500 ml of water for 3–5 min. The organic phase was washed with 200 ml of water, dried (sodium sulfate), and evaporated at reduced pressure. The orange residue was best recrystallized using the following procedure. The solid was dissolved by gentle warming in a mixture of 25 ml of absolute ethanol and 150 ml of toluene, and the resulting solution allowed to attain room temperature. Seven 20-ml portions of petroleum ether (bp 30–60°) were successively added with good mixing after each addition, and then the mixture kept 1 hr at room temperature, during which a crop of bright orange needles separated. Another 100-ml portion of petroleum ether was added, and the product was collected after another hour, washed with petroleum ether, and vacuum dried: yield 3.90 g; melting and resolidifying at 142°, followed by sharp melting at 151.5–152.5°. A second crop (1.05 g, mp 148–153°) was obtained by adding 300 ml of petroleum ether to the mother liquor and allowing the solution to stand at ~6°. Both crops were chromatographically uniform in solvent system A. The combined yield was 4.95 g (50%): infrared, 1700, 1685, 1650, and 1590 cm^{-1}; ultraviolet, λ_{max}^{MeOH} 258 mμ ($\epsilon \times 10^{-3} = 12.6$), 299 (27.4), 422 (9.75); nmr (trifluoroacetic acid solution containing 1 drop of deuterium oxide), δ 8.40 (singlet, 0.94 proton, NHC*H*=C<), 6.72 (singlet, 1.05 protons, quinone ring proton).

Anal. Calcd for $C_{18}H_{17}NO_6$ (343.3): C, 62.97; H, 4.99; N, 4.08. Found: C, 63.19; H, 5.05; N, 4.15.

Diethyl 4-(1,2-Naphthoquinonyl)aminomethylenemalonate (3).—A suspension of 5.0 g of 4-amino-1,2-naphthoquinone[12] was reduced and allowed to react with diethyl ethoxymethylenemalonate as described under the procedure for **2**. Evaporation of the reaction solution gave a crude quinhydrone, which without further manipulation was dissolved in a mixture of ethanol and chloroform. After the usual treatment with iron(III) solution, washing, and evaporation of the dried organic solution, the crude naphthoquinone **3** was isolated as an orange-brown crystalline solid. This solid was digested with 50 ml of ethanol, filtered, and washed with ether: yield 6.0 g (chromatographically impure, two zones). The product was recrystallized from approximately 1 l. of absolute ethanol (preheated to boiling before adding compound) to give 4.83 g (49%) of metallic-lustered orange platelets: mp 176–189° dec; the compound moved as one zone in solvent systems A and B; infrared, 1725, 1695, 1655 sh, 1643, 1625, and 1590 cm^{-1}; ultraviolet, λ_{max}^{MeOH} 255 mμ ($\epsilon \times 10^{-3} = 19.9$), 297 (12.0), 333 (12.8), 438 (7.60); λ_{sh}^{MeOH} 342 (12.5); nmr, δ 8.73 (singlet, 1.03 protons, NHC*H*=C<), 6.97 (singlet, 1.03 protons, quinone ring proton).

Anal. Calcd for $C_{18}H_{17}NO_6$ (343.4): C, 62.97; H, 4.99; N, 4.08. Found: C, 63.00; H, 5.00; N, 4.42.

3-Carboethoxybenzo[*g*]quinoline-4,5,10-trione (4).—A solution of 3.15 g of **2** in 50 ml of Dowtherm A was heated under reflux for 45 min and then kept at room temperature for 2 hr. The light yellow, crystalline product was filtered and washed with a little Dowtherm and then thoroughly with petroleum ether. After vacuum drying overnight, the product (2.1 g) still gave a strong diphenylether odor. The material was recrystallized from approximately 90 ml of toluene (activated charcoal) to give 1.37 g (50%), mp 226–228.5°, of soft yellow needles. The compound moved as one zone (tlc) when chromatograms were eluted with solvent systems A, C, and D. The compound crystallized from absolute ethanol as small yellow prisms: mp 224–226.5°; infrared, 1720, 1680, 1630, and 1580 cm^{-1}; ultraviolet, λ_{max}^{MeOH} 250 mμ ($\epsilon \times 10^{-3} = 23.2$), 320 (4.93), 390 (2.60); λ_{sh}^{MeOH} 260 (20.9), 274 (14.4), 280 (10.3); $\lambda_{max}^{6\ N\ HCl}$ 240 (24.0), 265 (22.5), 307 (5.25), 352 (4.15); $\lambda_{max}^{0.1\ N\ NaOH}$ 225 (24.6), 247 (28.6), 252 (28.2), 272 (18.7), 330 (3.62), 425 (4.80); nmr, δ 9.54 (singlet, 1.00 proton, heterocyclic ring proton).

Anal. Calcd for $C_{16}H_{11}NO_5$ (297.3): C, 64.65; H, 3.73; N, 4.71. Found: C, 64.86; H, 4.04; N, 4.81.

3-Carboethoxybenzo[*h*]quinoline-4,5,6-trione (5).—A solution of 3.0 g of **3** in 20 ml of Dowtherm A was heated under reflux for 45 min and then kept at room temperature for 4–5 hr. The crop of heavy, dark brown crystals (2.3 g) was collected, washed successively with Dowtherm and petroleum ether, and recrystallized from 60 ml of toluene (activated charcoal) to give golden brown crystals (1.7 g), mp 233–237° with a crystalline change occurring at ~185°. One further recrystallization using 40 ml of toluene (activated charcoal) gave 1.3 g of metallic-lustered gold plates, which melted and resolidified in the form of needles at 183–186°. The latter crystalline form then melted at 233–235°: the compound moved as one zone (tlc) in solvent systems A and B; infrared, 1715, 1690, 1630 and 1580 cm^{-1}; ultraviolet, λ_{max}^{MeOH} 261 mμ ($\epsilon \times 10^{-3} = 30.9$), 325 (4.42); λ_{sh}^{MeOH} 245 (22.0), 350 (3.62); $\lambda_{max}^{6\ N\ HCl}$ 278 (28.7), 363 (5.14); $\lambda_{sh}^{6\ N\ HCl}$ 320 (5.46); $\lambda_{max}^{0.1\ N\ NaOH}$ 254 (32.5), 328 (4.25), 430 (4.62); $\lambda_{sh}^{0.1\ N\ NaOH}$ 245 (28.2); nmr, δ 9.45 (singlet, 1.04 protons, heterocyclic ring proton).

Anal. Calcd for $C_{16}H_{11}NO_5$ (297.3): C, 64.65; H, 3.73; N, 4.71. Found: C, 64.65; H, 3.72; N, 4.91.

Quinoxaline Derivative of 5.—To a suspension of 100 mg of **5** in 5.0 ml of acetic acid was added a solution of 100 mg of *o*-phenylenediamine in 5.0 ml of acetic acid. After 15 min, the original suspension of **5** had passed to one consisting of a spongy, light yellow solid. The mixture was warmed until a clear solution had formed and then set aside until the contents formed a solid mass. The light yellow product (110 mg) was filtered and washed successively with acetic acid, ethanol, and ether. When recrystallized from approximately 5 ml of acetic acid, the derivative, mp 176°, had no definite crystalline form when examined under the microscope. The compound crystallized from absolute ethanol as canary yellow, microcrystalline needles: mp 178–179.5°; it moved as one zone in solvent systems A and B; ultraviolet, λ_{max}^{EtOH} 261 mμ ($\epsilon \times 10^{-3} = 77.0$), 381 (18.2), 402 (22.4).

Anal. Calcd for $C_{22}H_{15}N_3O_3$ (369.4): C, 71.53; H, 4.09; N, 11.38. Found: C, 71.28; H, 4.12; N, 11.56.

Some Properties of Compounds 2–5.—Aside from the fact that only **5** would form a quinoxaline derivative and the observation that the color of **4** in aqueous solution was completely bleached at moderate acid strength (10^{-4} to 10^{-5} *M* solutions in 6 *N* hydrochloric acid), the tricyclic azaquinones **4** and **5** exhibited some common properties, which in the past have been used qualitatively for differentiating between *o*- and *p*-quinones. Both **4** and **5** reacted with cold, saturated bisulfite solution[13] to give insoluble white precipitates and, in tests conducted by suspending a few crystals in the cold solution and allowing the suspension to stand at ~6°, the 1-azaanthraquinone **4** was observed to react more rapidly. Contrasting with the striking color differences of comparable heterocyclic *o*- and *p*-quinones,[14] the azaquinones **4** and **5** exhibited similar colors; in fact, the similarity in color allows aged or impure samples of **4** to be easily mistaken for **5**.

When *Phoma terrestris* Hansen was grown on a Czapek-Dox medium containing starch,[4a] the dark violet color contained on the underside of the mycelium was attributed to the presence of a sodium or potassium salt of the phomazarin. In this connection, we have tested the colors imparted to 0.1 *N* sodium hydroxide solution by the compounds prepared in this study. When relatively concentrated solutions of the azaquinones **4** and **5** in alcohol were treated with a few drops of 1% sodium hydroxide solution, neither a permanent nor transient violet color was imparted to the solution; alkaline solutions of **4** and **5** were yellow and yellow-orange, respectively. If, on the other hand, alcohol or acetone solutions of the intermediates **2** and **3** were treated with drops of dilute alkali, royal purple colors were immediately imparted. When stock solutions of compounds **2** and **3** in alcohol (10^{-4} *M*) were diluted with 0.1 *N* alkali, only transient violet colors were observed.

Registry No.—**2**, 13388-72-2; **3**, 13388-73-3; **4**, 13388-74-4; **5**, 13421-38-0.

(13) L. F. Fieser, *J. Am. Chem. Soc.*, **48**, 3201 (1926).

(14) (a) Quinolinequinones: J. Matheus, *Ber.*, **21**, 1887 (1888); R. Long and K. Schofield, *J. Chem. Soc.*, 3161 (1953). (b) Furanonaphthoquinones: S. C. Hooker, *J. Am. Chem. Soc.*, **58**, 1163 (1936).

The Selective Reduction of a Nitro and Pyridyl Group

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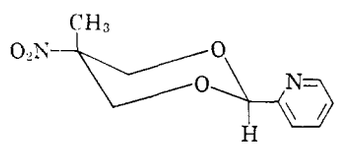
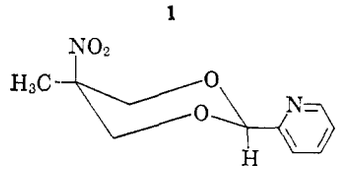
In this Note, we wish to report our findings on the stereochemistry of the 1,3-dioxane obtained from the condensation of 2-pyridinecarboxaldehyde and 2-nitro-2-methyl-1,3-propanediol and some selective hydro-

genations of the nitro and pyridyl group in this compound.

From the reaction of 2-nitro-2-methyl-1,3-propanediol and 2-pyridinecarboxaldehyde in the presence of *p*-toluenesulfonic acid there was obtained a 21% yield of a crystalline isomer of 2-α-pyridyl-5-nitro-5-methyl-1,3-dioxane. Careful investigation of the mother liquors by thin layer chromatography failed to uncover another isomer.[1] The nmr spectrum of this substance gave a methyl singlet at 1.38 ppm, while the four C-4,6 protons gave an AB pattern with the centers of gravity of the two doublets at 3.93 and 4.98 ppm (J = 13 cps). All four peaks were further split into triplets[2] with J = 1.5 cps. The C-2 proton gave a singlet at 5.58 and the α-pyridyl group gave characteristic bands in the 7.0–8.5-ppm region. If it is assumed that the 1,3-dioxane ring exists in the chair conformation[3] and that the 2-pyridyl group[4] occupies an equatorial position, the compound would be either **1** or **1a**. Dipole



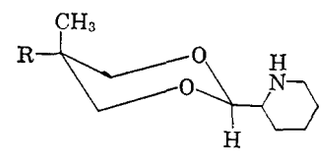
1



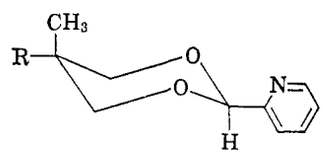
1a

moment calculations[5] on configurations **1** and **1a** gave theoretical values of 3.44 and 5.79D. respectively. The experimental value of 2.97. indicates that structure **1**, with the equatorial nitro group,[6] is the most probable conformational form of this isomer.

An acetic acid solution of **1** was hydrogenated in the presence of platinum until 3 moles of hydrogen was absorbed. There was obtained a 90% yield of 2-piperidyl-5-nitro-5-*cis*-methyl-1,3-dioxane (**2**). The presence of the nitro and 2-piperidyl groups was confirmed by characteristic infrared and nmr bands. When the platinum–acetic acid hydrogenation of **1** was carried out for 70 hr, there was obtained a 55% yield of **2** and a



2, R = NO_2
3, R = NH_2



4, R = NOH
5, R = NH_2

43% yield of 2-piperidyl-5-amino-5-*cis*-methyl-1,3-dioxane (**3**). The hydrogenation of an isopropyl alcohol solution of **1** in the presence of platinum gave 2-α-pyridyl-5-hydroxyamino-5-*cis*-methyl-1,3-dioxane (**4**) together with some starting material. The hydroxy amino group was supported by elemented analysis and the nmr spectrum. Raney nickel catalyzed hydrogenation of **1** resulted in the reduction of the nitro group to give 2-α-pyridyl-5-amino-5-*cis*-methyl-1,3-dioxane (**5**).

Earlier studies[7] on the platinum acetic acid hydrogenation of a nitro and pyridyl group have shown that the saturation of the pyridyl group occurs less readily than the nitro group. Our findings with the catalyst system in the reduction of **1** to **2** are just opposite. Undoubtedly the steric environment[8] that the nitro group occupies on C-4 of **1** offers some hindrance to approach on a catalytic surface. However, this effect cannot be the only factor operating in this system since the platinum-catalyzed hydrogenation of **1** in isopropyl alcohol results in the reduction of the nitro group to the hydroxyamino derivative **4**. It appears that the earlier conclusions[7] about the platinum-catalyzed hydrogenation of a nitro and pyridyl group are oversimplified and that additional studies are needed before any general statements can be made.

The Raney nickel catalyzed hydrogenation of **1** to the amine **5** proceeded in the expected manner[7] where the nitro group is reduced prior to the pyridyl system.

(1) The failure to isolate a second isomer does not rule out its presence. A similar reaction between 2-nitro-2-methyl-1,3-propanediol and isobutyraldehyde has been reported to give a mixture of isomeric 1,3-dioxanes of undetermined geometry in a ratio of 1.0:3.8: C. S. Rondestvedt, Jr., *J. Org. Chem.*, **26**, 2247 (1961).

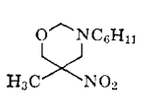
(2) The splitting pattern has been observed in a number of 1,3-dioxanes prepared in our laboratory. A more detailed analysis of the nmr pattern of these compounds will be forthcoming.

(3) Dipole and nmr studies have shown that 1,3-dioxane and 2- or 5-substituted 1,3-dioxanes (R. Walker and D. W. Davidson, *Can. J. Chem.*, **37**, 492 (1959); N. Baggett, B. Dobinson, A. B. Foster, J. Homer, and L. F. Thomas, *Chem. Ind.* (London), 106 (1961); G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961); C. Barbier, J. Delman, and J. Ranft, *Tetrahedron Letters*, 3339 (1964); and K. C. Ramey and J. Messick, *ibid.*, 4423 (1965)) exist in the chair conformation while 4,4-substituted 1,3-dioxanes exist in a twist form (J. Delmau and J. Duplan, *Tetrahedron Letters*, 2693 (1966)).

(4) Since the spatial requirements of the 2-pyridyl group have not been determined, this assignment is based on assuming that it has a conformational preference similar to that found for the phenyl group: E. W. Garbisch, Jr., and D. B. Patterson, *J. Am. Chem. Soc.*, **85**, 3228 (1963).

(5) The authors are grateful to Professor Edmund R. Malinowski, Stevens Institute of Technology, Hoboken, N. J., for performing the calculations.

(6) It is interesting to note that in the similar ring system 3-cyclohexyl-5-nitro-5-methyltetrahydro-1,3-oxazine (i), obtained by condensing formaldehyde, cyclohexylamine, and 2-nitroethane, the nitro group is reported to be in the axial position: T. Urbanski, D. Gurne, R. Kolinski, H. Piotrowska, A. Jonczyk, B. Serafin, M. Szretter-Szmid, and M. Witanosaki, Proceedings of the International Symposium on Nitro Compounds, Warsaw, 1963, publ 1964, pp 195–210; *Chem. Abstr.*, **63**, 16186 (1965); and D. Gurne and T. Urbanski, *Roczniki Chem.*, **34**, 881 (1960); *Chem. Abstr.*, **59**, 8414 (1961).



i

(7) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, p 104.

(8) An example in which a benzene ring has been reduced prior to a nitro group has been reported in the hydrogenation of 1-(α-carboethoxy-β-indolyl)-2-nitrobutane with 30% Pd–C in acetic acid. The result was attributed to a combination of steric and electronic factors that protect the nitro group and facilitated attack on the benzene portion of the indole system: D. T. Young and H. R. Snyder, *J. Am. Chem. Soc.*, **83**, 3160 (1961).

Experimental Section[9]

Dipole Moment.—The dielectric apparatus used in this study has been described in the literature.[10] Molar refractivities were calculated from atomic refractivities for the sodium D line. The dipole moment measurements were determined in *p*-xylene solutions at 25.0°. The P_μ value was calculated from eq 1[11]

$$P_\mu = M_2\left[\frac{3\alpha}{d_1(\epsilon_1+2)^2} - \frac{6\sqrt{\epsilon_1}\gamma}{d_1(\epsilon_1+2)^2}\right] \quad (1)$$

where M_2 is the molecular weight of solute, d_1 the density of solvent, ϵ_1 the dielectric constant of solvent, $\alpha = (\partial\epsilon_{sol}/\partial W_2)_{W_2\to 0}$ and $\gamma = (\partial_{sol}/\partial W_2)_{W_2\to 0}$, W_2 is the weight fraction of solute, and n is the refraction index. The data obtained for 2-α-pyridyl-5-nitro-5-methyl-1,3-dioxane (1) are given in Table I. The

TABLE I[a]

$W_2 \times 10^3$	$\epsilon \times 10^3$	$\Delta n \times 10^5$
1.577	6.81	5.8
3.047	12.75	11.2
4.521	19.12	14.3
6.026	25.92	19.3

[a] $\alpha = 4.2646$, $\gamma = 0.03274$, $M_2 = 224.218$, $\mu = 2.97$ D.

calculated dipole[12] values for the axial (**1a**) and equatorial (**1**) isomers were carried out by assuming a chair conformation[3] for the 1,3-dioxane ring system and free rotation for the α-pyridyl, methyl, and nitro groups. The bond moment values used in the calculations were 2.21 D. for α-pyridyl,[13a] 3.6 D. for nitro,[13b] and 2.14 D. for the 1,3-dioxane ring.[13c]

2-α-Pyridyl-5-nitro-5-*cis*-methyl-1,3-dioxane (1).—A mixture of 2-nitro-2-methyl-1,3-propanediol[14] (130 g, 0.96 mole), 2-pyridinecarboxaldehyde (103 g, 1.27 mole), *p*-toluenesulfonic acid monohydrate (205 g, 1.08 moles), and benzene (1000 ml) was placed in a flask equipped with a Dean–Stark water separator. The mixture was stirred and refluxed until a water phase (33 ml) failed to separate in the condensate. The reaction flask was then placed on a rotary evaporator and the solvent was removed *in vacuo*. The residue was cooled in ice and treated with 50% sodium hydroxide until basic to litmus. The caustic layer was extracted four times with chloroform. The chloroform layer was washed with water, dried with sodium sulfate, filtered, and then concentrated *in vacuo* on a rotary evaporator. There was obtained 84.9 g of material that was shown by tlc on silica gel plates to contain some unreacted diol. Chromatography of this material on a silica gel column ($CHCl_3$ eluant) gave 45.5 g of a substance, mp 105–106°, with R_f 0.54 ($CHCl_3$–CH_3OH, 95:5). Crystallization from a methylene chloride–ether–pentane mixture gave 36.9 g of 2-α-pyridyl-5-nitro-5-*cis*-methyl-1,3-dioxane, mp 105–107°.

Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.5; H, 5.4; N, 12.5; O, 28.6. Found: C, 53.5; H, 5.8; N, 12.5; O, 28.2.

2-α-Piperidyl-5-nitro-5-*cis*-methyl-1,3-dioxane (2).—A mixture of 2-α-pyridyl-5-nitro-5-*cis*-methyl-1,3-dioxane (11.2 g, 0.05 mole), platinum oxide (0.60 g), and acetic acid (100 ml) was placed in a Parr hydrogenation bottle and then attached to a Parr hydrogenation apparatus. The bottle was evacuated and then filled with hydrogen to a total pressure of 50 psi. After 1.25, hr, agitation at room temperature the hydrogen uptake (3 equiv of H_2) ceased. The catalyst was filtered off and the filtrate was concentrated *in vacuo* on a rotary evaporator. The residue was treated with 2 *N* sodium hydroxide until the aqueous phase had pH 9. It was then extracted with chloroform, dried with sodium sulfate, filtered, and concentrated on a rotary evaporator. There was obtained 13.3 g of oil that crystallized from an ether–pentane mixture to give 10.2 g (90%) of 2-α-piperidyl-5-nitro-5-*cis*-methyl-1,3-dioxane: mp 86–89°; infrared absorption (KBr) at 2.95 (NH), 6.48, and 7.28 (NO_2); nmr peaks ($CDCl_3$) at δ 1.10–3.20 (9 H, complex multiplet, C_5H_9N), 1.33 (3 H, singlet, CH_3), 1.82 (1 H, exchangeable with D_2O, NH), 3.68 and 4.82 (4 H, AB, J = 13.0, J' = 1.5[2], $OCH_2\overset{|}{C}CH_2O$), and at 4.32 (1 H, doublet, J = 6.5, OCHO). An analytical sample from a methylene chloride–ether mixture gave mp 87–89°.

Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.2; H, 7.8; N, 12.2; O, 27.8. Found: C, 52.3; H, 8.1; O, 27.3.

2-α-Piperidyl-5-amino-5-*cis*-methyl-1,3-dioxane (3).—A mixture of 2-α-pyridyl-5-nitro-5-methyl-1,3-dioxane (5.6 g, 0.025 mole), platinum oxide (0.60 g), and acetic acid (50 ml) was hydrogenated as above for a total of 70 hr. A total of 0.11 moles of hydrogen was absorbed. The catalyst was filtered off and the residue worked up as above. There was obtained 5.9 g of an oil that gave two spots on a thin layer plate. Chromatography on silica gel ($CHCl_3$ eluent) gave 2.4 g of 2-α-piperidyl-5-nitro-5-methyl-1,3-dioxane (R_f 0.1, $CHCl_3$–CH_3OH, 95:5) and 2.7 g of an oil (R_f 0.1, $CHCl_3$–CH_3OH, 95:5). Distillation of the oil gave 2.5 g of 2-α-piperidyl-5-amino-5-*cis*-methyl-1,3-dioxane, bp 95° (8 mm). The nmr spectrum (CCl_4) has δ 0.82 (3 H, singlet, CH_3), 1.00–3.20 (9 H, complex multiplet, C_5H_9N), 1.80 (3 H, exchangeable with D_2O, NH_2 and NH), 3.50 (4 H, singlet, $OCH_2\overset{|}{C}CH_2O$), and at 4.11 (1 H, doublet, J = 6.5, OCHO).

Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 60.0; H, 10.0; N, 14.0; O, 16.0. Found: C, 60.3; H, 9.9; N, 13.9; O, 16.6.

2-α-Pyridyl-5-hydroxyamino-5-*cis*-methyl-1,3-dioxane (4).—A mixture of 2-α-pyridyl-5-nitro-5-*cis*-methyl-1,3-dioxane (11.2 g, 0.05 mole), 5% platinum on carbon (0.60 g), and isopropyl alcohol (150 ml) was hydrogenated at room temperature and 50 psi initial pressure as described in the preparation of **2**. After 48 hr (0.08 moles H_2 uptake), the reaction was terminated. The catalyst was filtered off and the filtrate concentrated *in vacuo* on a rotary evaporator. The residue which gave three spots (R_f 0.05, 0.17, 0.52 with $CHCl_3$–CH_3OH, 95:5), on a silica gel thin layer plate was chromatographed on a silica gel column. After developing with benzene, the following fractions were eluted with $CHCl_3$: 7–11, 2.8 g (R_f 0.52); 12–13, 0.7 g (R_f 0.12, 0.52); 14–26, 5.6 g (R_f 0.17); 27–29, 0.6 g (R_f 0.05, 0.17), and 30–32, 0.6 g (R_f 0.05). Fractions 7–13 were crystallized from methylene chloride–pentane to give 2.3 g of starting material, mp 105–107°. Fractions 14–29 were crystallized from methylene chloride–pentane to give 5.5 g of 2-α-pyridyl-5-hydroxyamino-5-methyl-1,3-dioxane, mp 122–124°. The nmr spectrum ($CDCl_3$) has δ 1.00 (3 H, singlet, CH_3), 3.72 and 4.27 (4 H AB, J = 12.0, $OCH_2\overset{|}{C}CH_2O$), 5.53 (1 H, singlet, OCHO), 7.10–8.50 (4 H, complex, C_5H_4N), and 7.65 (2 H, exchangeable with D_2O, NHOH).

Anal. Calcd for $C_{10}H_{14}N_2O_3$: C, 57.1; H, 6.7; N, 13.3; O, 22.9. Found: C, 57.2; H, 6.7; N, 12.9; O, 22.4.

2-α-Pyridyl-5-amino-5-*cis*-methyl-1,3-dioxane (5).—A mixture of 2-α-pyridyl-5-nitro-5-methyl-1,3-dioxane (6.8 g, 0.03 mole), Raney nickel (1.5 g), and isopropyl alcohol (150 ml) was hydrogenated at room temperature and 50-psi initial pressure as described in the preparation of **2**. After 22 hr, 0.12 mole of hydrogen was absorbed. The catalyst was filtered off and the filtrate concentrated to about three-fourths of the original volume. The crystalline precipitate (2.5 g) was filtered off and identified as starting material. The filtrate was concentrated further to give 3.1 g of oil. Distillation gave 2.3 g of 2-α-pyridyl-5-amino-5-*cis*-methyl-1,3-dioxane, bp 110–120° (0.4–0.5 mm). The nmr spectrum ($CDCl_3$) of the free base **5** has δ 0.82 (3 H, singlet, CH_3), 1.99 (2 H, exchangeable with D_2O, NH_2), 3.68 (4 H, singlet, $OCH_2\overset{|}{C}CH_2O$), 5.32 (1 H, singlet, OCHO), and 7.0–8.4 (4 H, complex, C_5H_4N). Treatment of this material with D-tartaric acid (1.8 g) in methanol (15 ml) gave, after dilution with ethyl acetate, 2.6 g of the D-tartrate of **5**, mp 209–211°. A sample crystallized for analysis gave mp 210–212°.

Anal. Calcd for $C_{14}H_{20}N_2O_8$: C, 48.9; H, 5.8; N, 8.1; O, 37.2. Found: C, 48.8; H, 6.3; N, 8.0; O, 36.8.

Registry No.—**1**, 13509-70-1; **2**, 13557-42-1; **3**, 13509-66-5; **4**, 13509-67-6; **5**, 13509-68-7; **5** D-tartrate, 13509-69-8.

(9) Melting points were determined on a Thomas–Hoover capillary melting point apparatus and have not been corrected. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer and are recorded in parts per million from an internal tetramethylsilane standard (J, cps). Infrared spectra were determined with a Perkin-Elmer Infracord.

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Heterocyclic Analogs of Fulvene and Fulvalene. II. 1,4-Diazafulvenes[1]

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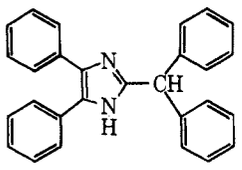
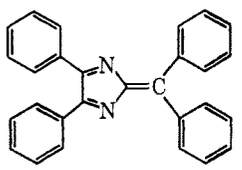
Several recent publications[2,3] dealing with nitrogen-containing analogs of fulvalene prompted us to present briefly some of our results in this general area. Earlier we showed[1] that $\Delta^{2,2'}$-bi-2H-benzimidazole could be readily prepared by oxidation of 2,2′-bibenzimidazole with lead peroxide. Recently the same method was used to prepare 2,3,6,7-tetraphenyl-1,4,5,8-tetraazafulvalene from 4,5,4′,5′-tetraphenyl-2,2′-biimidazole.[2] We have now found that examples of 1,4-diazafulvene derivatives can be prepared by oxidative methods and other reactions.

2-Benzhydryl-4,5-diphenylimidazole (I)[4] was converted into 2-benzhydrylidene-4,5-diphenyl-2H-imidazole (II) by two methods. Oxidation of I with freshly prepared lead peroxide gave an intense yellow solution from which II was isolated as orange needles. The spectroscopic properties were consistent with structure II: the infrared spectrum in CCl_4 showed no N–H absorption but had strong peaks at 3.25 and 3.29 μ (aromatic C–H) and at 6.02, 6.25, 6.71, and 6.92 μ (C=N and C=C). The visible spectra had maxima at 415 mμ (log ϵ 4.432) in ethanol and at 409 mμ (log ϵ 4.486) in cyclohexane. The nmr spectrum in $CDCl_3$ showed only a complex multiplet between τ 2.1 and 2.8 for the aromatic protons. An alternative though less efficient synthesis involved bromination of I with N-bromosuccinimide in $CHCl_3$ followed by dehydrobromination with triethylamine to yield a complex mixture from which II was isolated in low yield by column chromatography.

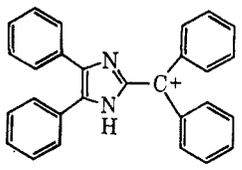
Behringer has recently described the properties of some 1,4-diazafulvenium ions obtained by the protonation with H_2SO_4 of 2-imidazolyldiphenyl carbinols, which were prepared by the reaction of aryl lithiums with 2-benzoylimidazoles.[5] When II was dissolved in concentrated H_2SO_4, a stable intense green solution resulted, with absorptions at 622 (log ϵ 4.396) and 458 mμ (log ϵ 4.006), which suggests that II was converted to a 1,4-diazafulvenium ion, presumably III. Quenching with water discharged the color and gave a product that was identified as 4,5-diphenyl-2-imidazolyldiphenyl carbinol (IV). In concentrated H_2SO_4, II and IV had identical absorption spectra. The easy reduction of II to I by $LiAlH_4$ indicated that no molecular rearrangement had occurred during oxidation.



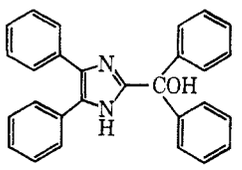
I



II

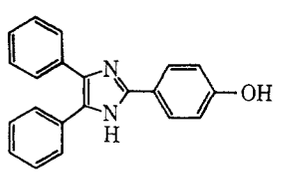


III

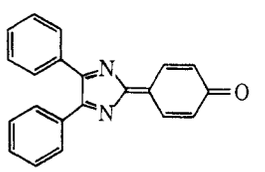


IV

2-(4-Hydroxyphenyl)-4,5-diphenylimidazole (V) was similarly oxidized by lead peroxide in warm $CHCl_3$ to 4-(4,5-diphenyl-2H-imidazol-2-ylidene)-2,5-cyclohexadien-1-one (VI).[3,6] Its infrared spectrum had intense absorption at 6.16 μ (C=O) and weaker absorptions at 3.22, 3.25, and 3.29 μ (=CH) and at 6.25, 6.77, and 7.00 μ (aromatic C=C). The visible spectra had maxima at 432 mμ (log ϵ 4.396) in ethanol and at 421 mμ (log ϵ 4.746) in cyclohexane. The nmr spectrum in $CDCl_3$ showed the cyclohexadienide protons as an AB system, with doublets at τ 1.55 and 3.44 (4 H, J_{AB} = 10 cps) and the aromatic protons as a multiplet centered at τ 2.5 (10 H). Compound VI decomposed in concentrated H_2SO_4. It was reduced in poor yield by hydrazine and Raney nickel.



V



VI

2-(4-Pyridyl)-4,5-diphenylimidazole (VII) was alkylated with methyl benzenesulfonate to yield 4-(4,5-diphenylimidazolyl)-1-methylpyridinium benzenesulfonate (VIII). Treatment of VIII with sodium methoxide gave 1,4-dihydro-4-(4,5-diphenyl-2H-imidazol-2-ylidene)-1-methylpyridine (IX) as small golden red crystals. Compound IX was somewhat sensitive to light and air. It behaved as an anhydro base and was decolorized in acid solution and regenerated when the acid solution was basified. Its spectral properties were consistent with the structure proposed. The infrared spectrum in $CHCl_3$ had no N–H absorption but showed absorption at 3.39 (=CH), 6.14, and 6.28 μ (C=C or C=N). Maxima at 451 mμ (log ϵ 4.377) in ethanol and at 501 mμ (log ϵ 4.534) in benzene were observed. The nmr spectrum in $CDCl_3$ had a singlet at τ 5.9 (>NCH_3, 3 H) and a complex multiplet from τ 1.95 to 3.1 (about 14 H) which was due to both the aromatic and 1,4-dihydropyridine protons. Compound VIII was also prepared by alkylation of pyridine-4-carboxaldehyde with methyl benzenesulfonate and reaction of the crude product with benzil and ammonium acetate in refluxing acetic acid. This showed that VII was alkylated on the pyridine and not the imidazole ring.

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