Reaction of 2,3-Diphenylpyrazine 1-Oxides with Acetic Anhydride

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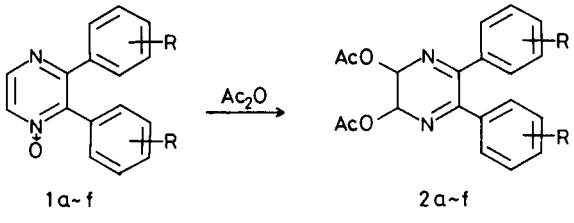
Received July 12, 1983

Some 2,3-diphenylpyrazine 1-oxides were heated with acetic anhydride to give the corresponding 2,3-diacetoxy-2,3-dihydro-5,6-diphenylpyrazines. By X-ray diffraction analysis, the configuration of two acetoxyl groups was determined to be *trans*.

J. Heterocyclic Chem., **21**, 103 (1984).

Recently we reported that the reaction of 2,3-diphenylpyrazine 1-oxide (**1a**) with acetic anhydride resulted in giving a 2,3-diacetoxy-2,3-dihydropyrazine(**2a**) [1]. However, the configuration of two acetoxyl groups was left unclear. This paper reports that some other 2,3-diphenylpyrazine 1-oxides **1b-f** underwent the same reaction to give the corresponding 2,3-diacetoxy-2,3-dihydropyrazines **2b-f** and that the X-ray diffraction analysis made clear the configuration of two acetoxyl groups in **2a** to be *trans*.

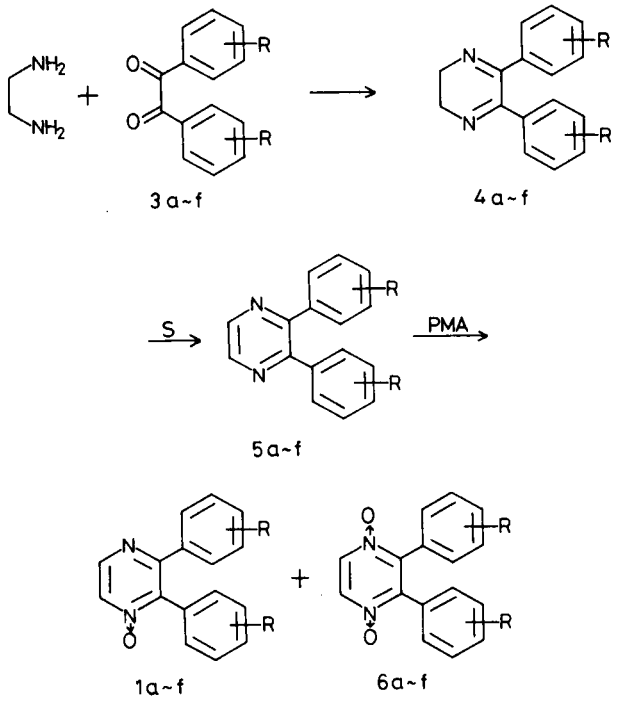


R: a=H, b=p-Cl, c=p-Br, d=p-CH_3, e=p-CH_3O, f=o-Cl

Scheme 1

Among the 2,3-diphenylpyrazines **5b-f** examined, 2,3-bis(*p*-methoxyphenyl)pyrazine (**5e**) [2] is already known in literature. However, all the 2,3-diphenylpyrazines **5b-f** were prepared in the present work by the same way as we previously reported [1]. Namely, benzils **3b-f** [3-5] were condensed with ethylenediamine in ethanol to afford 5,6-diphenyl-2,3-dihydropyrazines **4b-f** [6,7], which were dehydrogenated by heating with sulfur to yield the expected 2,3-diphenylpyrazines **5b-f**. The compounds **5b-f** thus obtained were oxidized with 1.5 equimolar permaleic acid and the products, mono- **1b-f** and dioxides **6b-f**, were separated from each other by silica gel column chromatography.

The monoxides **1b-f** thus synthesized were treated with acetic anhydride under the same conditions as reported [1]. The crystalline products were obtained after purification by a silica gel column chromatography in all cases. The acetyl carbonyl absorption of all the products **2b-f** ap-



R: a=H, b=p-Cl, c=p-Br, d=p-CH_3, e=p-CH_3O, f=o-Cl

Scheme 2

peared as a single band in the region of 1750-1770 cm^{-1} in the ir spectra. The pmr spectra of **2b-f** showed a singlet (6.23-6.51 ppm) according to the dihydropyrazine ring protons, being similar to the pmr spectrum of **2a**.

Since the configuration of two acetoxyl groups could not be made clear on the basis of the pmr spectral data, the single crystal X-ray diffraction analysis of **2a** was performed. The final atomic parameters are listed in Table 1 and a perspective drawing of **2a** is shown in Figure 1. Consequently, these data indicated that the configuration of the acetoxyl groups of **2a** is *trans*.

The ir and pmr spectral data of **2b-f** are very similar to those of **2a**. Therefore, one might conclude that the acetoxyl groups of **2b-f** are situated as same as those of **2a**.

Table 1

Atomic Positional Parameters ($\times 10^4$ for C, N, and O, and $\times 10^3$ for H) and Equivalent Thermal Parameters with e.s.d.'s in Parenthese.

Atom	X	Y	Z	Beq(Å^2)
N(1)	8939(3)	2980(3)	6783(3)	3.61(0.11)
C(2)	9291(3)	2821(3)	8334(4)	3.45(0.12)
C(3)	8180(4)	1538(3)	8117(4)	3.56(0.13)
N(4)	6680(3)	1515(3)	7551(3)	3.46(0.11)
C(5)	6399(3)	2076(3)	6557(4)	3.05(0.11)
C(6)	7557(3)	2643(3)	5939(4)	3.11(0.12)
C(7)	7140(3)	2756(3)	4317(4)	3.26(0.13)
C(8)	5886(4)	1806(4)	2933(4)	3.89(0.14)
C(9)	5626(4)	1917(4)	1417(4)	4.50(0.16)
C(10)	6569(4)	2970(4)	1293(5)	4.78(0.18)
C(11)	7789(4)	3925(4)	2661(5)	4.95(0.18)
C(12)	8087(4)	3821(4)	4173(5)	4.42(0.15)
C(13)	4947(3)	2214(3)	6103(4)	3.17(0.12)
C(14)	3716(4)	1303(4)	6116(4)	4.04(0.14)
C(15)	2395(4)	1490(4)	5819(5)	5.11(0.17)
C(16)	2294(4)	2574(4)	5540(5)	5.16(0.18)
C(17)	3500(5)	3477(4)	5525(5)	5.34(0.19)
C(18)	4826(4)	3293(4)	5797(5)	4.25(0.15)
C(19)	11895(4)	3808(4)	9974(5)	4.70(0.15)
C(20)	13274(4)	3549(5)	10330(6)	6.13(0.19)
C(21)	8362(4)	349(4)	9852(5)	4.18(0.15)
C(22)	8784(5)	542(5)	11624(5)	5.83(0.21)
O(1)	10723(2)	2738(2)	8764(3)	4.25(0.10)
O(2)	11808(3)	4813(3)	10644(5)	9.00(0.16)
O(3)	8527(3)	1519(3)	9733(3)	4.48(0.11)
O(4)	7966(4)	-664(3)	8704(4)	6.43(0.14)
H(1)	382(4)	53(3)	629(4)	4.8(0.8)
H(2)	155(4)	87(3)	582(4)	5.2(0.9)
H(3)	138(4)	275(4)	539(4)	5.9(0.9)
H(4)	345(4)	425(4)	541(4)	5.6(0.9)
H(5)	568(4)	396(3)	583(4)	5.0(0.8)
H(6)	525(3)	108(3)	305(4)	4.0(0.7)
H(7)	477(4)	125(3)	47(4)	5.1(0.8)
H(8)	637(4)	305(4)	21(4)	5.5(0.9)
H(9)	848(4)	473(3)	269(4)	5.6(0.9)
H(10)	894(4)	456(3)	521(4)	4.5(0.8)
H(11)	823(3)	67(3)	734(4)	4.1(0.8)
H(12)	936(3)	365(3)	926(3)	3.0(0.6)
H(13)	1419(4)	442(3)	1075(4)	5.8(0.9)
H(14)	1329(4)	288(3)	936(4)	5.7(0.9)
H(15)	1340(4)	321(4)	1124(4)	6.0(0.9)
H(16)	855(4)	129(4)	1228(4)	5.7(0.9)
H(17)	825(4)	-35(4)	1170(4)	6.0(0.9)
H(18)	993(4)	81(4)	1218(4)	6.1(0.9)

EXPERIMENTAL

Melting points were recorded on a Yanagimoto micro-melting point apparatus and are uncorrected. The uv spectra were taken in 95% ethanol using Hitachi Model 557 spectrophotometer, ir spectra on a Shimadzu IR-400 spectrometer, and pmr spectra in deuteriochloroform using JEOL PS-100 and Varian EM-360 instruments with tetramethylsilane as an internal standard. Mass spectra were obtained with Hitachi RMU-7L and M-80 spectrometers. For silica gel column chromatography, Wakogel C-200 (Wako Pure Chemical Industries, Ltd., Tokyo) was used.

General Procedure for Preparation of 5,6-Diphenyl-2,3-dihydropyrazines **4b-f**.

To a solution of a benzil (23.7 mmoles) dissolved in ethanol (100 ml), ethylenediamine (28.8 mmoles) was added dropwise at room temperature under stirring, and then the reaction mixture was refluxed for 30 minutes. After cooling, yellow crystals were collected by suction and recrystallized from ethanol or isopropanol to furnish pale yellow prisms.

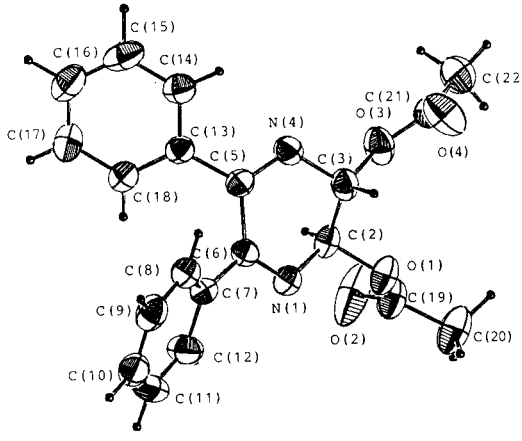


Figure 1. A Perspective View of **2a**, Showing the Crystallographic Numbering [11].

5,6-Bis(*p*-chlorophenyl)-2,3-dihydropyrazine (**4b**).

This compound was obtained in a yield of 79%, mp 155-156° (from ethanol); uv: λ max 227.5 (log ε = 4.35), 286 (3.92) nm; pmr: δ 3.70 (4H, s, pyrazine H), 7.38 (8H, s, benzene H) ppm; ms: m/e 302 (M^+).

Anal. Calcd. for $C_{16}H_{12}Cl_2N_2$: C, 63.38; H, 3.99; N, 9.24. Found: C, 63.17; H, 3.97; N, 9.42.

5,6-Bis(*p*-bromophenyl)-2,3-dihydropyrazine (**4c**).

This compound was obtained in a yield of 90%, mp 205-207° (from ethanol); uv: λ max 231.5 (log ε = 4.09), 285 (3.67) nm; pmr: δ 3.66 (4H, s, pyrazine H), 7.25-7.60 (8H, m, benzene H) ppm; ms: m/e 390 (M^+).

Anal. Calcd. for $C_{16}H_{12}Br_2N_2$: C, 49.01; H, 3.09; N, 7.15. Found: C, 48.88; H, 3.20; N, 7.12.

5,6-Bis(*p*-methylphenyl)-2,3-dihydropyrazine (**4d**).

This compound was obtained in a yield of 85%, mp 185-186.5° (from ethanol) (lit [6], mp 179°); uv: λ max 227 (log ε = 4.23), 295 (3.84) nm; pmr: δ 2.17 (6H, s, CH_3), 3.43 (4H, s, pyrazine H), 6.77 (4H, d, J = 8 Hz, benzene H), 7.09 (4H, d, J = 8 Hz, benzene H) ppm; ms: m/e 262 (M^+).

Anal. Calcd. for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.44; H, 6.94; N, 10.69.

5,6-Bis(*p*-methoxyphenyl)-2,3-dihydropyrazine (**4e**).

This compound was obtained in a yield of 88%,mp 134-135° (from isopropanol) (lit [2], mp 118-122°); uv: λ max 235 (log ε = 4.12), 289 (3.67, shoulder), 312.5 (3.75) nm; pmr: δ 3.69 (4H, s, pyrazine H), 3.81 (6H, s, OCH_3), 6.90 (4H, d, J = 8 Hz, benzene H), 7.53 (4H, d, J = 8 Hz, benzene H) ppm: ms: m/e 294 (M^+).

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.19; N, 9.52. Found: C, 73.74; H, 6.12; N, 9.63.

5,6-Bis(*o*-chlorophenyl)-2,3-dihydropyrazine (**4f**).

This compound was obtained in a yield of 78%, mp 136-137° (from ethanol); uv: λ max 208.5 (log ε = 4.22), 272.5 (3.36) nm; pmr: δ 3.80 (4H, s, pyrazine H), 7.20-7.50 (6H, m, benzene H), 7.70-7.95 (2H, m, benzene H) ppm; ms: m/e 302 (M^+).

Anal. Calcd. for $C_{16}H_{12}Cl_2N_2$: C, 63.38; H, 3.99; N, 9.24. Found: C, 63.60; H, 3.98; N, 9.42.

General Procedure for Preparation of 2,3-Diphenylpyrazines **5b-f**.

A mixture of a 5,6-diphenyl-2,3-dihydropyrazine (10 mmoles) and sulfur (20 mmoles) was heated at 140° for 30 minutes, and then chroma-

tographed on a silica gel (Wakogel C-200, 75 g) column, eluting with benzene, chloroform, and ethyl acetate, successively. The benzene fractions afforded sulfur. The aimed substance was obtained from the chloroform-ethyl acetate (10:1) fractions as a solid and recrystallized from ethanol or hexane to furnish pale yellow leaflets.

2,3-Bis(*p*-chlorophenyl)pyrazine (**5b**).

This compound was obtained in a yield of 72%, mp 133-135° (from hexane); uv: λ max 223.5 (log ε = 4.35), 278 (4.12, shoulder), 285.5 (4.13) nm; pmr: δ 7.47 (8H, s, benzene H), 8.70 (2H, s, pyrazine H) ppm; ms: m/e 300 (M^+).

Anal. Calcd. for $C_{16}H_{10}Cl_2N_2$: C, 63.81; H, 3.35; N, 9.30. Found: C, 63.58; H, 3.32; N, 9.22.

2,3-Bis(*p*-bromophenyl)pyrazine (**5c**).

This compound was obtained in a yield of 55%, mp 158-160° (from hexane); uv: λ max 224.5 (log ε = 4.24), 278 (4.06, shoulder), 286.5 (4.07) nm; pmr: δ 7.30-7.68 (8H, m, benzene H), 8.73 (2H, s, pyrazine H) ppm; ms: m/e 388 (M^+).

Anal. Calcd. for $C_{16}H_{10}Br_2N_2$: C, 49.26; H, 2.58; N, 7.18. Found: C, 49.10; H, 2.59; N, 7.04.

2,3-Bis(*p*-methylphenyl)pyrazine (**5d**).

This compound was obtained in a yield of 46%, mp 118-121° (from hexane); uv: λ max 223 (log ε = 4.33), 276-286 (4.07), 315 (3.95) nm; pmr: δ 2.36 (6H, s, CH_3), 7.20 (4H, d, J = 8 Hz, benzene H), 7.50 (4H, d, J = 8 Hz, benzene H), 8.70 (2H, s, pyrazine H) ppm; ms: m/e 260 (M^+).

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.91; H, 6.16; N, 10.73.

2,3-Bis(*p*-methoxyphenyl)pyrazine (**5e**).

This compound was obtained in a yield of 87%, mp 141-143° (from ethanol) (lit [2], mp 136-137°); uv: λ max 230 (log ε = 4.25), 290 (4.14), 325.5 (3.96) nm; pmr: δ 3.65 (6H, s, OCH_3), 6.60 (4H, d, J = 8 Hz, benzene H), 7.22 (4H, d, J = 8 Hz, benzene H), 8.32 (2H, s, pyrazine H) ppm; ms: m/e 292 (M^+).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.70; H, 5.64; N, 9.45.

2,3-Bis(*o*-chlorophenyl)pyrazine (**5f**).

This compound was obtained in a yield of 89%, mp 82-84° (from ethanol); uv: λ max 211.5 (log ε = 4.27), 245 (3.87), 267-273 (3.88) nm; pmr: δ 7.20-7.53 (8H, m, benzene H), 8.93 (2H, s, pyrazine H) ppm; ms: m/e 300 (M^+).

Anal. Calcd. for $C_{16}H_{10}Cl_2N_2$: C, 63.81; H, 3.35; N, 9.30. Found: C, 63.51; H, 3.28; N, 9.29.

General Procedure for Preparation of 2,3-Diphenylpyrazine *N*-Oxides **1b-f** and **6b-f**.

A solution of a 2,3-diphenylpyrazine (4 mmoles), 90% hydrogen peroxide (6 mmoles), and maleic anhydride (7 mmoles) in chloroform (50 ml) was refluxed for 2 hours, and then washed with water, 10% potassium bicarbonate and water, successively. The chloroform layer was dried over sodium sulfate, and the solvent was distilled off *in vacuo*. The residual solid was chromatographed on a silica gel (Wakogel C-200, 35 g) column and eluted with chloroform, containing an increasing amount of ethyl acetate. A mixture of chloroform and ethyl acetate (7:1) eluted a monoxide and ethyl acetate fractions afforded a dioxide. Both compounds were recrystallized from ethanol or methanol to furnish colorless prisms.

2,3-Bis(*p*-chlorophenyl)pyrazine 1-Oxide (**1b**).

This compound was obtained in a yield of 63%, mp 211-212° (from ethanol); uv: λ max 223.5 (log ε = 4.34), 265.5 (4.41), 322 (3.58) nm; pmr: δ 7.41-7.67 (8H, m, benzene H), 8.43 (1H, d, J = 4 Hz, pyrazine H), 8.73 (1H, d, J = 4 Hz, pyrazine H) ppm; ms: m/e 316 (M^+), 300 (M^+-O), 299 (M^+-OH).

Anal. Calcd. for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.83. Found: C, 60.58; H, 3.20; N, 8.77.

2,3-Bis(*p*-chlorophenyl)pyrazine 1,4-Dioxide (**6b**).

This compound was obtained in a yield of 14%, mp 259-261° (from methanol); uv: λ max 220.5 (log ε = 4.28), 267 (3.97), 282 (3.98), 318 (4.13) nm; pmr: δ 6.98-7.34 (8H, m, benzene H), 8.08 (2H, s, pyrazine H) ppm; ms: m/e 332 (M^+).

Anal. Calcd. for $C_{16}H_{10}Cl_2N_2O_2$: C, 57.68; H, 3.03; N, 8.41. Found: C, 57.50; H, 3.23; N, 8.40.

High resolution ms: Calcd: for $C_{16}H_{10}Cl_2N_2O_2$: 332.0119. Found: 332.0080.

2,3-Bis(*p*-bromophenyl)pyrazine 1-Oxide (**1c**).

This compound was obtained in a yield of 59%, mp 226-227° (from ethanol); uv: λ max 210.5 (log ε = 4.35, shoulder), 226 (4.40), 266.5 (4.47), 321.5 (3.65) nm; pmr: δ 6.90-7.44 (8H, m, benzene H), 8.08 (1H, d, J = 4 Hz, pyrazine H), 8.38 (1H, d, J = 4 Hz, pyrazine H) ppm; ms: m/e 404 (M^+), 388 (M^+-O), 387 (M^+-OH).

Anal. Calcd. for $C_{16}H_{10}Br_2N_2O$: C, 47.32; H, 2.48; N, 6.90. Found: C, 47.19; H, 2.37; N, 6.91.

2,3-Bis(*p*-bromophenyl)pyrazine 1,4-Dioxide (**6c**).

This compound was obtained in a yield of 7%, mp 250-251° (from methanol); uv: λ max 221.5 (log ε = 4.53), 269 (4.26), 284 (4.28), 318 (4.39) nm; pmr: δ 7.19 (4H, d, J = 8 Hz, benzene H), 7.52 (4H, d, J = 8 Hz, benzene H), 8.20 (2H, s, pyrazine H) ppm; ms: m/e 420 (M^+).

Anal. Calcd. for $C_{16}H_{10}Br_2N_2O_2$: C, 45.53; H, 2.39; N, 6.64. Found: C, 45.37; H, 2.37; N, 6.59.

2,3-Bis(*p*-methylphenyl)pyrazine 1-Oxide (**1d**).

This compound was obtained in a yield of 71%, mp 207-208° (from methanol); uv: λ max 222 (log ε = 4.38), 268 (4.40), 332 (3.67) nm; pmr: δ 2.36 (3H, s, CH_3), 2.46 (3H, s, CH_3), 7.07-7.44 (8H, m, benzene H), 8.36 (1H, d, J = 4 Hz, pyrazine H), 8.65 (1H, d, J = 4 Hz, pyrazine H) ppm; ms: m/e 276 (M^+), 260 (M^+-O), 259 (M^+-OH).

Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.08; H, 5.87; N, 10.14.

2,3-Bis(*p*-methylphenyl)pyrazine 1,4-Dioxide (**6d**).

This compound was obtained in a yield of 6%, mp 235-236° (from ethanol); uv: λ max 220 (log ε = 4.34), 293 (4.11, shoulder), 317 (4.22) nm; pmr: δ 2.30 (6H, s, CH_3), 7.23 (8H, s, benzene H), 8.27 (2H, s, pyrazine H) ppm; ms: m/e 292 (M^+).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.87; H, 5.58; N, 9.59.

2,3-Bis(*p*-methoxyphenyl)pyrazine 1-Oxide (**1e**).

This compound was obtained in a yield of 73%, mp 209-211° (from ethanol); uv: λ max 227 (log ε = 4.40), 276.5 (4.40), 343 (3.79) nm; pmr: δ 3.70 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 6.67-7.37 (8H, m, benzene H), 8.23 (1H, d, J = 4 Hz, pyrazine H), 8.52 (1H, d, J = 4 Hz, pyrazine H) ppm; ms: m/e 308 (M^+), 292 (M^+-O), 291 (M^+-OH).

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.14; H, 5.23; N, 9.09. Found: C, 69.84; H, 5.25; N, 8.94.

2,3-Bis(*p*-methoxyphenyl)pyrazine 1,4-Dioxide (**6e**).

This compound was obtained in a yield of 13%, mp 217-218° (from methanol); uv: λ max 224-229 (log ε = 4.65), 306 (4.67) nm; pmr: δ 3.73 (6H, s, OCH_3), 6.73 (4H, d, J = 8 Hz, benzene H), 7.10 (4H, d, J = 8 Hz, benzene H), 8.06 (2H, s, pyrazine H) ppm; ms: m/e 324 (M^+).

Anal. Calcd. for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.70; H, 4.96; N, 8.58.

2,3-Bis(*o*-chlorophenyl)pyrazine 1-Oxides (**1f**).

This compound was obtained in a yield of 67%, mp 168-169° (from ethanol); uv: λ max 220 (log ε = 4.24), 268 (4.18) nm; pmr: δ 7.10-7.33 (8H, m, benzene H), 8.25 (1H, d, J = 4 Hz, pyrazine H), 8.53 (1H, d, J = 4 Hz, pyrazine H) ppm; ms: m/e 317 (M^+ + 1), 281 (M^+-Cl).

Anal. Calcd. for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.83. Found: C, 60.59; H, 3.50; N, 8.66.

2,3-Bis(*o*-chlorophenyl)pyrazine 1,4-Dioxide (**6f**).

This compound was obtained in a yield of 12%, mp 245-246° (from methanol); uv: λ max 218 (log ε = 4.57), 256-257 (4.07), 317.5 (4.48) nm; pmr: δ 7.10-7.46 (8H, m, benzene H), 8.25 (2H, s, pyrazine H) ppm; ms: m/e 332 (M^+).

Anal. Calcd for $C_{16}H_{10}Cl_2N_2O_2$: C, 57.68; H, 3.03; N, 8.41. Found: C, 57.54; H, 2.99; N, 8.44.

Reaction of 2,3-Diphenylpyrazine 1-Oxides **1b-f** with Acetic Anhydride.

A mixture of a 2,3-diphenylpyrazine 1-oxide (4 mmoles) and acetic anhydride (20 ml) was heated at 130° for one hour, and then poured into ice-water. Yellow precipitates were extracted with methylene chloride, and the organic layer was washed with 10% potassium bicarbonate and water, successively. A usual work-up of the organic layer gave a yellow solid, which was chromatographed on silica gel (Wakogel C-200, 35 g) column, eluting with methylene chloride, to give colorless prisms.

5,6-Bis(*p*-chlorophenyl)-2,3-diacetoxy-2,3-dihydropyrazine (**2b**).

This compound was obtained in a yield of 88%, mp 192-194° (from methanol); uv: λ max 230.5 (log ε = 4.34), 297.5 (4.00) nm; ir (potassium bromide): 1750 cm^{-1} (C=O); pmr: 2.20 (6H, s, $OCOCH_3$), 6.36 (2H, s, pyrazine H), 7.36 (8H, s, benzene H) ppm; ms: m/e 418 (M^+), 316 (M^+-$(CH_3CO)_2O$).

Anal. Calcd. for $C_{20}H_{16}Cl_2N_2O_4$: C, 57.29; H, 3.85; N, 6.68. Found: C, 57.00; H, 3.83; N, 6.60.

5,6-Bis(*p*-bromophenyl)-2,3-diacetoxy-2,3-dihydropyrazine (**2c**).

This compound was obtained in a yield of 63%, mp 220-222° (from ethanol); uv: λ max 234 (log ε = 4.37), 298 (4.06) nm; ir (potassium bromide): 1750 cm^{-1} (C=O); pmr: δ 2.19 (6H, s, $OCOCH_3$), 6.23 (2H, s, pyrazine H), 7.22-7.55 (8H, m, benzene H) ppm; ms: m/e 506 (M^+), 404 (M^+-$(CH_3CO)_2O$).

Anal. Calcd. for $C_{20}H_{16}Br_2N_2O_4$: C, 47.25; H, 3.17; N, 5.51. Found: C, 47.13; H, 3.14; N, 5.46.

5,6-Bis(*p*-methylphenyl)-2,3-diacetoxy-2,3-dihydropyrazine (**2d**).

This compound was obtained in a yield of 44%, mp 90-92° (from hexane); uv: λ max 228 (log ε = 4.21), 297 (3.87) nm; ir (potassium bromide): 1754 cm^{-1} (C=O); pmr: δ 2.23 (6H, s, $OCOCH_3$), 2.33 (6H, s, CH_3), 6.36 (2H, s, pyrazine H), 7.16 (4H, d, J = 8 Hz, benzene H), 7.46 (4H, d, J = 8 Hz, benzene H) ppm; ms: m/e 378 (M^+), 276 (M^+-$(CH_3CO)_2O$).

Anal. Calcd. for $C_{22}H_{22}N_2O_4$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.40; H, 6.08; N, 7.14.

5,6-Bis(*p*-methoxyphenyl)-2,3-diacetoxy-2,3-dihydropyrazine (**2e**).

This compound was obtained in a yield of 95%, mp 72-74° (from hexane); uv: λ max 237 (log ε = 4.28), 290 (3.91), 326 (3.92) nm; ir (potassium bromide): 1758 cm^{-1} (C=O); pmr: δ 2.17 (6H, s, $OCOCH_3$), 3.70 (6H, s, OCH_3), 6.17 (2H, s, pyrazine H), 6.75 (4H, d, J = 8 Hz, benzene H), 7.43 (4H, d, J = 8 Hz, benzene H) ppm; ms: m/e 410 (M^+), 308 (M^+-$(CH_3CO)_2O$).

Anal. Calcd. for $C_{22}H_{22}N_2H_6$: C, 64,38; H, 5.40; N, 6.83. Found: C, 64.55; H, 5.44; N, 6.84.

High resolution ms: Calcd. for $C_{22}H_{22}N_2O_6$: 410.1478. Found: 410.1469.

5,6-Bis(*o*-chlorophenyl)-2,3-diacetoxy-2,3-dihydropyrazine (**2f**).

This compound was obtained in a yield of 58%, mp 200-202° (from ethanol); uv: λ max 209 (log ε = 4.27), 280 (3.51) nm; ir (potassium bromide): 1750 cm^{-1} (C=O); pmr: δ 2.16 (6H, s, $OCOCH_3$), 6.50 (2H, s, pyrazine H), 7.20-7.50 (6H, m, benzene H), 7.67-7.87 (2H, m, benzene H) ppm; ms: m/e 418 (M^+), 316 (M^+-$(CH_3CO)_2O$).

Anal. Calcd. for $C_{20}H_{16}Cl_2N_2O_4$: C, 57.29; H, 3.85; N, 6.68. Found: C, 57.14; H, 3.86; N, 6.61.

Crystal Data for 2,3-Diacetoxy-5,6-diphenyl-2,3-dihydropyrazine (**2a**).

The crystals are triclinic, with the space group $P\bar{1}$, a = 10.206(4)Å, b = 11.480(8)Å, c = 9.197(9)Å, α = 106.96(7)°, β = 106.27(5)°, γ = 106.63(1)°, Z = 2, D_x = 1.283, μ(MoKα, λ = 0.7107) = 0.98 cm^{-1}. Lattice parameters were obtained by a least-squares refinement of 46 values of 2θ (28° ≤ 2θ ≤ 36°) measured on a Rigaku AFC-5 automatic four-circle diffractometer with graphite-monochromated MoKα radiation. A total of 5549 reflections was collected up to 2θ = 55.0° by the θ-2θ scan method, of which independent 2469 reflections with $|Fo| > 3\sigma(|Fo|)$ were considered as "observed". The structure was solved by the direct method using Multan 78 Program [8], and refined by the block-diagonal least-squares method. The final R was 0.059 for 2469 unique reflections. Atomic scattering factors were taken from International Tables for X-ray Crystallography [9]. All the calculations were carried out on the FACOM-M160F computer in the computer center of Josai University by the use of the UNICS-111 program [10] and Multan 78 program [8].

Acknowledgements.

The authors are grateful to Dr. H. Miyamae, Josai University, for allowing us to use automated diffractometer and for helpful discussions.

REFERENCES AND NOTES

[1] A. Ohta, S. Masano, S. Iwakura, A. Tamura, H. Watahiki, M. Tsutsui, Y. Akita and T. Watanabe, *J. Heterocyclic Chem.*, **19**, 465 (1982).

[2] P. England and R. H. McDougall, *J. Chem. Soc. C*, 2685 (1971).

[3] Compounds **3b**, **3d** and **3f**; C. W. N. Cumper and A. P. Thurston, *J. Chem. Soc., Perkin Trans. II*, 106 (1972).

[4] Compound **3c** was prepared from *p*-bromobenzaldehyde by a similar method to the literature [3] in a total yield of 50%, mp 227-228° [T. van Es and O. G. Backenberg, *J. Chem. Soc.*, 1371 (1963); mp 223-224°].

[5] Compound **3e**.

[6] Compound **4d**; J. van Alpen, *Rec. Trav. Chim.*, **54**, 443 (1935).

[7] Compound **4e**, *cf.* lit [2].

[8] P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain, Belgium.

[9] "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham (1974).

[10] T. Sakurai and K. Kobayashi, *Rika Gaku Kenkyusho Hokoku (Rep. Inst. Phys. Chem. Res.)*, **55**, 69 (1978).

[11] C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).