Oxidations of Tetraphenylpyrroles[1,2]

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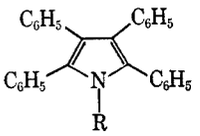
2,3,4,5-Tetraphenylpyrrole (**1**) is oxidized by nitric acid, nitrous acid, lead tetraacetate, chromic–acetic acids, or phosphorus pentachloride–phosphorus oxychloride, to 2-hydroxytetraphenylpyrrolenine (**3**) [obtainable also by ammonolysis of *cis*-dibenzoylstilbene (**7**)]. Compound **3** undergoes reversible hydrochloride formation and acid-catalyzed etherification, rearrangement by acid or base to 3,3,4,5-tetraphenylpyrrolinone (**5**), hydrolysis to **7** by nitrous acid (not by nitric acid), and reductions to **1** by hydriodic acid, sodium hydrosulfite, zinc–acetic acid, phosphorus trichloride and sodium borohydride. Oxidation of **1** by hydrogen peroxide–acetic acid gives *cis*-dibenzoylstilbene oxide (**11**) and α-N-benzamido-α′-benzoylstilbene (**12**) which is obtainable also by ammonolysis of **11**. N-Methyltetraphenylpyrrole (**2**) is oxidized by chromic acid to **11**, by hydrogen peroxide–acetic acid to **11** and α-N-methylbenzamido-α′-benzoylstilbene (**13**), and by nitric acid, nitrous acid, or phosphorus pentachloride–phosphorus oxychloride to N-methylpyrrolenineonium salts, which are convertile by base to 1-methyl-3,3,4,5-tetraphenylpyrrolinone (**6**). Mechanisms are discussed.

While a number of pyrrole oxidations have been reported, there has been no extensive comparison of oxidations of a given pyrrole by a variety of such reagents.[4,5] Our recent study of the oxidations[3,6] of tetraphenylfuran[3a] led us to compare, with these, the several oxidations of 2,3,4,5-tetraphenylpyrrole (**1**) and its N-methyl derivative (**2**).

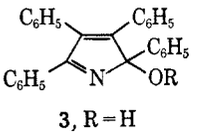
The pyrrole oxidations may be conveniently divided into two classes: *monooxidation*, to pyrrolenines **3** and **4**, which may be accompanied by hydrolysis to *cis*-dibenzoylstilbene (**7**) or 2- to 3-phenyl group migration leading to the 2-pyrrolinones **5** or **6**; and *dioxidation* which also includes attack at one or both of the β positions and leads to **11**, **12**, or **13**.

Monooxidations.—These are brought about by chromic acid, lead tetraacetate, phosphorus pentachloride, nitric acid, and nitrous acid, and they are in analogy with the comparable and facile oxidations of furans.[3a,6]

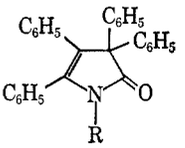
Tetraphenylpyrrole (**1**), by the action of chromic acid in refluxing glacial acetic acid, produces only the monooxidation and rearrangement product, 3,3,4,5-tetraphenylpyrrolinone-2 (**5**). Investigation of this reaction under various conditions revealed that the conversion **1** → **5** is primarily a monooxidation to the 2-hydroxypyrrolenine followed in a second and discrete step by 2- to 3-phenyl group migration. Under milder conditions (55°) a compound is obtained which is assigned the structure 2-hydroxy-2,3,4,5-tetraphenylpyrrolenine (**3**), *vide infra*, and which in a separate experiment in refluxing acetic acid without chromic acid rapidly underwent rearrangement to the 2-pyrrolinone (**5**).



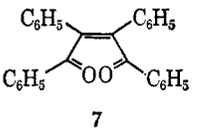
1, R = H
2, R = CH_3



3, R = H
4, R = CH_3



5, R = H
6, R = CH_3



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Lead tetraacetate oxidation of tetraphenylpyrrole (**1**) in refluxing chloroform has been shown to give tetraphenylpyrazine,[7a] whereas we find that in glacial acetic acid at room temperature the product of this oxidation is the 2-hydroxypyrrolenine (**3**).

Phosphorus pentachloride, studied as an oxidizing agent for furans[3] but not used to any significant extent in the pyrrole field,[4,5] converts tetraphenylpyrrole (**1**) to a phosphorus complex which is hydrolyzed by water to the hydrochloride of 2-hydroxypyrrolenine **3** (interconvertible with its base **3**). The methyl ether of **3**, the 2-methoxypyrrolenine (**4**), is obtained when the crude phosphorus pentachloride complex is treated with sodium methoxide.

Nitric acid has long been used as an oxidizing agent in the pyrrole field[8] and in porphyrin degradations.[4,5] Furthermore, it was reported recently[7b] that nitrous acid oxidation of tetraphenylpyrrole (**1**) under mild conditions gave the compound now known to be the 2-hydroxypyrrolenine (**3**), but under vigorous conditions gave *cis*-dibenzoylstilbene (**7**). In accord with these results we find that oxidation of the pyrrole (**1**) by an excess of nitric or of nitrous acid in acetic acid at 80° gives good yields of *cis*-dibenzoylstilbene (**7**), paralleling the oxidations of analogous furans.[3,6,9] Under these same conditions in acetic acid, treatment of the 2-hydroxypyrrolenine (**3**) with nitrous acid

(1) (a) Supported in large part by a National Science Foundation Grant; (b) Eastman Kodak Co. Fellowship, 1964–1965.

(2) (a) D. W. Boykin, Jr., M.S. Thesis (1963), from which the major part of this work is taken; (b) D. W. Boykin, Jr., Ph.D. Dissertation University of Virginia, 1965; (c) specific mention of this work was made in ref 3a.

(3) (a) R. E. Lutz and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **85**, 755 (1963); (b) O. W. Rigdon, Ph.D. Dissertation, University of Virginia, 1965; (c) J. I. Dale, Ph.D. Dissertation, University of Virginia, 1962.

(4) E. Baltazzi and L. I. Krimen, *Chem. Rev.*, **63**, 511 (1963).

(5) H. Fischer and H. Orth, "Die Chemie Des Pyrrols," Academische Verlagsgesellschaft M. B. H., Leipzig, 1934.

(6) *Cf.* furan oxidation: (a) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934); (b) R. E. Lutz and W. P. Boyer, *ibid.*, **63**, 3189 (1941); (c) C.-K. Dien and R. E. Lutz, *J. Org. Chem.*, **22**, 55 (1957); (d) R. E. Lutz and C.-K. Dien, *ibid.*, **23**, 1861 (1958); (e) R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, **81**, 3396 (1959); (f) *cf.* β nitration of 2,5-dimesityl-3-phenylfuran where the α-mesityl groups hinder 2,5-hydrolysis and oxidation: R. E. Lutz and C. J. Kibler, *ibid.*, **61**, 3010 (1939).

(7) (a) R. Kuhn and H. Kainer, *Ann.*, **578**, 226 (1952); (b) *ibid.*, **578**, 228 (1952).

(8) (a) V. Sprio and P. Madonia, *Gazz. Chim. Ital.*, **85**, 965 (1955); (b) T. Aiello and S. Giambrone, *Chem. Abstr.*, **49**, 6226*g* (1955).

(9) A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953.

produces the *cis*-diketone (**7**), whereas treatment with nitric acid even at higher temperature (80°) gives a difficultly purifiable salt-like compound which is undoubtedly the nitrate and which on treatment with base at 25° liberates the hydroxypyrrolenine (**3**). The nitrous acid reaction thus appears to involve specific hydrolysis of the hydroxypyrrolenine **3**, doubtless by attack directly on the nitrogen atom, a reaction of interest mechanistically (*vide infra*) and potentially useful synthetically.

The oxidations of N-methyl-2,3,4,5-tetraphenylpyrrole (**2**) with phosphorus pentachloride, nitric acid, or nitrous acid, give difficultly purifiable N-methylpyrrolenineonium salts, treatment of which with base in refluxing ethanol brings about rearrangement with phenyl group migration and produces the N-methyl-2-pyrrolinone (**6**). These salts, although not rigorously characterized, are evidently related to those of **3** and they are distinguishable from salts of the type **5** and **6** by their lack of carbonyl group absorption. The base-induced rearrangement of these compounds is analogous to the base-catalyzed rearrangements of the 2-hydroxypyrrolenine **3** itself, *vide infra*.

The Structure of the 2-Hyroxypyrrolenine (3).—The early reports on the preparation of **3** by the action of ammonia on *cis*-dibenzoylstilbene (**7**)[10a] described the thermal rearrangement of **3** to the 2-pyrrolinone (**5**) but did not include definite structural assignment. Suggested structures[7,8,10b] included **3**,[7] a structure containing a 2,5-oxygen bridge[10b] (excluded by strain considerations and spectral data), the monoimine of *cis*-dibenzoylstilbene,[7] and 2,3-epoxytetraphenyldihydropyrrole.[7] The absence of a carbonyl band in the infrared spectrum and the noncomparability of the ultraviolet spectra of **3** and **7** eliminate the imine structure. The absence of a band at *ca.* 300 mμ in the ultraviolet analogous to that of the aminostilbene system in pyrrolinone (**5**) and in 1-methyl-2-hydroxy-2,3,3,4,5-pentaphenyldihydropyrrole,[3c] and the absence of an epoxide infrared band at *ca.* 890 cm^{-1} which has been identified in **11** and in tetraphenylfuran diepoxide by O^{18} shift[3b] and which appears in the spectrum of **15**, provide evidence against the epoxydihydropyrrole structure.

In support of structure **3** are the following distinctive infrared and ultraviolet absorptions: a strong band for bonded OH in the 3050-cm^{-1} region, a band for the α,β-unsaturated imine group at 1630 cm^{-1},[11] and absorption at 320 mμ (ε 5900), which is in the region expected for a chalcone-type chromophore.

Supporting this spectroscopic evidence for structure **3** is the following chemical behavior: facile conjugate reductions to the pyrrole **1** by a variety of agents (see the Experimental Section),[3c,12] acid-catalyzed interconvertibility[13] with its methyl ether (**4**), and its formation from *cis*-dibenzoylstilbene (**7**) by ammonolysis. The ultraviolet spectra of **3** and its methyl ether (**4**) are close to superimposable, and notably absent in the infrared spectrum of the methyl ether (**4**) is absorption in the 3300-cm^{-1} region.

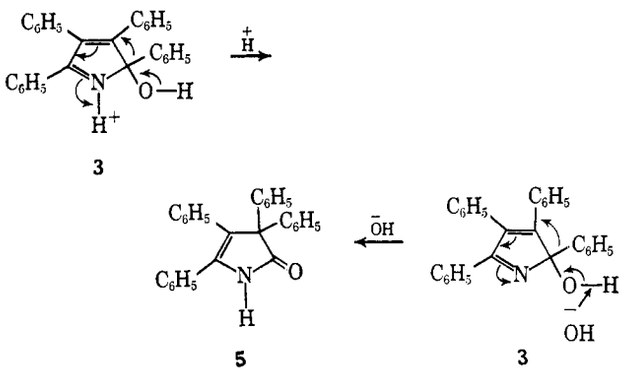
(10) (a) F. Klingemann and W. F. Laycock, *J. Chem. Soc.*, **59**, 140 (1891); (b) F. R. Japp and A. Tingle, *ibid.*, **71**, 1138 (1897).

(11) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 37.

(12) *Cf.* R. E. Lutz, *J. Am. Chem. Soc.*, **56**, 1378 (1934).

(13) *Cf.* R. E. Lutz and F. B. Hill, Jr., *J. Org. Chem.*, **6**, 1975 (1941).

Hydroxypyrrolenine **3** is rearranged readily by both acid and base to the 2-pyrrolinone (**5**), which is readily rationalized in terms of benzilic acid type rearrangements.



Wasserman and Liberles[14] found that photooxidation of tetraphenylpyrrole (**1**) in basic solution produced the pyrrolinone (**5**), and they suggested involvement of a benzilic acid type rearrangement. Since hydroxypyrrolenine **3** is readily obtained from pyrrole **1** by oxidation, and because it is rearranged by base to pyrrolinone **5**, it or its equivalent is perhaps intermediate in the photooxidation of pyrrole **1** to pyrrolinone **5**.

The Mechanism of Monooxidation.—The oxidations of the pyrrole to hydroxypyrrolenine **3** doubtless involve mechanisms typical of other five-membered ring heterocycles.[6,15] The initial step is assumed to be attack at the α position by the electrophile generated from the appropriate reagent.[15,16] The resonance-stabilized cations resulting from the electrophilic attack can lead to hydroxypyrrolenine **3** by a variety of paths.[6,15]

The oxidations of tetraphenylpyrrole (**1**) with nitric and nitrous acids present an intriguing mechanistic problem, which appears to be atypical in heterocyclic oxidations. One mole of nitric acid oxidizes the pyrrole to *cis*-dibenzoylstilbene (**7**), whereas 1 mole of nitrous acid produces instead chiefly hydroxypyrrolenine **3**. The fact that the latter compound (**3**) can subsequently be hydrolyzed by more nitrous acid *but not by nitric acid*, to *cis* diketone **7**, suggests that the nitric acid oxidation of pyrrole **1** is a process involving two, discrete steps, first an electrophilic attack giving pyrrolenine **3**, followed by hydrolysis to *cis* diketone **7** through the action of the nitrous acid generated from the nitric acid which was consumed in the initial step.

The identity of the nitrous species attacking hydroxypyrrolenine **3** is probably the nitrosonium ion or its equivalent.[16e,f] In the highly acidic nitric–acetic acid solution the predominant electrophile would be the proton, and the extensive protonation of hydroxy-

(14) H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.*, **82**, 2086 (1960).

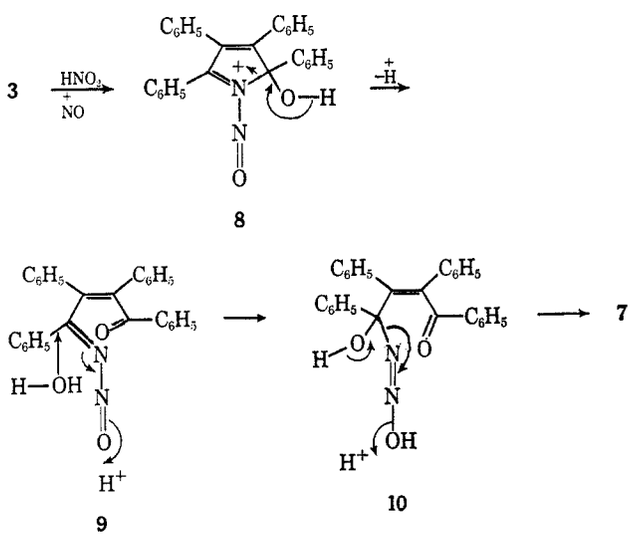
(15) (a) R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962); (b) W. J. Welstead, Jr., Ph.D. Dissertation, University of Virginia, 1961; (c) R. G. Bass, Ph.D. Dissertation, University of Virginia, 1961.

(16) (a) K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., p 69, 1965; (b) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955); (c) R. Criegee in ref 16a, p 278; (d) M. W. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959); (e) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953; (f) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964.

pyrrolenine **3** would thus provide considerable protection from further reaction. On the other hand, in the weakly acidic or slightly basic sodium acetate–acetic acid solution, the nitrosonium ion or its equivalent could conceivably be the important electrophile, attacking the imine nitrogen and leading to ready hydrolysis. The suggestion that electrophilic attack occurs directly on the imine nitrogen atom of **3** is supported by the observation (*vide supra*) that N-methylpyrrole **2**, which can only give a quaternary analog of **3**, is not oxidized to *cis* diketone **7** by nitric or nitrous acid.

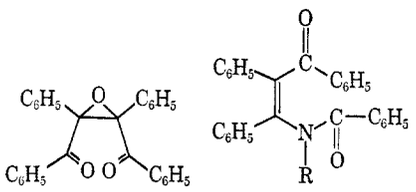
To test the hypothesis that generated nitrous acid actually participated in the nitric acid oxidation, an experiment was carried out using 0.5 mole of nitric acid to 1 mole of pyrrole **1**. If nitrous acid generated from reduction of the nitric acid were participating in an important way in the reaction, and if nitric acid oxidized the pyrrole only to hydroxypyrrolenine **3**, one would expect to obtain either complete conversion of the pyrrole to the hydroxypyrrolenine, or conversion of only one-half of the pyrrole to *cis* diketone **7** and recovery of the remaining pyrrole, or something between these extremes, depending on the course and rates of the reactions of nitrous acid with the pyrrole and the hydroxypyrrolenine. Complete conversion of the pyrrole to hydroxypyrrolenine **3** would indicate that nitrosonium ion attack on the pyrrole is much more efficient than its hydrolytic action on the hydroxypyrrolenine. Actually, the hydroxypyrrolenine was obtained as the main product although only in 60% yield, and 26% of *cis*-dibenzoylstilbene was isolated. These results indicate that, after the nitric acid was consumed, the generated nitrous acid oxidized the remaining pyrrole to the hydroxypyrrolenine somewhat faster than it hydrolyzed the hydroxypyrrolenine to the *cis*-diketone, and they support the earlier conclusion that for the nitric acid oxidation of the pyrrole to the *cis* diketone the generated nitrous acid is necessary to complete the reaction through its unique ability to hydrolyze the hydroxypyrrolenine.

A mechanism which is consonant with these results is outlined as shown. Assuming as before that hydroxypyrrolenine **3** or its equivalent is produced by the action of nitric or nitrous acid, the nitrosonium ion could attack the imine nitrogen to form **8**, whereupon



hydrolytic release of nitrogen would lead through **9** and **10** to *cis* diketone **7**.

Dioxidation.—Oxidation of pyrroles with peroxidic reagents involves dioxidation to the ketoenamides by 2,3 bond cleavage, in competition with monooxidation and hydrolysis to the *cis* diketones.[17] We find that tetraphenylpyrrole (**1**) is oxidized by hydrogen peroxide–acetic acid mixture, mainly to *cis*-dibenzoylstilbene oxide (**11**), but also to a significant amount of the 2,3-cleavage product, α-N-benzamide-α′-benzoylstilbene (**12**). Similarly, N-methylpyrrole **2** was oxidized by the same peroxidic reagent to a mixture of epoxide **11** and analogous N-methylketoenamide **13**. In contrast to earlier work[17] we find no evidence of *cis*-diketone formation.



11 **12**, R = H; **13**, R = CH_3 **14**, R = H (not isolated); **15**, R = CH_3

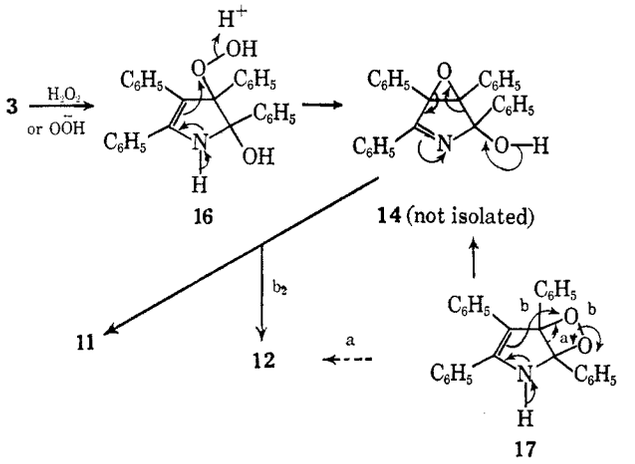
The hydrogen peroxide–acetic acid oxidations of pyrroles **1** or **2** are of special interest because the results are similar to those obtained from the photooxidation in methanol of tetraphenylpyrrole by Wasserman and Liberles[14] who reported the formation of both benzamidostilbene **12** (30%) and 2-methyl-3,4-epoxypyrroline **15** (55%). The hydrogen peroxide–acetic acid oxidations gave similar yields of **12** or **13** and of **11** (the hydrolysis product of either **14** or **15**), which implies that the mechanisms of the photo- and peroxide oxidations have some similarity.

Unexpectedly, chromic acid in acetic acid converts N-methylpyrrole **2** mainly to *cis*-dibenzoylstilbene oxide (**11**) which is the result of hydrolysis and twofold oxidation involving both the α and β positions. Welstead[15b] and Bass[15c] have shown that *cis*-dibenzoylstilbene (**7**) is not oxidized to epoxide **11** by chromic acid and therefore can not be a precursor of it in the oxidation of pyrrole **1**. This case of epoxidation in the reaction of pyrrole **2** with chromic acid appears to be novel, and it is in contrast to the chromic acid oxidations, of tetraphenylpyrrole itself (**1**), and of tetraphenylfuran[15a] which gives *cis*-dibenzoylstilbene.

Mechanistic Aspects of the Dioxidations.—Since *cis*-dibenzoylstilbene (**7**) has previously been shown to give only 4% of *cis*-dibenzoylstilbene oxide (**11**) on treatment with hydrogen peroxide–acetic acid,[15a] it must therefore be assumed that hydrogen peroxide epoxidations in the oxidations of pyrroles **1** and **2** occur *prior* to ring opening. Because the hydrogen peroxide–acetic acid oxidation of tetraphenylfuran under these conditions gave none of the epoxide **11**,[15b] it is reasonable to assume that the oxidations of the pyrroles involve some intermediate state not possible with tetraphenylfuran and *cis*-dibenzoylstilbene. Hydroxypyrrolenine **3**, which is capable of epoxidation, but which was not isolated in the reaction **1** → **11** and **12**, is

(17) (a) V. Sprio and P. Madenia, *Gazz. Chim. Ital.*, **86**, 101 (1956); (b) V. Sprio, *ibid.*, **85**, 569 (1955); (c) *cf.* also A. Pieroni and P. Veremenco, *ibid.*, **56**, 455 (1926).

shown probably to be the intermediate by the fact that in a separate experiment under the same conditions it is completely consumed and gives **11** and **12** in the same ratio as did pyrrole **1**. A rational mechanism for epoxidation of hydroxypyrrolenine **3** or its equivalent is the addition of hydrogen peroxide or its anion to the α,β-unsaturated imine system[18] to give **16**, followed by consummation of the epoxidation to epoxypyrrolinine **14** as depicted, whereupon competitive hydrolysis and rearrangement would give *cis*-dibenzoylstilbene oxide (**11**) and the benzamidostilbene **12**, respectively.



Of particular interest is the facile ammonolysis of *cis*-dibenzoylstilbene oxide (**11**) which simultaneously brings about rearrangement to benzamidostilbene **12**, thus furnishing a novel and possibly useful route to protected ketoenamines, and offering evidence that hydroxypyrrolenine oxide **14** may well be a precursor to **12** which is able actually to rearrange as depicted. The reasonableness of this picture is supported by the following facts: both *cis*-dibenzoylstilbene (**7**) and its epoxide (**11**) readily form cyclic diketals,[15b,19] and *cis*-dibenzoylstilbene (**7**) reacts equally readily with ammonia to give hydroxypyrrolenine **3**.

An alternative rationalization of the formation of **11** and **12** by peroxide oxidation of pyrrole **1** without involving hydroxypyrrolenine **3**, which may be only incidental, is to assume intermediacy of, or transannular tautomerism with, the 2,3-peroxide (**17**) from which benzamidostilbene **12** might readily be formed, directly by path a, or indirectly by path b_1b_2 through **14** which is capable of forming either **11** or **12** as previously indicated.

The action of chromic acid on the N-methylpyrrole **2** differs from the reaction with **1** in producing *cis*-dibenzoylstilbene oxide (**11**). This unexpected generation of an epoxide by chromic acid starting with a 5-nitrogen heterocycle appears to be unique, although epoxidations with chromic acid are known to occur [*e.g.*, *trans*- (but not *cis*-) dibenzoylstilbene is oxidized by chromic acid to *trans*-dibenzoylstilbene oxide[15b]]. The mechanism for this oxidation of **2** is presumably similar to that of hydrogen peroxide oxidation; however, the other product expected from such a route, the benzamidostilbene (**13**), has not been isolated.

In conclusion it is noted that pyrrole **1** and N-methylpyrrole **2** behave similarly toward the oxidizing agents considered, with the exception of chromic acid where the major difference is in susceptibility of the latter toward epoxidation.

(18) (a) C. A. Bunton and G. J. Mincoff, *J. Chem. Soc.*, 665 (1949); (b) H. H. Wasserman and H. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955); (c) R. E. Lutz and J. O. Weiss, *ibid.*, **77**, 1814 (1955).

(19) *Cf.* R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 2763 (1962).

Experimental Section[20]

Oxidations of Tetraphenylpyrrole[21] (1). A. Chromic Acid.—To a slurry of 1.0 g of **1** in 100 ml of refluxing AcOH was added 0.2 g of CrO_3. Refluxing for 30 min, pouring into an equal volume of cold water, filtering, washing with 20 ml of cold water, and recrystallizing from ethanol gave pyrrolinone **5** (0.85 g, 85%), mp 210–212° (lit.[10a,3c] 211–213°).

In an experiment similar to the above but at 55°, the mixture was stirred for 10 min, quenched in ice water, and extracted with ether. The ether extract upon washing (H_2O–Na_2CO_3), drying (Na_2SO_4), and evaporating yielded 0.6 g (58%) of the 2-hydroxy-2,3,4,5-tetraphenylhydroxypyrrolenine (**3**): mp 183–185° (lit. 204–205°,[21a] 170–173°[7b]); λ_{max} 233, 246, 320 mμ (ϵ 20,000, 18,700, 5900); ν 3050 (bonded OH) and 1630 cm^{-1} (α,β-unsaturated C=N).

Anal. Calcd for $C_{28}H_{21}NO$: C, 86.78; H, 5.47; N, 3.62. Found: C, 86.55; H, 5.36; N, 3.50.

Hydroxypyrrolenine **3** was prepared in quantity by the action of ammonia in 1:1 ethanol–benzene solution, on *cis*-dibenzoylstilbene (**7**) (the *trans* isomer of **7** did not react under these conditions). The experiment with **3** at 25° (12 hr) was repeated in ethanol at 55°[21a] (8 hr) with similar results.

Hydrochloride of Hydroxypyrrolenine 3.—A solution of 0.4 g of **3** in 30 ml of dry benzene, to which was added 4–5 drops of concentrated HCl (stirred 5 min), was slowly evaporated at atmospheric pressure, giving 0.43 g (97%): mp 189–191° dec, λ_{max}^{KBr} 335 mμ, ν 3000–2600 cm^{-1} (broad band).

Anal. Calcd for $C_{28}H_{22}ClNO$: C, 79.45; H, 5.19. Found: C, 79.65; H, 5.37.

Hydrolysis of hydrochloride of **3** by ethanolic KOH (15 min at 25°) regenerated hydroxypyrrolenine **3**.

B. Lead Tetraacetate.—To a vigorously stirred slurry of 1 g of **1** in 50 ml of AcOH was added 2.0 g of $Pb(OAc)_4$,[22] and stirring was continued for *ca.* 30 min. The resulting solution contained a slight excess of $Pb(OAc)_4$ (KI–starch paper) which was destroyed by addition of a few drops of glycerol. Pouring into water, extracting with ether, washing (H_2O, Na_2CO_3), drying (Na_2SO_4), evaporating, and crystallization of the gummy residue, once from *n*-hexane [0.6 g (63%), mp 172–180°] and finally from ethanol, gave hydroxypyrrolenine **3**, mp 178–181°.

C. Phosphorus Pentachloride.—The mixture of 2.0 g of **1**, 40 ml of $POCl_3$, and 4.0 g of PCl_5 was allowed to react at 25° for 30 min. The red oil obtained by removal of $POCl_3$ under reduced pressure was cooled to 0° and treated with ice water. The product, the hydrochloride of **3**, was crystallized from benzene: 0.85 g (77%), mp 175–183° dec; recrystallized, mp 187–189° dec. In a second expriment the red oil (above) was treated at 0° with a solution of 6.0 g of sodium in 100 ml of methanol. Pouring into cold water, extracting with ether, washing (H_2O), drying (Na_2SO_4), evaporating, and crystallization of the residual oil from *n*-hexane gave 1.2 g (56%) of 2-methoxy-2,3,4,5-tetraphenylpyrrolenine (**4**): mp 122–124°; λ_{max} 233, 249, 320 mμ (ϵ 20,300, 17,000, 6300); ν 2830 (OCH_3), 1640 cm^{-1} (α,β-unsaturated C=N); nmr peaks at τ 6.5 (3 H singlet, CH_3) and 2.8 (broad 20 H aromatic multiplet).

(20) Identification of all known and recovered compounds was by mixture melting point and infrared comparison with an authentic sample. Infrared absorptions were determined by KBr pellet on a Perkin-Elmer Infracord. Ultraviolet absorptions in absolute ethanol solution on a Perkin-Elmer Model 4000A Spectracord. Nmr spectra in $CDCl_3$ on a Varian A-60.

(21) D. Davidson, *J. Org. Chem.*, **3**, 361 (1938).

(21a) NOTE ADDED IN PROOF.—G. Rio, A. Ranjon, and O. Pouchot, *Compt. Rend.*, **263**, 634 (1966); C. Dufraisse, G. Rio, A. Ranjon, and O. Pouchot, *ibid.*, **261**, 3133 (1965). Compounds **3**, its hydrochloride, and **4** were reported but with melting points differing from ours. Our pertinent experiments have now been repeated with results the same as those given in the Experimental Section.

(22) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1955, p 325.

Anal. Calcd for $C_{29}H_{23}NO$: C, 86.80; H, 5.78. Found: C, 86.43; H, 5.75.

Evaporation of the above *n*-hexane solution gave 0.1 g (5%) of pyrrolinone **5** (rearrangement product of **3**, *vide supra*).

D. Nitric Acid. 1. Excess HNO_3 in AcOH at 80°.—To a suspension of 1 g of **1** in 20 ml of AcOH (80°) was added 1 ml of concentrated nitric acid (70–71%, specific gravity 1.42) in 5 ml of AcOH. Solution occurred during 30 min with ebullition of oxides of nitrogen. Pouring into water, filtering the precipitate, washing, and recrystallizing from ethanol yielded *cis*-dibenzoylstilbene (**7**) (0.07 g, 65%), mp 211–213°.

2. One Mole of HNO_3 in AcOH at 55°.—A stirred suspension of 1.0 g (0.0027 mole) of **1** in 50 ml of AcOH dissolved upon addition of 0.2 ml (0.003 mole) of concentrated HNO_3 (70–71%, specific gravity 1.42) (55°, 1 min). Work-up as in A gave **7**: (0.75 g, 70%), mp 208–212°, recrystallized, mp 213–215°.

3. One-Half Mole of HNO_3 in AcOH at 55° (as in B).—The product failed to coagulate and was extracted with ether. After evaporating, the residue was dissolved in benzene and placed on an alumina column (60 g, 0.8 in. i.d., packed in petroleum–pentane). Elution was by petroleum pentane–benzene, benzene, and 1:1 benzene ether mixtures. The benzene effluent contained **7** (0.27 g, 26%), mp 212–214°. Evaporation of the ether–benzene effluent and recrystallization from ethanol gave **3** (0.61 g, 59%), mp 180–182°.

In a separate experiment, **3** was passed through an alumina column packed as above and was recovered unchanged from the 1:1 ether–benzene effluent.

E. Nitrous Acid in AcOH.—Attempts to obtain **3** by the reported procedure[7b] failed, but the following was successful. A stirred suspension of 1.0 g of **1** in 50 ml of AcOH at 55° dissolved upon treatment with 0.2 g $NaNO_2$ (1 min). The products, obtained by hydrolysis, extraction with ether, washing (H_2O), drying (Na_2SO_4), concentrating, and chromatographing as in D3, were **7**, 0.1 g (10%), mp 211–214°; **3**, 0.35 g (34%), mp 182–184°, recrystallized from ethanol; and unchanged **1**, 0.23 g (23%), mp 212–214°.

F. Hydrogen Peroxide.—A slurry of 2 g of **1** in 50 ml of refluxing AcOH plus 1.5 ml of 30% hydrogen peroxide after 30 min was poured into ice water. Fractional crystallization of the precipitate from absolute ethanol gave **11** (1.45 g, 67%), mp 170–172°. Partial evaporation of the filtrate gave **12** (0.4 g, 19%), mp 190–192°.

Reactions of 2-Hydroxy-2,3,4,5-tetraphenylpyrrolenine (3).

A. Rearrangement of 0.15 g by refluxing AcOH (15 ml, 1.5 hr) gave **5** (0.13 g, 86%), mp 210–211°, recrystallized from ethanol.

B. Alcoholysis of 0.5 g of **4** in 50 ml of absolute methanol plus 1 drop of concentrated H_2SO_4 (refluxed for 1 hr) gave the 2-methoxypyrrolenine **4** (0.2 g, 38%), mp 119–121°.

Hydrolysis of 0.3 g of **4** in 3 ml of water, 3 ml of concentrated HCl, and 20 ml of methanol (refluxing for 1 hr) gave 0.07 g (22%) of the hydrochloride of **3** mp 188–191° dec. The filtrate was extracted with ether, washed (H_2O), dried (Na_2SO_4), and evaporated, and the resulting oil upon repeated crystallization from *n*-hexane–benzene gave **3** (0.15 g, 52%), mp 180–182°.

C. Rearrangement of 0.3 g of **3** by 0.6 g of KOH in 28 ml of 85% methanol (refluxed 1 hr) yielded pyrrolinone **5** (0.28 g, 93%), mp 209–211°.

D. Hydrolysis. 1. By Excess Nitrous Acid.—A solution of 0.3 g of **3** and 0.6 g of $NaNO_2$ in 30 ml of AcOH, after heating at 55° (30 min), was poured into water and crystallized from benzene, yielding **7**, 0.28 g (90%), mp 212–214°.

2. By 1 Mole of Nitrous Acid.—Compound **3** (0.5 g) and 0.01 g (0.0015 m) of $NaNO_2$ were allowed to react in 50 ml of AcOH at 55° (1 min). Crystallization from ethanol yielded **7** (0.35 g, 70%), mp 212–214°.

E. Oxidation of 1 g of **3** by 1.5 ml of 30% hydrogen peroxide in 50 ml of refluxing AcOH (5 min), pouring into ice water, and fractionally crystallizing the product from ethanol gave *cis*-dibenzoylstilbene oxide (**11**) (0.60 g, 64%), mp 170–172°, and the benzamidostilbene (**12**) (0.22 g, 20%), mp 190–192°.

F. Reduction. 1. By Hydriodic Acid.—A solution of 0.1 g of **3** or its hydrochloride in 0.4 ml of 47% HI in 20 ml of AcOH (85° for 1 hr) upon pouring into ice water and crystallizing from ethanol yielded **1** (0.08 g, 89%). The infrared spectrum of the crude product indicated the presence of a small amount of pyrrolinone **5** (not isolated).

2. By Sodium Hydrosulfite.—A mixture of 0.2 g of **3**, 0.4 g of $Na_2S_2O_4$, and 20 ml of 87% ethanol, after refluxing for 30 min, pouring into water, and crystallization of the precipitate from ethanol, gave **1**, 0.18 g (95%).

3. By Sodium Borohydride.—A suspension of 1.0 g of 50 ml of methanol containing 0.21 g of $NaBH_4$ was stirred at 25° for 30 min. An additional 0.21 g of $NaBH_4$ was added with stirring for 1 hr. Neutralization with 5% HCl and recrystallization of the precipitate from ethanol gave **1**, 0.92 g (94%).

Similar results were obtained using methoxypyrrolenine **4**.

4. By Phosphorus Trichloride.—Refluxing a solution of 0.5 g in 25 ml of PCl_3 (30 min), evaporation under reduced pressure, addition of water, and crystallization of the resulting solid from ethanol gave **1** (0.44 g, 97%).

Similar results were obtained from methoxypyrrolenine **4**.

Oxidations of N-Methyltetraphenylpyrrole (2). A. Chromic Acid.—A slurry of 0.5 g of **2** and 0.1 g of CrO_3 in 50 ml of AcOH after 5 min at 55° was poured into water. The product, dissolved in benzene, was placed on a Florosil column (50 g, 0.8-in. i.d., packed with petroleum pentane) and chromatographed. The initial elution [7.5% benzene–petroleum pentane] gave unchanged **2** (0.25 g, 50%). Elution with benzene gave *cis*-dibenzoylstilbene oxide (**11**) (0.12 g, 50% allowing for recovered starting material). Final elution with 20% ether–benzene gave 0.05 g of benzil, mp 94–96°.

B. Nitric Acid.—A solution of 0.2 g of **2** in 5 ml of AcOH and 0.2 ml of concentrated HNO_3 was heated on a steam bath for 30 min and poured into water. The crude, yellow precipitate, mp 173–178° dec, evidently a mixture of salts, was not purified: λ_{max} *ca.* 247–248, 304–306 mμ; ν broad band centered at *ca.* 3000, 1610, and no band at 1640–1670 cm^{-1} (carbonyl).

In a separate experiment a solution of the salt from 0.2 g of **2**, and 0.2 g of KOH in 10 ml of 95% ethanol, after refluxing for 1 hr, was poured into water. Crystallization of the precipitate from ethanol the N-methylpyrrolinone **6** (0.15 g, 72%), mp 158–160° (lit.[3c,10a] 161°).

Reaction of **2** with $NaNO_2$ in AcOH as above gave similar results.

C.—Phosphorus Pentachloride (in $POCl_3$), like the reaction with **1**, gave a crude salt (λ_{max} 247, 302 mμ; ν 3000, 1620 cm^{-1}) which was converted by base, as in B (above), to N-methylpyrrolinone **6**.

D. Hydrogen Peroxide.—To a refluxing slurry of 2.0 g of **2** in 50 ml of AcOH was added 2.0 ml of 30% hydrogen peroxide. After refluxing for 20 min and pouring into ice water, the resulting solid was dissolved in benzene and placed on an alumina column (80 g, 0.8-in. i.d. packed in petroleum–pentane). Elution with benzene gave 0.08 g of unchanged **2** (4%). Ether–benzene elution yielded the N-methylbenzamidostilbene **13** (0.55 g, 25%): mp 192–195°; λ_{max} 257, 294 mμ (ϵ 11,400, 22,400); ν 1650 and 1630 cm^{-1}; nmr peaks at τ 6.8 (3 H singlet, CH_3) and 2.8 (broad, 20 H aromatic multiplet).

Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.50; H, 5.56. Found: C, 83.61; H, 5.87.

Final elution with ether and acetone yielded *cis*-dibenzoylstilbene oxide (**11**) (1.18 g, 61%), mp 170–172°.

Rearrangement of *cis*-Dibenzoylstilbene Oxide (17) to the Benzamidobenzoylstilbene (12).—Dry NH_3 was passed through a solution of 0.5 g of **11** in 300 ml of refluxing methanol for *ca.* 6 hr. Evaporation and repeated recrystallizations from absolute ethanol gave benzamidostilbene **12** (0.35 g, 70%), mp 189–191°.

Registry No.—**3**, 4793-86-6; hydrochloride of **3**, 7731-71-7; **4**, 7731-72-8; **7**, 6313-26-4; **1**, 3263-79-4; **11**, 7731-74-0; **12**, 7731-75-1; **5**, 4793-85-5; benzil, 134-81-6; **6**, 7731-77-3; **13**, 7731-78-4.