acid or base; however both chlorine atoms can be displaced by alkoxide ions. Treatment of the dibenzyloxy-derivative with acid gives 1,5-dihydroxy-3,6-dimethylpyrazin-2(1*H*)-one 4-oxide, related to pulcherriminic acid. Oxidation of 2-chloro-3,6-dimethylpyrazine 4-oxide with trifluoroperacetic acid gives the di-*N*-oxide, which can react further, by oxidative deoxygenation, to give 2-chloro-3,6-dimethylpyrazine 1-oxide.

A POTENTIAL route to the fungal metabolite myceliamide (I) [1,2] can be envisaged as proceeding *via* its tautomer (II). The latter structure contains an oxidised pyrazine nucleus such as exists in pulcherriminic acid (III) [3] and for which a synthesis has been claimed.[4] We describe here an alternative route to the related compound 1,5-dihydroxy-3,6-dimethylpyrazin-2(1*H*)-one 4-oxide (IV; R = OH).

Reaction of alanine anhydride with phosphoryl chloride gave two products.[5] The minor, neutral material was the dichloropyrazine (V; $R^2 = R^1 = Cl$); the major product was the monochloropyrazine (V; $R^1 = H$, $R^2 = Cl$). Use of mild oxidising agents, such as air or phosphorus pentachloride, did not increase the proportion of dichloropyrazine formed. In order to obtain more of this material the monochloropyrazine was selectively oxidised with peracetic acid. The mono-*N*-oxide (VI) obtained was rearranged further by

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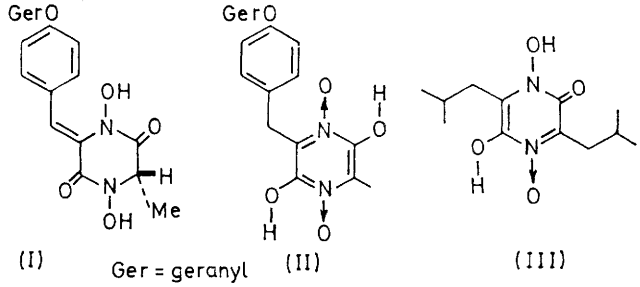
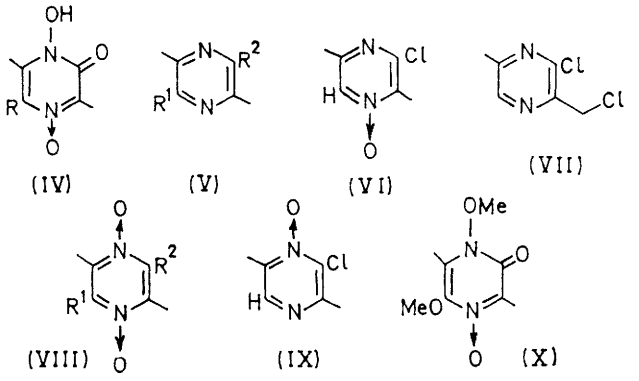
[2] R. B. Bates, J. H. Schauble, and M. Soucek, *Tetrahedron Letters*, 1963, 1683; A. J. Birch, R. A. Massy-Westropp, and R. W. Rickards, *J. Chem. Soc.*, 1956, 3717.
[3] J. C. MacDonald, *Canad. J. Chem.*, 1963, **41**, 165.
[4] A. Ohta, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 125.
[5] R. A. Baxter and F. S. Spring, *J. Chem. Soc.*, 1947, 1179.

phosphoryl chloride [6] to give two products, the dichloropyrazine (V; $R^1 = R^2 = Cl$) and the previously unknown chloromethyl derivative (VII).[7]

Oxidation of the monochloropyrazine *N*-oxide (VI) with trifluoroperacetic acid [8] gave two new products, the di-*N*-oxide (VIII; $R^1 = H$, $R^2 = Cl$) and 2-chloro-

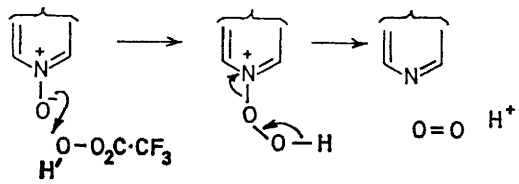




3,6-dimethylpyrazine 1-oxide (IX). The latter was similar in its physical properties to the starting oxide (VI). However, after mild alkaline hydrolysis oxide (VI) gave a negative iron(III) chloride reaction, whereas the oxide (IX) gave a positive response, indicating formation of a hydroxamic acid. Control experiments showed that the new mono-*N*-oxide was formed by further reaction of the di-*N*-oxide with trifluoroperacetic acid. The di-*N*-oxide was unaffected by trifluoroacetic acid under the reaction conditions. Similarly, no interconversion of the two mono-*N*-oxides took place in the acid and no deoxygenation of the di-*N*-oxide was effected by the mono-*N*-oxide (VI).

Thus the isomeric *N*-oxide (IX) must be formed by an oxidative deoxygenation of the type depicted in the Scheme.[9] The oxygen atom attached to position 4 in the di-*N*-oxide would be expected to be more nucleophilic than that at position 1, which is adjacent to the electronegative chlorine atom.

Whereas oxidation of the dichloropyrazine (V; $R^1 = R^2 = Cl$) with peroxymaleic acid [10] gave only a mono-*N*-oxide,[4] use of pertrifluoroacetic acid gave the



SCHEME

dichloro-di-*N*-oxide (VIII; $R^1 = R^2 = Cl$).[11] Treatment of this di-*N*-oxide with aqueous sodium hydroxide rapidly yielded the monohydroxamic acid (IV; R = Cl) which resisted further basic hydrolysis. The inert character of the second chlorine atom is probably due to the formation of the anion of the hydroxamic acid function which inhibits further attack.[12] Vigorous treatment with base destroyed the monohydroxamic acid. In contrast, sodium ethoxide readily displaced both chlorine atoms to form the corresponding diethoxypyrazine (VIII; $R^1 = R^2 = EtO$). Although base-induced alkyl-oxygen cleavage of alkoxy-groups in such an environment has been observed,[13] and was used by Ohta in his synthesis of pulcherriminic acid,[4] the diethoxy-derivative (VIII; $R^1 = R^2 = EtO$) was stable to prolonged treatment with sodium ethoxide. Mild acid hydrolysis gave the monoethoxy-hydroxamic acid (IV; R = EtO) only; more vigorous acid hydrolysis caused decomposition.

The hydroxamic acid (IV; R = OH) was synthesised by treating the dichloro-di-*N*-oxide (VIII; $R^1 = R^2 =$ Cl) with benzyloxysodium to give the dibenzyloxy-derivative (VIII; $R^1 = R^2 = PhCH_2{\cdot}O$) and some of the monobenzyloxy-hydroxamic acid (IV; R = $PhCH_2{\cdot}O$). The benzyl groups were readily removed by mild treatment with acid in aqueous solution. The product (IV; R = OH) precipitated as a pale yellow solid, only slightly soluble in water. It was extremely sensitive to iron(III) ions; the deep red complex formed tended to precipitate from the solution. Esterification of the hydroxamic acid (IV; R = OH) with diazomethane [14] gave the dimethyl ester (X). The structure of the former was tentatively assigned on the basis of the similarity of its u.v. absorption to those of the series of monohydroxamic acids prepared (see Table). Since the latter all possess an absorption at longer wavelengths than the di-*N*-oxides (see Table) and also have a strong i.r. carbonyl absorption band in the region of 1660 $cm.^{-1}$, they have been tentatively identified as monohydroxamic

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[12] G. W. H. Cheeseman and E. S. G. Törzs, *J. Chem. Soc.*, 1965, 6681.
[13] G. Karmas and P. E. Spoerri, *J. Amer. Chem. Soc.*, 1957, **79**, 680.
[14] A. H. Cook and C. A. Slater, *J. Chem. Soc.*, 1956, 4133.

U.v. absorption maxima (nm.)*; ε in parentheses

(*a*) Monohydroxamic acids	
(IV; R = Cl)	238 (18,600), 282 (4400) 350 (4800)
(IV; R = EtO)	230 (19,000), 282 (6400), 352 (5900)
(IV; R = $PhCH_2$·O)	233 (19,500), 282 (6000), 353 (5600)
(X)	229 (19,500), 282 (6400), 347 (5700)
Dimethyl pulcherriminate	233 (24,500), 289 (6400), 354 (7400) [a]
(IV; R = OH)	237 (8500), 281 (5800), 375 (3900) [b]
(*b*) Pyrazine *N*-oxides	
(VI)	231 (13,800), 271 (10,500)
(IX)	230 (15,500), 268 (9100)
(VIII; R^1 = H, R^2 = Cl)	242 (24,000), 309 (20,900)
(VIII; R^1 = R^2 = Cl)	250 (29,500), 311 (19,900)
(VIII; R^1 = R^2 = EtO)	245 (20,100), 303 (14,500)
(VIII; R^1 = R^2 = $PhCH_2O$)	249 (24,000), 304 (15,100)

* Solutions in ethanol.

[a] A. H. Cook and C. A. Slater, *J. Chem. Soc.*, 1956, 4133. [b] Recorded for solution in water; insufficiently soluble in ethanol.

acids rather than as tautomeric hydroxypyrazine di-*N*-oxides.

EXPERIMENTAL

I.r. spectra were recorded with a Unicam SP 200 spectrometer for Nujol mulls unless otherwise specified. U.v. spectra were measured with a Unicam SP 800 instrument for solutions in ethanol. ^{1}H N.m.r. spectra were recorded with a Varian A60 spectrometer (on permanent loan from the Wellcome Trust), with tetramethylsilane as internal reference for solutions in deuteriochloroform. Solutions were dried with anhydrous magnesium sulphate. Light petroleum refers to the fraction of boiling range 60—80°. M.p.s were determined with a Kofler hot-stage apparatus.

Preparation of 2,5-*Dichloro*-3,6-*dimethylpyrazine* (V; R^1 = R^2 = Cl).[5]—3,6-Dimethylpiperazine-2,5-dione (15 g.) and phosphoryl chloride (75 ml.) were gradually heated to 100° for 1 hr. Excess of solvent was distilled off under reduced pressure and the residue was carefully treated with ice–water (100 ml.). The solid precipitate was collected and dried to give the dichloropyrazine (2·4 g., 12%), m.p. 72° (lit.,[5] 73°). The filtrate was extracted with dichloromethane (5 × 30 ml.); the extracts were washed with water (2 × 30 ml.), dried, and evaporated to leave a yellow oil, which was distilled at 82—84°/20 mm. (lit.,[5] b.p. 78°/15 mm.), to give 2-chloro-3,6-dimethylpyrazine (V; R^1 = H, R^2 = Cl) (9·2 g., 61%).

2-*Chloro*-3,6-*dimethylpyrazine* 4-*Oxide* (VI).—2-Chloro-3,6-dimethylpyrazine (9·0 g.) was heated at 80° with acetic acid (40 ml.) containing hydrogen peroxide (85% w/w; 7·6 ml.) for 4 hr. Excess of acetic acid was distilled off under reduced pressure, water was added, and the mixture was neutralised with sodium carbonate and extracted with chloroform. Evaporation of the extract gave the crystalline *N*-oxide (7·5 g., 75%), m.p. (from benzene–light petroleum) 116—117° (lit.,[6] 113—115°), $\lambda_{max.}$ 231 and 271 nm. (ε 13,800 and 10,500). After mild alkaline hydrolysis and reacidification a specimen gave a negative neutral iron(III) chloride test.

Rearrangement of the N-*Oxide* (VI).—The oxide (9·9 g.) and phosphoryl chloride (60 ml.) were gently heated at 100° for 1 hr. Excess of reagent was distilled off and the residue was extracted with dichloromethane. The organic extract was washed with water, dried, and evaporated to give a semicrystalline mass (9·5 g.). Chromatography through alumina (700 g., grade 5), with light petroleum as eluant gave, initially, the dichloropyrazine (V; R^1 = R^2 = Cl) (4·8 g., 44%), m.p. 72°. Further elution with light petroleum gave a colourless oil, identified as 2-*chloro*-3-*chloromethyl*-6-*methylpyrazine* (VII) (3·6 g., 33%), b.p. 70°/3 mm., $\nu_{max.}$ (film) 1570, 1460, 1340, 1140, 1090, 940, 780, and 700 cm.$^{-1}$, $\lambda_{max.}$ 230 and 270 nm. (ε 15,000 and 10,000), τ 7·4(3H, s), 5·21(2H, s), and 1·63(1H, s) (Found: C, 40·9; H, 3·5; Cl, 39·7; N, 16·1. $C_6H_6Cl_2N_2$ requires C, 40·7; H, 3·4; Cl, 40·1; N, 15·8%).

Trifluoroperacetic Acid Oxidation of (VI).—2-Chloro-3,6-dimethylpyrazine 4-oxide (2·0 g.) in trifluoroacetic acid (20 ml.) was treated with hydrogen peroxide (85% w/w; 2·5 ml.) and the solution was warmed to 70° for 14 hr. Excess of trifluoroacetic acid was then distilled off under reduced pressure, saturated aqueous sodium carbonate solution was added and the mixture was extracted with chloroform. The extract was washed with water, dried, and concentrated to dryness. The crude product gave crystals of 2-*chloro*-3,6-*dimethylpyrazine* 1,4-*dioxide* (VIII; R^1 = H, R^2 = Cl) (1·0 g., 47%), m.p. 203—204° (from benzene–light petroleum), $\nu_{max.}$ 3050, 1760w, 1470, 1350, 1285, 1215, 1140, 1055, 915, 900, and 715 cm.$^{-1}$, $\lambda_{max.}$ 242 and 309 nm. (ε 24,000 and 20,900), τ 7·54(3H, s), 7·39(3H, s), and 1·91(1H, s) (Found: C, 41·3; H, 4·0; Cl, 20·3; N, 16·0%. $C_6H_7ClN_2O_2$ requires C, 41·3; H, 4·1; Cl, 20·3; N, 16·1%). A sample gave a positive iron(III) chloride test after mild basic hydrolysis.

The filtrate from the crystallisation of the product was shown, by t.l.c. on silica gel (1 : 9 acetone–chloroform), to contain another, less polar product which was slightly more polar than the starting material. A sample of this compound was isolated by preparative layer chromatography on silica gel to give 2-*chloro*-3,6-*dimethylpyrazine* 1-*oxide* (IX), m.p. (from benzene–light petroleum) 106—109°, $\nu_{max.}$ 1585, 1470, 1355, 1315, 1275, 1215, 1070, 1025, 960, 910, 765, and 740 cm.$^{-1}$, $\lambda_{max.}$ 230 and 268 nm. (ε 15,500 and 9100), τ 7·51(3H, s), 7·44(3H, s), and 1·76(1H, s) (Found: C, 45·7; H, 4·7; N, 17·6%. $C_6H_7ClN_2O$ requires C, 45·5; H, 4·45; N, 17·6%). A sample gave a positive iron(III) chloride test after mild basic hydrolysis.

Control Reactions with the Di-N-*oxide* (VIII; R^1 = H, R^2 = Cl).—The di-*N*-oxide (100 mg.) was heated at 70° in trifluoroacetic acid (1 ml.) for 15 hr. No reaction occurred in this time (t.l.c. analysis). Addition of hydrogen peroxide (85% w/w; 0·2 ml.) and further heating at 70° gave the two mono-*N*-oxides (VI) and (IX), with the latter predominating. Separation by preparative layer chromatography gave traces of (VI), (IX) (9 mg.), and starting di-*N*-oxide (70 mg.). Heating the mono-*N*-oxide (VI) together and the di-*N*-oxide (VIII; R^1 = H, R^2 = Cl) at 70° in trifluoroacetic acid gave none of the isomeric mono-*N*-oxide during 15 hr.

Oxidation of 2,5-*Dichloro*-3,6-*dimethylpyrazine* (V; R^1 = R^2 = Cl).—The pyrazine (1·65 g.) was oxidised with trifluoroperacetic acid [from the acid (20 ml.) and 85% w/w hydrogen peroxide (2·2 ml.)] at 70° for 30 min. After evaporation of excess of trifluoroacetic acid under reduced pressure, water (20 ml.) was added, followed by sodium carbonate until the mixture was alkaline, then chloroform

(3 × 25 ml.). Work-up in the usual way gave, from benzene–carbon tetrachloride, colourless prisms of *2,5-dichloro-3,6-dimethylpyrazine* 1,4-*dioxide* (VIII; $R^1 = R^2 =$ Cl) (1·17 g., 60%), m.p. 231° (decomp.), $\nu_{max.}$ 1490, 1470, 1320, 1120, 1030, and 930 cm.$^{-1}$, $\lambda_{max.}$ 250 and 311 nm. (ε 29,600 and 19,900), τ 7·3 (only) (Found: C, 34·2; H, 3·0; Cl, 34·6; N, 13·3. $C_6H_6Cl_2N_2O_2$ requires C, 34·45; H, 2·9; Cl, 34·4; N, 13·4%).

Alkaline Hydrolysis of the Di-N-oxide (VIII; $R^1 = R^2 =$ Cl).—The di-*N*-oxide (100 mg.) was stirred with 0·5N-sodium hydroxide (5 ml.) for 5 hr. at room temperature. After acidification with dilute hydrochloric acid, continuous dichloromethane extraction eventually afforded a crystalline solid (60 mg.). Recrystallisation from benzene–carbon tetrachloride gave *5-chloro-3,6-dimethyl-1-hydroxypyrazin-2(1H)-one 4-oxide* (IV; R = Cl), m.p. 170—180° (decomp.), $\nu_{max.}$ 3500—2500, 1630, 1590, 1470, 1370, 1340, 1250, 1140, 1050, 850, and 720 cm.$^{-1}$, $\lambda_{max.}$ 238, 282, and 350 nm. (ε 18,600, 4400, and 4800), τ 7·27(3H, s) and 7·20(3H, s) (Found: C, 37·8; H, 3·85; Cl, 19·3; N, 14·1. $C_6H_7ClN_2O_3$ requires C, 37·8; H, 3·7; Cl, 18·6; N, 14·7%).

Heating either this product or the starting material at 100° with 2N-sodium hydroxide gave a product mixture which gave a negative iron(III) chloride test.

2,5-Diethoxy-3,6-dimethylpyrazine 1,4-*Dioxide* (VIII; $R^1 = R^2 =$ EtO).—The dichloropyrazine (VIII; $R^1 = R^2 =$ Cl) (200 mg.) was stirred with sodium ethoxide [from sodium (132 mg.)] in absolute ethanol (10 ml.) at room temperature for 2 hr. The solvent was removed *in vacuo* and the residue was dissolved in 0·5N-sodium hydroxide (25 ml.) before extraction with dichloromethane (2 × 20 ml.). Work-up gave crystals of the *diethoxypyrazine* (216 mg., 99%), m.p. (from benzene–light petroleum) 158—159°, $\nu_{max.}$ 1525, 1345, 1320, 1265, 1175, 1090, 1010, 970, 925, and 840 cm.$^{-1}$, $\lambda_{max.}$ 245 and 303 nm. (ε 20,100 and 14,800), τ 8·56(6H, t, *J* 7 Hz), 7·52(6H, s), and 5·53(4H, q, *J* 7 Hz) (Found: C, 52·2; H, 6·9; N, 11·8. $C_{10}H_{16}N_2O_4$ requires C, 52·6; H, 7·0; N, 12·3%). This material gave a negative iron(III) chloride test and was unaffected by heating with sodium ethoxide in ethanol.

Acid Hydrolysis of 2,5-Diethoxy-3,6-dimethylpyrazine 1,4-Dioxide.—The pyrazine (VIII; $R^1 = R^2 =$ EtO) (100 mg.) in 2N-hydrochloric acid (10 ml.) was heated at 70° for 4 hr. Continuous extraction of the product with chloroform eventually gave a crystalline solid. Recrystallisation from benzene–light petroleum gave *5-ethoxy-1-hydroxy-3,6-dimethylpyrazin-2(1H)-one 4-oxide* (IV; R = EtO) (50 mg.), m.p. 164—165° (decomp.), $\nu_{max.}$ 3200—3080, 1655, 1600, 1530, 1470, 1330, 1230, 1165, 1100, 1075, 1025, and 920 cm.$^{-1}$, $\lambda_{max.}$ 230, 282, and 352 nm. (ε 19,000, 6400, and 5900), τ 8·56(3H, t, *J* 7 Hz), 7·57(3H, s), 7·58(3H, s), 5·55(2H, q, *J* 7 Hz), −0·41(1H, s, exchangeable) (Found: C, 48·2; H, 5·95; N, 13·8. $C_8H_{12}N_2O_4$ requires C, 48·0; H, 6·0; N, 14·0%).

Further treatment of the product with 2N-hydrochloric acid for 1 hr. at 100° gave a mixture which gave no colouration with iron(III) chloride.

2,5-Dibenzyloxy-3,6-dimethylpyrazine 1,4-*Dioxide* (VIII; $R^1 = R^2 = PhCH_2{\cdot}O$).—Similar reaction of the dichloropyrazine (VIII; $R^1 = R^2 =$ Cl) (200 mg.) with sodium benzyloxide [from sodium hydride (90 mg.) and dry benzyl alcohol (450 mg.)] in benzene (10 ml.) at room temperature for 2 hr., followed by extraction with 0·5N-sodium hydroxide (20 ml.) gave, in the organic phase, the *dibenzyloxy-derivative* (92 mg., 27%), m.p. (from benzene–light petroleum) 108—110°, $\nu_{max.}$ 1530, 1470, 1355, 1320, 1215, 1170, 1100, 960, 930, 760, and 710 cm.$^{-1}$, $\lambda_{max.}$ 249 and 304 nm. (ε 24,000 and 15,100), τ 7·77(6H, s), 4·55(4H, s), and 2·65(10H) (Found: C, 68·0; H, 5·6; N, 7·8. $C_{20}H_{20}N_2O_4$ requires C, 68·2; H, 5·7; N, 8·0%).

The sodium hydroxide extract was acidified with 2N-hydrochloric acid then extracted with chloroform to give *5-benzyloxy-1-hydroxy-3,6-dimethylpyrazin-2(1H)-one 4-oxide* (IV; R = $PhCH_2{\cdot}O$) (74 mg., 29%), m.p. (from benzene–light petroleum) 158—160°, $\nu_{max.}$ 2800—2400, 1650, 1580, 1520, 1470, 1330, 1280, 1210, 1160, 1100, 1075, 970, 955, 760, and 705 cm.$^{-1}$, $\lambda_{max.}$ 233, 282, and 353 nm. (ε 19,000, 6000, and 5600), τ 7·81(3H, s), 7·54(3H, s), 4·77(2H, s), 2·52(5H), and 0·2(1H, s, exchangeable) (Found: C, 59·15; H, 5·2; N, 9·9. $C_{13}H_{14}N_2O_4$ requires C, 59·5; H, 5·3; N, 10·7%).

1,5-Dihydroxy-3,6-dimethylpyrazin-2(1H)-one 4-Oxide (IV; R = OH).—The dibenzyloxy-derivative (VIII; $R^1 = R^2 =$ $PhCH_2{\cdot}O$) (67 mg.) was stirred in 10N-hydrochloric acid at room temperature. After 30 min. a crystalline precipitate formed. This was left at room temperature overnight, then collected to give the *hydroxamic acid* (24 mg.), m.p. 200° (decomp.), $\nu_{max.}$ 2800—2400, 1660, 1585, 1535, 1475, 1420, 1385, 1325, 1200, 1175, 1080, and 970 cm.$^{-1}$, $\lambda_{max.}$ (H_2O) 237, 281, and 375 nm. (ε 8500, 5800, and 3900), τ ($CF_3{\cdot}CO_2H$) 7·37 (only) (Found: C, 41·7; H, 4·75; N, 16·0. $C_6H_8N_2O_4$ requires C, 41·9; H, 4·65; N, 16·3%). The material was very insoluble in most solvents, but slightly soluble in methanol and water. With aqueous iron(III) chloride it gave an intense violet colour, and a dark red precipitate was eventually deposited.

Methylation of the Hydroxamic Acid (IV; R = OH).—The acid (100 mg.) was stirred as a suspension in ether (5 ml.) containing excess of diazomethane. After 1 hr. at room temperature the solution was concentrated and the residue was purified by preparative layer chromatography (1 : 9 acetone–chloroform). The major product (50 mg.) crystallised on trituration with light petroleum. Sublimation at 100°/10^{-4} mm. gave a pale yellow solid, *3,6-dimethyl-1,5-dimethoxypyrazin-2(1H)-one 4-oxide* (X), m.p. 151—152° (decomp.), $\nu_{max.}$ 1660, 1620, 1355, 1235, 1155, 1100, 1075, and 1030 cm.$^{-1}$, $\lambda_{max.}$ 229, 282, and 347 nm. (ε 19,500, 6400, and 5700), τ 7·61(6H, s), 6·08(3H, s), and 5·94(3H, s) (Found: C, 48·2; H, 6·1; N, 13·85. $C_8H_{12}N_2O_4$ requires C, 48·0; H, 6·0; N, 14·0%).

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