B. Preparation of *N*-Acetyl-2,3,4,5-tetrahydro-1*H*-naphth-[1,8-*de*]azocine (5).—In another reduction 0.51 g (0.0024 mol) of **3** in tetrahydrofuran was boiled under reflux under nitrogen for 5 hr with 35 ml of a solution of diborane in tetrahydrofuran (1 *M* BH_3, Ventron Corp.). Boiling the mixture under reflux with hydrochloric acid and the usual work-up yielded a crystalline product, 80% of which was dissolved in ether and acetylated with 1.11 g (0.014 mol) of acetyl chloride added in portions to the stirred solution with concurrent additions of 1 *N* sodium hydroxide. The usual isolation and recrystallization of the product from ether yielded **5** as white crystals: 0.25 g; mp 133–135°; ir (Nujol) 1630 cm^{-1} (amide C=O); uv (hexane) 228 mμ (log ε 4.78), 287 (3.87), 317 (2.7), 322 (2.65); nmr ($CDCl_3$) δ 1.30 [3 H, singlet, $CH_3C(=O)$, the Dreiding molecular model shows that the methyl group is held over by naphthalene moiety with the result that the methyl group is shielded by the diamagnetic ring current], 3.72 (8 H, center of broad overlapping signals, two $-CH_2CH_2-$ groups), 7.14–7.48 (4 H, multiplet, naphthalene β protons), 7.52–7.84 (2 H, multiplet, naphthalene α protons) (Figure 1); nmr [toluene-d_8, 40°, $(Me_3Si)_2$ internal reference] δ 3.1 and 3.8 (broad overlapping signals, aliphatic protons); nmr (toluene-d_8, 117°) δ 3.18 (4 H, triplet, two $-CH_2-$ groups), 3.54 (4 H, triplet, two $-CH_2-$ groups); mass spectrum, molecular ion *m/e* 239.

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.34; H, 7.27; N, 5.85.

Continuous Titration of Protons Generated during Photolyses of Compound 2.—In all cases 0.15×10^{-3} mol of the substrate was dissolved in 20 ml of methanol and that solution was diluted with 80 ml of water. The solution was placed in a semicircular two-neck quartz cell with an inner radius of 3.8 cm and a distance between inner cell walls of 0.7–1 cm. The electrode was introduced through one opening and the other was available for withdrawal of aliquots, etc. The cell was placed in a stainless steel cylinder with a polished inner surface with inner diameter of 15 cm and was supported by hooks on the wall of the cylinder. The water-cooled well containing the lamp and filter was also placed within the cylinder. The substrate solution was agitated by a vigorous stream of a gas which was introduced through two polyethylene tubes. A steel shield supported in grooves on the inner surface of the metal cylinder was positioned between the substrate cell and the immersion well. This shield could be removed rapidly after the lamp had been allowed a warm-up period of 3 min. In doing a series of phototitrations, a given arrangement of equipment could be reproduced precisely. During irradiation the protons produced were titrated with a Radiometer Titrator, type TTTlC, fitted with an Ole Dich No. 38 recorder and a Radiometer GK 2302C glass electrode which was immersed in the substrate solution. The titration curves obtained with this equipment indicate that relative rates of production of protons under various conditions. Reaction half-lives were taken from the curves (Figure 2). Each reaction was allowed to continue nearly to completion and then was taken to dryness *in vacuo*. Examination of the residues in methanol solution by uv spectroscopy and tlc afforded information on the character of the product mixtures. Tlc plates (0.25 mm, silica gel GF, Analtech, Inc.) were developed with ether–methanol (9:1, v/v) or benzene–methanol (3:1, v/v). Developing solvents were allowed to evaporate before visualization with a uv lamp or iodine vapor.

Registry No.—**2**, 25055-69-0; **3**, 25055-70-3; **4**, 26630-82-0; **4** HCl, 26595-66-4; **5**, 26595-67-5.

Acknowledgment.—The author wishes to thank Dr. E. D. Becker of the National Institute of Arthritis and Metabolic Diseases for assistance in the interpretation of nmr spectra and Mr. E. A. Sokoloski of the Laboratory of Chemistry of the National Heart Institute, who determined all of the nmr spectra, for his generous and skillful assistance.

Some Unusual Oxidation Reactions of 1,3-Diaryl-3,4-dihydro-7-methoxy-2(1*H*)-quinoxalinones

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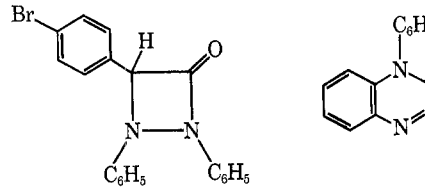
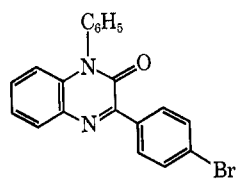
Acid-catalyzed air oxidation of 3-aryl-3,4-dihydro-7-methoxy-1-(*p*-methoxyphenyl)-2(1*H*)-quinoxalinones (**4**) proceeded rapidly to give the corresponding 3,4-dehydro compounds **5**. In contrast, a similar oxidation of the 4-methyl derivative **9** afforded anisic acid and 5-methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (**10**). Photolytic oxidation of 3,4-dihydroquinoxalinones by 4,4′-dimethoxyazobenzene proceeded smoothly to give the quinoxalinones **5** and *p*-anisidine.

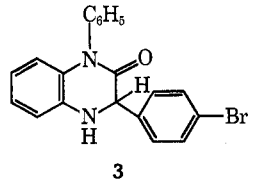
The acid-catalyzed ortho-semidine type of rearrangement of 4-aryl-1,2-diphenyldiazetidinones (*e.g.*, **1**) to 3-aryl-1-phenyl-2(1*H*)-quinoxalinones (**2**) was reported in 1967 by Fischer and Fahr.[2] Surprisingly, no notice appeared to be taken at that time of the unusual oxidation of the expected product, a 3,4-dihydro-2(1*H*)-quinoxalinone (**3**), to the compound which was actually isolated. We have investigated this reaction and found that, in the absence of air, none of the quinoxalinone **2** was formed, and that 3-aryl-3,4-dihydro-2(1*H*)-quinoxalinones readily undergo a novel acid-catalyzed air oxidation.



1



2



3

We have prepared a series of 7-methoxydihydroquinoxalinones (**4**) in good yield by catalytic reduction of the corresponding quinoxalinones **5**. These compounds were found to be stable to air in the presence of small amounts of base (*e.g.*, triethylamine or sodium bicarbonate), but in slightly acidic solutions were rapidly reoxidized to the quinoxalinones by air. The dihydro compounds were also stable to acid in the absence of air and were recovered unchanged under these conditions. The *N*-acetyl derivative of the dihydroquinoxalinone **6**

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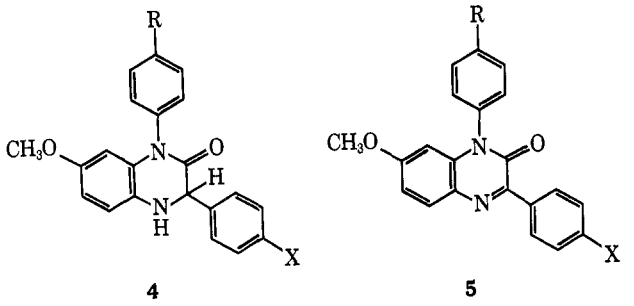
(2) W. Fischer and E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **6**, 630 (1967).

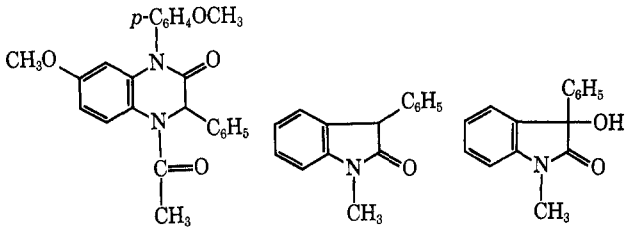
was stable to air in acidic solution, indicating the necessity for a protonated basic center at the 4 position for oxidation to occur.



4 5

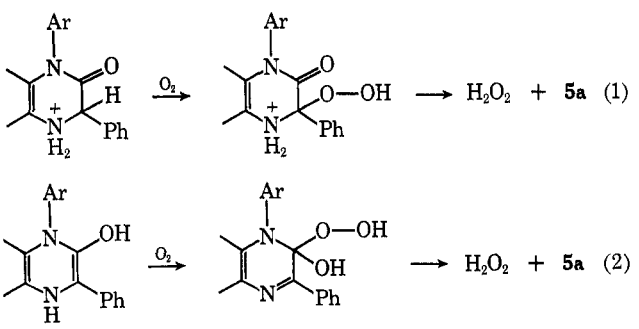
a, R = OCH_3; X = H
b, R = OCH_3; X = OCH_3
c, R = H; X = OCH_3

We have been unable to find any precedent in the literature for an acid-catalyzed air oxidation of this type. However, a structurally similar *base*-catalyzed air oxidation of oxindoles (**7** → **8**) has been reported,[3] in which a methine hydrogen flanked by two phenyls and a carboxamide group was readily converted to a hydroxyl group.

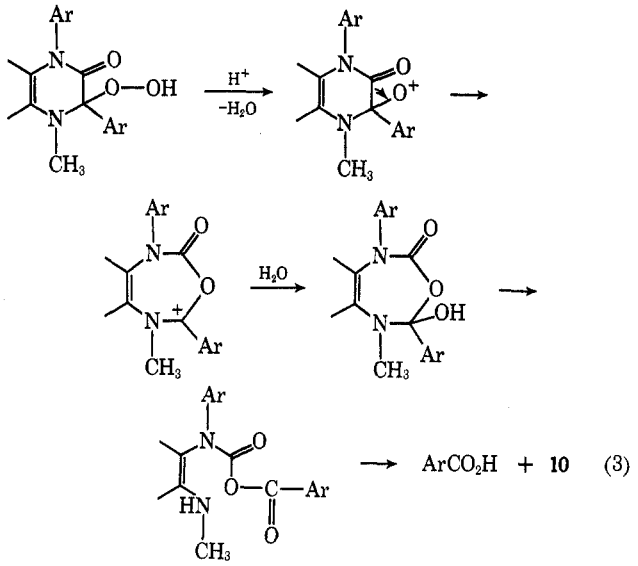


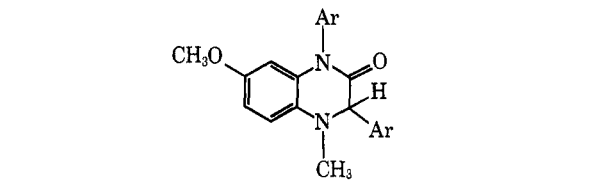
6 7 8

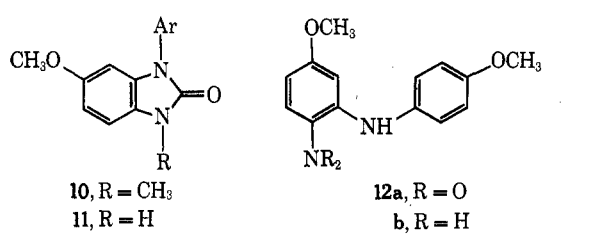
One possible process through which the oxidation of **4** to **5** could proceed involves a free-radical oxidation at the highly activated 3 position to give a hydroperoxide, followed by elimination of hydrogen peroxide (eq 1). Alternatively, an allylic enamine oxidation, similar to that in the formation of 3-hydroperoxyindolenines from indoles,[4] could be postulated (eq 2).



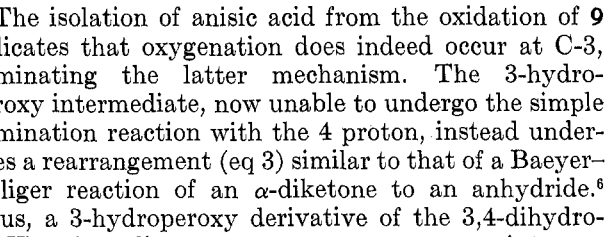
In order to distinguish between these possible mechanisms, the 4-methyl derivative **9** was prepared by alkylation of **4b** and subjected to treatment with air and acid. By blocking a possible elimination reaction, we hoped to be able to isolate the 3-hydroperoxy or 3-hydroxy derivative which would be formed if eq 1 were operative. However, the air oxidation of **9** gave instead anisic acid and 5-methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (**10**) in good yield. The structure of **10** was proven by an independent unambiguous synthesis from *m*-fluorophenol. Nitration by known methods[5] gave the 4-nitrophenol, which was converted to the methyl ether. The fluorine atom was readily displaced by *p*-anisidine to give 3,4′-dimethoxy-6-nitrodiphenylamine (**12a**), which was easily reduced to the corresponding diamine **12b**. Ring closure with phosgene afforded 6-methoxy-1-(*p*-methoxyphenyl)-2(3*H*)-benzimidazolone (**11**), which was alkylated with methyl iodide to give the 1-methyl derivative, 5-methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (**12**), identical in all respects with the air oxidation product of **9**.







9, Ar = *p*-$C_6H_4OCH_3$



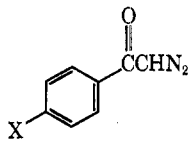
10, R = CH_3 12a, R = O
11, R = H b, R = H

The isolation of anisic acid from the oxidation of **9** indicates that oxygenation does indeed occur at C-3, eliminating the latter mechanism. The 3-hydroperoxy intermediate, now unable to undergo the simple elimination reaction with the 4 proton, instead undergoes a rearrangement (eq 3) similar to that of a Baeyer–Villiger reaction of an α-diketone to an anhydride.[6] Thus, a 3-hydroperoxy derivative of the 3,4-dihydro-2(1*H*)-quinoxalinones can serve as a common intermediate to explain the products formed from the oxidation reaction of both **4** and **9**.

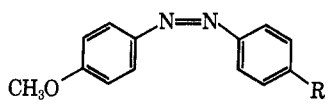
The starting quinoxalinones, **5a** and **5b**, were prepared by photolysis of the appropriate diazoacetophenone **13**

(3) P. Aeberli and W. J. Houlihan, *J. Org. Chem.*, **33**, 1640 (1968).
(4) B. Witkop, *J. Amer. Chem. Soc.*, **72**, 1428 (1950).
(5) H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, 1879 (1928).
(6) C. H. Hasall, *Org. React.*, **9**, 73 (1957).

with 4,4′-dimethoxyazobenzene (**14a**). The structure of the photoproducts **5** was proven by an unambiguous synthesis from the diamine **12b**. This was condensed[7] with benzoylformic acid to give 7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (**5a**), which was identical in all respects with the photoproduct **5a**. The use of 4-methoxyazobenzene (**14b**)[8] in place of **14a** afforded the corresponding 7-methoxy-1-phenylquinoxalinone (**5c**), rather than the 7-unsubstituted 1-(*p*-methoxyphenyl) isomer, as shown by both the ultraviolet and nmr spectra of the product.

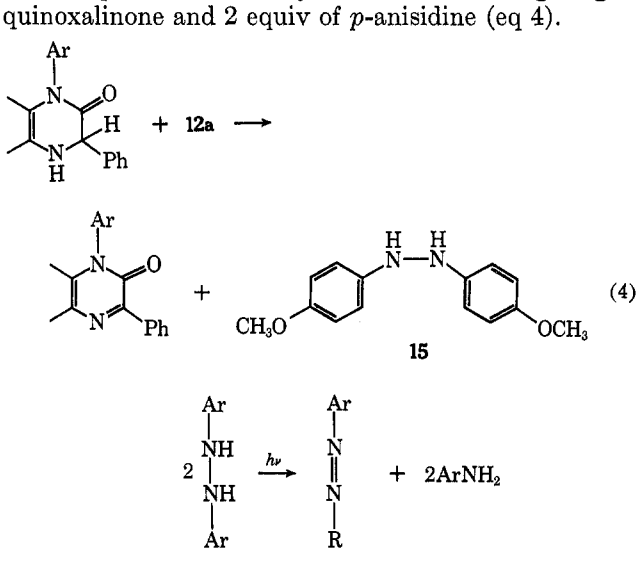


13a, X = H
b, X = OCH_3



14a, R = OCH_3
b, R = H

The photosynthesis of **5** from **13** and **14** probably proceeds through an initially formed diazetidinone,[9] which, presumably catalyzed by a trace of HCl present in the dichloromethane, undergoes an ortho-semidine rearrangement such as that reported by Fischer and Fahr,[2] to a 3,4-dihydro-2(1*H*)-quinoxalinone (**4**), which is then dehydrogenated to the quinoxalinone product **5**. This oxidation must, however, occur by a quite different process, for the reaction was run under an inert atmosphere of helium. That this dehydrogenation had indeed occurred during the photolysis and not by air oxidation during the work-up procedure was shown by the presence of **5** by tlc in the reaction mixture immediately after photolysis, and by direct crystallization, under an atmosphere of nitrogen, of **5a** in 8% yield from this mixture. The agent responsible for this dehydrogenation was shown to be 4,4′-dimethoxyazobenzene (**14a**). Irradiation of **4a** with 0.5 equiv of **14a** in the absence of air rapidly produced *p*-anisidine and the quinoxalinone **5a** in good yield. Although it is not possible to rule out a direct reduction of **14a** to *p*-anisidine by **4a**, a more likely process would involve a dehydrogenation of **4a** to give 4,4′-dimethoxyhydrazobenzene (**15**).[10] We have shown that **15** rapidly disproportionates to *p*-anisidine and dimethoxyazobenzene under photolytic conditions, so that the overall stoichiometry of the reaction involves 2 equiv of dihydroquinoxalinone and 1 equiv of dimethoxyazobenzene reacting to give quinoxalinone and 2 equiv of *p*-anisidine (eq 4).



(4)

Experimental Section[11]

7-Methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (5a).—A solution of 6.05 g (0.025 mol) of 4,4′-dimethoxyazobenzene (**14a**)[12] and 3.65 g (0.025 mol) of diazoacetophenone (**13a**)[13] in 900 ml of dichloromethane was irradiated for 6 hr with a Hanovia 450-W lamp (Model 679A), using a Vycor filter, while a slow stream of helium was bubbled through the solution. At the end of this time, the solution was concentrated to dryness under reduced pressure. The dark residue was combined with that from another similar run and chromatographed on Florisil. The first fraction eluted with benzene was shown by vpc to contain mostly *N*-benzylidine-*p*-methoxyaniline, contaminated with smaller amounts of benzaldehyde, phenacyl chloride, and unreacted 4,4′-dimethoxyazobenzene. Further elution with 10% ether in benzene afforded the product, which was recrystallized from acetonitrile to give 2.71 g (15%) of **5a**: mp 208.5–209.5°; ir (KBr) 1652 cm^{-1} (C=O); nmr 8.4 (m, 2, *o*-H's of 3-Ph), 7.84 (d, 1, J = 9 Hz, 5 H), 7.40 (m, 3, *m*- and *p*-H's of 3-Ph), 7.16 (d, 4, J = 3 Hz, 1-C_6H_4OMe), 6.87 (dd, 1, J = 3, 9 Hz, 6 H), 6.13 (d, 1, J = 3 Hz, 8 H), 3.83 (s, 3, 4′-OMe), and 3.68 (s, 3, 7-OMe); uv max 368 mμ (ε 20,800), 271 (11,000), and 221 (43,300).

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.69; H, 5.16; N, 7.90.

7-Methoxy-1,3-bis(*p*-methoxyphenyl)-2(1*H*)-quinoxalinone (5b).—A similar photolysis of 4-methoxydiazoacetophenone (**14b**) with **13a** afforded **5b** in 13% yield: mp 204–205° (MeOH); uv max 375 mμ (ε 25,100), 273 (11,200), and 224 (43,400).

Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21. Found: C, 71.09; H, 5.19; N, 7.13.

7-Methoxy-3-(*p*-methoxyphenyl)-1-phenyl-2(1*H*)-quinoxalinone (5c).—A similar photolysis of diazoacetophenone (**14a**) with 4-methoxyazobenzene (**13b**)[8] afforded **5c** in 14% yield: mp 215–217° (MeOH); uv max 373 mμ (ε 25,700), 273 (9700), and 223 (42,200).

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.67; H, 4.95; N, 7.94.

3,4-Dihydro-7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (4a).—A solution of 1.00 g of 7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (**5a**) in 40 ml of tetrahydrofuran and 40 ml of ethanol was added to a prereduced suspension of 1.0 g of 10% platinum on carbon in 20 ml of tetrahydrofuran and 20 ml of ethanol and hydrogenated at atmospheric pressure and room temperature. Hydrogen uptake ceased when 1 equiv of hydrogen had been absorbed (*ca.* 5 min). The solution was filtered and concentrated to dryness under reduced pressure. The residue was crystallized from ether affording 0.82 g (82%) of product: mp 153–155°; ir ($CHCl_3$) 1687 (C=O), 3400 cm^{-1} (NH); uv max 322 mμ (ε 4200), 223 (40,300); nmr 3.55 (s, 3, OMe), 3.78 (s, 3, OMe), 4.00 (s, 1, NH), 5.03 (s, 1, 3 H), 5.97 (d, 1, J = 3 Hz, 8 H), 6.32–6.87 (m, 2, 5 H and 6 H), 7.04 (d, 4, J = 3 Hz, 1-$C_6H_4OCH_3$), 7.33 (m, 5, C_6H_5). A small amount of acid was added to the ultraviolet solution which was left exposed to the air. A peak at 368 mμ began to appear, ε 4570 (1 min), 8100 (5 min), 18,600 (16 hr).

(7) A. H. Cook and C. A. Perry, *J. Chem. Soc.*, 394 (1943).

(8) J. Burns, H. McCombie, and H. A. Scarborough, *ibid.*, 2982 (1928).

(9) It has previously been shown that photolysis of equimolar mixtures of substituted diazoacetophenones and azobenzene in dichloromethane solution afforded 4-aryl-1,2-diphenyl-1,2-diazetidinones, such as **1**: W. Fischer and E. Fahr, *Tetrahedron Lett.*, 5245 (1966). Similarly, photolysis of preformed diphenylketene and 4,4′-dimethoxyazobenzene in benzene or ether solution has been shown to give the corresponding 1,2-bis(*p*-methoxyphenyl)-4,4-diphenyl-1,2-diazetidin-3-one: J. H. Hall and R. Kellogg, *J. Org. Chem.*, **31**, 1079 (1966).

(10) Other photochemical dehydrogenations with an azo compound have been reported: G. O. Schwenck and H. Formaneck, *Angew. Chem.*, **70**, 505 (1958); R. C. Cookson, I. D. R. Stevens, and C. T. Watt, *Chem. Commun.*, 259 (1965).

(11) Melting points were determined on a Fisher–Johns block and are corrected. The ultraviolet spectra were run in methanol. The nmr spectra were obtained on a Varian A-60 instrument; the spectra were determined in deuteriochloroform solutions, and the shifts are expressed as parts per million downfield from Me_4Si used as an internal standard. The infrared spectra were determined on a Beckman IR-9 instrument. All compounds had infrared and nmr spectra which agreed with the assigned structures.

(12) Prepared by lithium aluminum hydride reduction of 4,4′-dimethoxyazoxybenzene (Aldrich Chemical Co.): T. Rotarski, *Ber.*, **36**, 3158 (1903); R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3738 (1948).

(13) A. Burger and S. Avakian, *J. Org. Chem.*, **5**, 606 (1940).

Anal. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.15; H, 5.34; N, 7.60.

3,4-Dihydro-7-methoxy-1,3-bis(*p*-methoxyphenyl)-2(1*H*)-quinoxalinone (4b).—A similar hydrogenation of **5b** afforded **4b** in 80% yield: mp 145–147° (ether); uv max 322 mμ (ε 4220), 225 (45,600), shifting to 375 mμ (ε 22,000) 16 hr after acidification.

Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.18. Found: C, 70.98; H, 5.70; N, 7.14.

3,4-Dihydro-7-methoxy-3-(*p*-methoxyphenyl)-1-phenyl-2(1*H*)-quinoxalinone (4c).—A similar reduction of **5c** afforded **4c** in 80% yield: mp 133–135° (ether); uv max 322 mμ (ε 4180), 224 (38,900), changing to 374 mμ (ε 22,900) 18 hr after acidification.

Anal. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.41; H, 5.79; N, 7.76.

4-Acetyl-3,4-dihydro-7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (6).—The crude oily **4a** prepared by reduction of 1.00 g of **5a** was dissolved in 100 ml of ether and treated with 3 ml of triethylamine and 1 ml of acetic anhydride. The solution was left at room temperature overnight and then washed with sodium carbonate solution and with water. The dried solution was concentrated to give an oil which was chromatographed on Florisil. Elution with 10% ether in benzene gave an early fraction containing 0.05 g of **5a**. Further elution with 50% ether in benzene afforded the product, which was recrystallized from ether to give 0.73 g (65%) of **6**: mp 120–122°; ir (KBr) 1693 (2 C=O) and 1672 (NAc) cm^{-1}; uv max 229 mμ (ε 37,800), no change with acid; nmr 2.37 (s, 3, NAc), 3.58 (s, 3, OMe), 3.82 (s, 3, OMe), 6.02 (d, 1, J = 2.5 Hz, 8 H), 6.48–6.93 (m, 2, 5 H and 6 H), 7.11 (d, 4, J = 3.5 Hz, $C_6H_4OCH_3$), and 7.29 (s, 6, C_6H_5 and 3 H).

Anal. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.85; H, 5.67; N, 7.04.

Air Oxidation of 3,4-Dihydro-7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone.—A solution of 4.20 g of **4a** in 750 ml of methanol was treated with 1 ml of 12 *N* hydrochloric acid, and air was bubbled through the solution for 2 hr. The precipitate which had formed was filtered, affording 2.34 g (56%) of 7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2-(1*H*)-quinoxalinone (**5a**), mp 208–209°, uv max 368 mμ (ε 20,800). The mother liquors were concentrated to about 250 ml and air was bubbled through for another 2 hr. Filtration yielded 1.60 g (38%) of **5a**, mp 207–209°, uv max 368 mμ (ε 20,400). Similarly a third crop of **5a** was obtained, 0.15 g (3.6%), mp 205–208°, uv max 368 mμ (ε 19,800).

A similar oxidation of 50 mg of **4a** in 10 ml of benzene and 0.4 ml of acetic acid for 3 hr afforded 30 mg (60%) of **5a**, mp 206–207°, uv max 369 mμ (ε 19,900).

3,4-Dihydro-7-methoxy-1,3-bis(*p*-methoxyphenyl)-4-methyl-2(1*H*)-quinoxalinone (9).—A solution of 3.12 g of 3,4-dihydro-7-methoxy-1,3-bis(*p*-methoxyphenyl)-2(1*H*)-quinoxalinone (**4b**) in 75 ml of acetonitrile was treated with 1.5 g of potassium carbonate and 6 ml of methyl iodide. The mixture was stirred and refluxed under an atmosphere of nitrogen for 24 hr. The mixture was then filtered, and the filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane and water, and the organic layer was separated, dried, and concentrated to dryness under reduced pressure. The residue was crystallized from methanol containing a little triethylamine, affording 2.61 g (81%) of product, mp 154–157°. Concentration of the mother liquors yielded a second crop, 0.22 g (7%), mp 153–156°. Recrystallization from methanol (plus Et_3N) afforded analytically pure material: mp 156–158°; ir (KBr) 1688 cm^{-1} (C=O); nmr 2.83 (s, 3, NMe), 3.63 (s, 3, OMe), 3.73 (s, 3, OMe), 3.80 (s, 3, OMe), 4.95 (s, 1, 3 H), 6.05 (dd, 1, J = 1, 2 Hz, 8 H), 6.56–7.24 [m, 10, 5 H, 6 H, $(C_6H_4OCH_3)_2$]; uv max 328 mμ (ε 4040), 226 (42,000). A peak at 426 mμ developed after acidification in the presence of air which rose to ε 22,100 after 18 hr. However, the original spectrum was obtained again immediately after the acidic solution was basified with potassium hydroxide. (Attempts to isolate the 426 mμ product gave a red oil which could not be crystallized or characterized.)

Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found: C, 71.37; H, 5.94; N, 7.01.

Air Oxidation of 3,4-Dihydro-7-methoxy-1,3-bis(*p*-methoxyphenyl)-4-methyl-2(1*H*)-quinoxalinone.—A solution of 0.69 g of **9** in 70 ml of benzene was treated with 3.5 ml of acetic acid, and air was bubbled through the solution for 4 hr. The solution was washed with a small amount of sodium bicarbonate solution and with water. The dried solution was concentrated to dryness, and the residue was recrystallized from methanol, affording 0.40 g (82%) of 5-methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (**10**), mp 152–155°. A sample was recrystallized from methanol for analysis: mp 155.5–156°; ir (KBr) 1708 cm^{-1} (C=O); uv max 290 mμ (ε 8450); nmr 3.43 (s, 3, NMe), 3.74 (s, 3, OMe), 3.86 (s, 3, OMe), 6.5–7.5 (m, 7, aromatic H's).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.31; H, 5.64; N, 9.77.

The sodium bicarbonate solution was washed with benzene, acidified with dilute hydrochloric acid, saturated with sodium chloride, and extracted with dichloromethane. The extract was dried and concentrated, and the residue was recrystallized from aqueous ethanol, affording 0.12 g (48%) of anisic acid, mp 182–183° (lit.[14] mp 185°). A mixture melting point with known anisic acid (mp 182–183°) showed no depression.

3-Fluoro-4-nitroanisole.—A solution of 42.1 g of 3-fluoro-4-nitrophenol, prepared by nitration of *m*-fluorophenol,[5,15] in 840 ml of acetonitrile was treated with 37.1 g of potassium carbonate and 126 ml of methyl iodide. The mixture was stirred and refluxed for 3 hr and then concentrated to dryness under reduced pressure. The residue was dissolved in ether and water, and the ether layer was washed with water, dried, and concentrated. The residue was crystallized from methanol to give 39.8 g (87%) of product, mp 55–57° (lit.[5] mp 56.5°).

3,4′-Dimethoxy-6-nitrodiphenylamine (12a).—A solution of 10.0 g of 3-fluoro-4-nitroanisole in 100 ml of dimethyl sulfoxide was treated with 15.0 g of *p*-anisidine and heated at 60–65° under an atmosphere of nitrogen for 24 hr. The solution was cooled and poured into 3 l. of dilute (2%) hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallized from 95% ethanol, affording 15.30 g (96%) of product, mp 103.5–104.5° (lit.[16] mp 106–106.5°).

6-Methoxy-1-(*p*-methoxyphenyl)-2(3*H*)-benzimidazolone (11).—A solution of 1.00 g of 3,4′-dimethoxy-6-nitrodiphenylamine (**12a**) in 40 ml of tetrahydrofuran and 40 ml of ethanol was added to a prereduced suspension of 10% platinum on carbon in 20 ml of tetrahydrofuran and 20 ml of ethanol and hydrogenated at atmospheric pressure and room temperature. Hydrogen uptake ceased after 3 equiv had been absorbed (*ca.* 15 min). The solution of 2-amino-4′,5-dimethoxydiphenylamine (**12b**)[16] was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in 10 ml of methanol and 50 ml of 1.2 *N* hydrochloric acid, and phosgene was bubbled into the solution for 1 hr.

The mixture was cooled and the precipitate was collected by filtration, washed with water, and dried, affording 0.42 g (43%) of **11**: mp 249–251° (lit.[17] mp 245–246°); ir (KBr) 1700 cm^{-1} (C=O); uv max 297 mμ (ε 8200).

The mother liquors were cooled in ice and again treated with phosgene for 1 hr. The new precipitate was collected, washed, and dried, yielding an additional 0.43 g (44%) of **11**, mp 249–251°.

5-Methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (10).—A suspension of 0.83 g of 6-methoxy-1-(*p*-methoxyphenyl)benzimidazolone (**11**) in 30 ml of dimethyl sulfoxide was treated with 0.25 g of a 55% dispersion of sodium hydride in mineral oil and then with 1 ml of methyl iodide. The mixture was stirred overnight at room temperature and then poured into water. The precipitate was collected by filtration, washed with a little petroleum ether to remove the mineral oil, and recrystallized from methanol, affording 0.59 g (68%) of **10**, mp 154–155°. A mixture melting point with the product of air oxidation of **9** melted at 154–155°, and the infrared spectra of the two compounds were identical.

Concentration of the mother liquors afforded a second crop of **10**, 0.08 g (9%), mp 152.5–154°. The overall yield of **10** from **12a** was 67%.

7-Methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone (5a).—A solution of 2-amino-4′,5-dimethoxydiphenylamine (**12b**), prepared as before by catalytic reduction of 1.0 g of **12a**, was treated with 0.62 g of phenylglyoxylic acid and left at room tem-

(14) E. E. Harris and G. B. Frankforter, *J. Amer. Chem. Soc.*, **48**, 3144 (1926).

(15) T. L. Fletcher, M. J. Namkung, W. H. Wetzel, and H.-L. Pan, *J. Org. Chem.*, **25**, 1342 (1960).

(16) A. P. Kottenkahn, E. T. Seo, and H. W. Stone, *ibid.*, **28**, 3114 (1963).

(17) L. Rosnati, *Gazz. Chim. Ital.*, **86**, 275 (1950).

perature for 3 hr. The solution was concentrated to dryness under reduced pressure, and the residue was crystallized by trituration with ethanol to give 0.85 g of fairly pure product. This was recrystallized from acetonitrile, affording 0.75 g (58%) of **5a**, mp 206–207°. A mixture melting point with the photochemical product **5a** was 207–208°.

Photochemical Oxidation of 3,4-Dihydro-7-methoxy-1-(*p*-methoxyphenyl)-3-phenyl-2(1*H*)-quinoxalinone.—A solution of 0.79 g (2.20 mmol) of **4a** and 0.26 g (1.07 mmol) of 4,4′-dimethoxyazobenzene (**14a**) in 250 ml of deoxygenated dichloromethane was irradiated for 4 hr at 300 mμ in a quartz vessel in a Rayonet photochemical reactor Model RPR-100 while a stream of helium was passed through the solution. At the end of this time, tlc indicated the presence of **5a** and no **14a** or **4a**. The solution was treated with 2 ml of triethylamine and concentrated to dryness under reduced pressure. The residue was recrystallized from methanol (containing a little triethylamine), affording 0.58 g (74%) of **5a**, mp 203–206°, uv max 368 mμ (ε 19,800). The mother liquors contained *p*-anisidine as shown by vpc.

4,4′-Dimethoxyhydrazobenzene (18).—A solution of 2.42 g of 4,4′-dimethoxyazobenzene (**14a**) in 50 ml of tetrahydrofuran and 50 ml of ether was treated with 0.35 g of lithium aluminum hydride and then with an ether solution of 0.10 g of ferric chloride.[18] The mixture was stirred at room temperature for 2 hr, and then treated successively with 0.35 ml of water, 0.35 ml of 15% sodium hydroxide solution, and 1.05 ml of water. The mixture was filtered, and the filtrate was concentrated to dryness at room temperature under reduced pressure. The residue contained about 15% of the azo compound **14a** (by uv), but could not be purified further. Mild heating, such as attempted recrystallization from ether, effected disproportionation to **14a** and *p*-anisidine: ir (KBr) 3355, 3340 (NH); uv max 353 mμ (ε 4830) and 311 (5650).

(18) G. A. Olah, *J. Amer. Chem. Soc.*, **81**, 3165 (1959).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.94; H, 6.56; N, 11.66.

Photochemical Disproportionation of 4,4′-Dimethoxyhydrazobenzene.—A solution of 0.40 g of the above crude 4,4′-dimethoxyhydrazobenzene in 40 ml of dichloromethane was irradiated for 30 min at 300 mμ in a Rayonet photochemical reactor. The solution turned dark, and the ultraviolet spectrum showed an intense peak at 354 mμ due to the azobenzene. (A control solution of **15** in dichloromethane in the dark showed little change in its ultraviolet spectrum after 1 hr at 25°.) The solution was concentrated to dryness under reduced pressure. The residue was extracted with ether and water, leaving a large amount of black insoluble material. The ether layer, concentrated under reduced pressure, afforded 0.14 g of 4,4′-dimethoxyazobenzene, mp 163–164°. Concentration of the aqueous solution gave a residue which was recrystallized from acetonitrile, affording 0.04 g of *p*-anisidine hydrochloride, mp 208–212°, having an infrared spectrum identical with that of an authentic sample.

Registry No.—**4a**, 26596-02-1; **4b**, 26596-03-2; **4c**, 26596-04-3; **5a**, 26596-05-4; **5b**, 26596-06-5; **5c**, 26596-07-6; **7**, 26596-08-7; **9**, 26596-09-8; **10**, 26596-10-1; **11**, 19950-86-8; **18**, 1027-40-3.

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The Singlet Oxygen Oxidation of *N*-Phenylpyrroles. Its Application to the Synthesis of a Model Mitomycin

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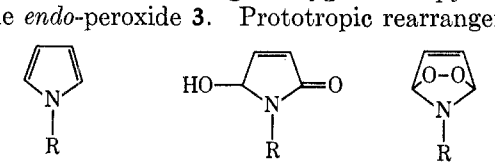
The photooxygenation of *N*-phenylpyrroles to produce pyrrolinones is described. The conversion of pyrrolinone **14** to a tetracyclic framework **22** related to the aziridine-containing mitomycin antibiotics is elucidated. A tabulation of nmr data for protons on the ring fusion of bicyclic fused aziridines is presented.

The photooxygenation of heterocycles is an area in which a steady level of interest has been maintained through the years.[2] The precedent for our research in pyrrole oxidations was based on the report of De Mayo and Reid,[3] on the photooxidation of pyrrole **1a** and *N*-methylpyrrole **1b** to form the hydroxylactams **2a** and **2b**. A possible mechanism for the reaction invokes the Diels–Alder reaction of singlet oxygen with pyrrole to form the *endo*-peroxide **3**. Prototropic rearrangement



1a, R = H
b, R = CH_3

2a, b

3

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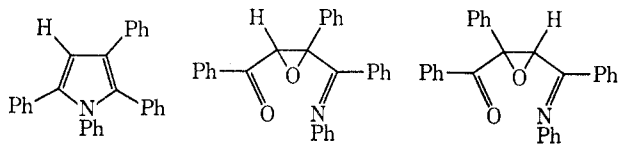
(2) S. T. Reid, *Advan. Heterocycl. Chem.*, **11**, 116 (1970).

(3) P. De Mayo and S. T. Reid, *Chem. Ind. (London)*, 1576 (1962).

including O–O bond fission affords **2**. Other oxidations of pyrroles that appear to be reactions with singlet oxygen have been reported.[4,5] In the case of highly substituted pyrroles such as **4**, Wasserman and Miller have isolated photooxidation products **5** and **6** whose formation can be rationalized by postulating rearrangements of an initially formed *endo*-peroxide.



4 **5** **6**

Our research on the singlet oxygen oxidation of *N*-phenylpyrrole (**7**) began because we saw a similarity between the predicted oxidation product **8** and certain features of the mitomycin antibiotics **9**.[6] The double bond

(4) A. R. Katritzky and E. Hoft, *Tetrahedron Lett.*, 2028 (1968).

(5) H. H. Wasserman and A. H. Miller, *Chem. Commun.*, 199 (1969).

(6) (a) J. S. Webb, D. B. Cosulich, J. H. Mowat, J. B. Patrick, R. W. Broschard, W. E. Meyer, R. P. Williams, C. F. Wolf, W. Fulmore, C. Pidacks, and J. E. Lancaster, *J. Amer. Chem. Soc.*, **84**, 3187 (1962); (b) J. B. Patrick, R. P. Williams, W. E. Meyer, W. Fulmor, D. B. Cosulich, R. W. Broschard, and J. S. Webb, *ibid.*, **86**, 1889 (1964).