hydroxide was added and the mixture was evaporated to one-half volume, *in vacuo*, on a steam bath. A yellow solid formed. The mixture was cooled and filtered, giving 0.5 g. (46.7%). The infrared spectrum of this compound was superimposable upon that of a sample of 3-oximinoimidazo[1,2-*a*]pyridin-2-one, prepared according to the method of Tschitschibabin.[11]

Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.5; H, 3.08; N, 25.7. Found: C, 51.7; H, 3.38; N, 25.41.

3-N-Acetylaminoimidazo[1,2-*a*]pyridine[10] (X).—To 100 ml. of absolute ethanol was added 0.75 g. of 3-nitroimidazo[1,2-*a*]pyridine (IX) and a small amount of Raney nickel catalyst. This mixture was hydrogenated on a low-pressure Parr shaker at 42 p.s.i. of hydrogen for 16 hr. The solution was then filtered through a Celite pad and ethereal hydrogen chloride was added to the filtrate. The filtrate was then evaporated to dryness, the resulting solid was dissolved in water, and the solution made basic with aqueous ammonia and extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and evaporated to give 0.43 g. of an oil. This oil was dissolved in 10 ml. of acetic anhydride and the solution was refluxed for 45 min. The excess acetic anhydride was removed and the residue was triturated with iced aqueous ammonia and extracted with chloroform. Evaporation of the chloroform gave a residue which was triturated with benzene, leaving a brown solid (0.45 g.). This crude solid was recrystallized from water (charcoal added) to yield 0.22 g. of white solid, m.p. 197°. An authentic sample of 3-N-acetylaminoimidazo[1,2-*a*]pyridine prepared by the method of Bristow, *et al.*,[10] melted at 197–198° (lit.[10] m.p. 196–199°). A mixture melting point showed no depression. Infrared spectra of the two samples were identical in every respect.

Reduction of Pyrrolyl-2,3,4,5-tetramercuric Acetate with Ferrocene

GRACE N. O'CONNOR,[1a] JEAN V. CRAWFORD, AND CHI-HUA WANG[1b]

Department of Chemistry, Wellesley College, Wellesley, Massachusetts 02181

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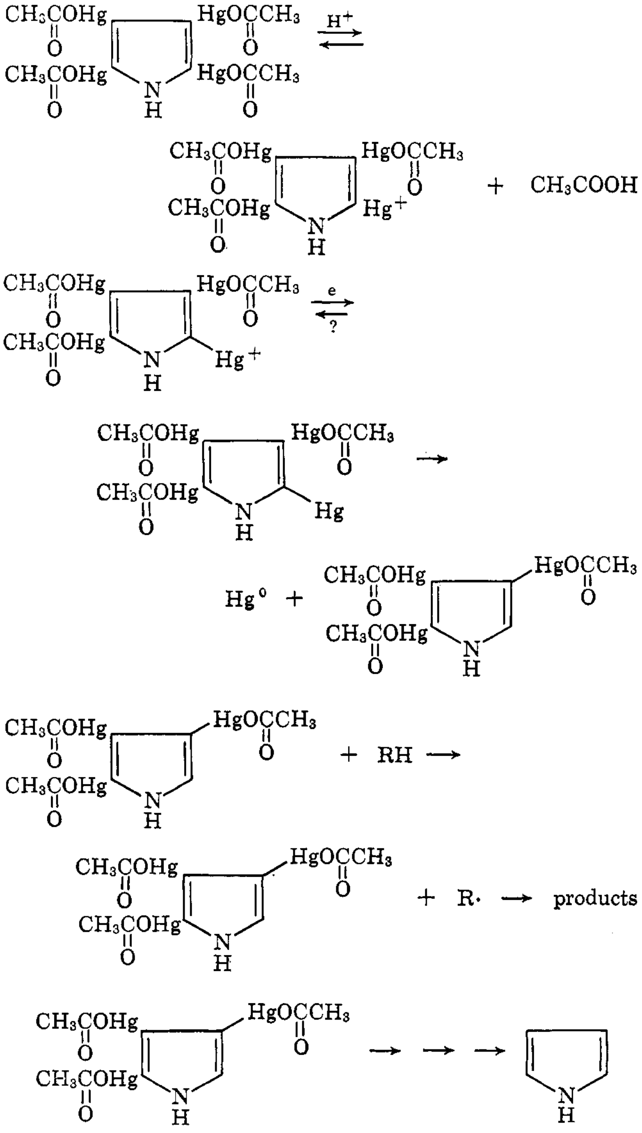
Pyrrolyltetramercuric acetate was prepared and characterized by elementary and infrared spectral analysis. The pyrrolylmercuric cation from solvolysis of the parent compound in acetic acid–toluene was reduced by ferrocene and the major product of the reaction was identified as pyrrole. The free-radical mechanism of the reaction was presented.

To continue our study of the reduction of organometallic cations as a means of generation of free radicals in solution, we have examined the solvolysis and reduction of pyrrolyl-2,3,4,5-tetramercuric acetate, an example of heteroaromatic mercuric compound, for comparison with that of phenylmercuric acetate.[2]

Under rather mild conditions, pyrrole and mercuric acetate furnished pyrrolyltetramercuric acetate and no monomercuric acetate or other identifiable products. Nevertheless, pyrrolyltetramercuric acetate underwent acid-catalyzed hydrolysis in acetic acid–toluene, and subsequent reduction with ferrocene to give pyrrole in good yield. We believe that the observed reaction follows a parallel route with that of phenylmercuric acetate, *e.g.*, Chart I.

CHART I



Pyrrolyl-2,3,4,5-tetramercuric Acetate.—Mercuric compounds of pyrrole have been investigated by Kottnitz,[3] Willestatter and Asahina,[4] Fischer and Muller,[5] and Cuisa and Grillo.[6] Treating mercuric chloride with pyrrole, Kottnitz obtained a compound with the composition $C_4H_5N \cdot 2HgCl_2$. Willestatter showed that mercuration occurred on the carbon atoms rather than on the nitrogen atom. However, under different conditions, using mercuric chloride, Fischer isolated a double compound, $(C_4H_4N)_2Hg(HgCl_2)_4$, the empirical formula of which is based on elementary analysis. Cuisa and Grillo, treating mercuric acetate, reported the preparation of pyrrolyltetramercuric acetate based on mercury and nitrogen analysis. Because the lack of definitive information about the chemistry of this type of compound, we decided to follow up the more recent work of Cuisa and Grillo. Pyrrolyltetramercuric acetate was prepared and

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[1] (a) Participant of the Wellesley College Institute of Chemistry supported by the National Science Foundation. (b) To whom inquiries should be addressed.

[2] C.-H. Wang, *J. Am. Chem. Soc.*, **85**, 2339 (1963).

[3] M. Kottnitz, *J. Prakt. Chem.*, **6**, 136 (1872).

[4] R. Willestatter and Y. Asahina, *Ann.*, **385**, 188 (1911).

[5] H. Fischer and R. Muller, *Z. physiol. Chem.*, **148**, 156 (1925).

[6] R. Cuisa and G. Grillo, *Gazz. chim. ital.*, **57**, 323 (1926).

studied. We repeated the procedure of the authors and obtained a product with the molecular formula $C_{12}H_{13}Hg_4NO_8$. Infrared spectral analysis of this compound indicates the presence of an N–H peak at 3450 cm.$^{-1}$ and an acetate peak at 1610 cm.$^{-1}$. The structure of the compound was thus identified as pyrrolyl-2,3,4,5-tetramercuric acetate.

Solvolysis and Reduction.—When the solution of pyrrolyl-2,3,4,5-tetramercuric acetate in acetic acid–toluene (65:35) was treated with ferrocene under comparable conditions as that for phenylmercuric acetate,[2] we observed the characteristic blue color of ferrocenium ion. Pyrrole was formed in 58% yield. Using acetic acid alone as solvent, no pyrrole was obtained from the reaction mixture, but some polymeric substances resulted with unsaturation bands in the 6-μ region. Further characterization of this substance was not fruitful at this time.

The appearance of blue ferrocenium ion and subsequent detection of pyrrole strongly suggests that there is similarity between this reaction and the reduction of phenylmercuric cation. The absence of pyrrolyl acetate also supports the assumption that the pyrrolylmercuric cation does not demercurate to yield the corresponding carbonium ion.[7] The formation of polymeric substances in acetic acid may reflect that the pyrrolyl radical is relatively stable, incapable of abstracting hydrogen from acetic acid. Thus, recombination of radicals leading to polymeric products becomes more important.

The solvolysis and reduction are perhaps stepwise. Simultaneous reduction and demercuration should provide a benzyne type intermediate, for which we have not secured any evidence. Experiments with polymercuric acetates of thiophene and benzene are in progress in this laboratory.

Experimental Section

Preparation of Pyrrolyl-2,3,4,5-tetramercuric Acetate.—Mercuric acetate (15 g., 0.042 mole, Merck Co.) was dissolved in 60 ml. of hot water and some red precipitate was filtered immediately. Pyrrole (1.0 g., 0.015 mole, Eastman, freshly distilled, b.p. 130–131°) was added to the freshly filtered solution of mercuric acetate. The mixture was allowed to stand for 1 hr. A white precipitate, 2.9 g. (20%), was collected. It decomposed above 200° with the formation of mercury beads. The analytical sample was obtained by recrystallization from an acetic acid–ethanol mixture.

Anal.[8] Calcd. for $C_{12}H_{13}Hg_4NO_8$: C, 13.06; H, 1.13; Hg, 72.80; N, 1.27. Found: C, 12.88; H, 1.26; Hg, 72.08; N, 1.27.

Other mole ratios of pyrrole and mercuric acetate were tried in acetic acid as well as water as solvent, but many difficulties were encountered. Using a mole-to-mole ratio of pyrrole and mercuric acetate, a dark blue viscous mess was obtained. When the amount of water was reduced, a gelatinous mixture resulted which made filtration impossible.

Solvolysis and Reduction of Pyrrolyl-2,3,4,5-tetramercuric Acetate.—To a solution containing 0.2 g. (2×10^{-4} mole) of pyrrolyltetramercuric acetate in 1 ml. of glacial acetic acid with trace amounts of *p*-toluenesulfonic acid (Matheson Coleman and Bell), 0.15 g. (8×10^{-4} mole) of ferrocene (Aldrich Chemical Co., m.p. 173–174°) in 0.5 ml. of toluene was added. The yellowish reaction mixture turned dark bluish green gradually upon standing at room temperature. At the end of 24 hr., 5 μl. of the reaction mixture was analyzed by v.p.c. at 150–155°, with a helium flow rate of 60 cc./min. The yield of pyrrole was 58%. In the blank run, with all the components but ferrocene, under identical conditions, no pyrrole was detected.

The remainder of the reaction mixture was concentrated to almost dryness. A gummy mess resulted. Purification and identification were not successful.

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(7) F. Jensen and R. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961).

(8) The analysis was performed by Dr. M. S. Nagy of Massachusetts Institute of Technology.

Stereochemistry of the Additions of Acids to Stilbene and Styrene Oxides[1]

GIANCARLO BERTI, FRANCESCO BOTTARI, PIER LUIGI FERRARINI, AND BRUNO MACCHIA

Institutes of Organic and Pharmaceutical Chemistry, University of Pisa, Pisa, Italy

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threo-2-Chloro-1,2-diphenylethanol was the main or only product of the reaction of *trans*- and *cis*-stilbene oxide with hydrogen chloride in several different solvents. The *erythro*-chlorohydrin was formed in slight excess only in the reaction of the *trans*-oxide in ether containing water. *trans*-Stilbene oxide was transformed into its *cis* isomer in better than 90% yield by reaction with hydrogen chloride, followed by treatment with alkali. The steric course of the reaction of (+)-styrene oxide with hydrogen chloride to give 2-chloro-2-phenylethanol was found to depend greatly on the solvent, as percentages of inversion ranging from 24% in dioxane to 83% in chloroform were observed. Additions of several organic acids to (+)-styrene oxide in different solvents were also investigated. Absolute configurations were deduced for *threo*-2-chloro-1,2-diphenylethanol, 1,2-diphenylethanol, and 2-chloro-2-phenylethanol.

It appears that, in all known cases, additions of nucleophiles to epoxides in basic or neutral media take place with complete inversion.[2] On the other hand, the stereochemistry of additions which take place in acidic solutions, with formation of glycols, glycol esters, or halohydrins, is much less straightforward and deserves further investigation. While purely aliphatic or cycloaliphatic epoxides open mostly in a *trans* fashion, it is now clear that this does not hold when aryl substituents are present on the oxirane ring: several recent examples in the literature show that retention, rather than inversion, takes place as a rule in this case.[3]

Apparent exceptions to this rule are the reactions of *cis*- (**1**) and *trans*-stilbene oxide (**4**) with hydrogen chloride. According to Reulos and Collin,[4] this reaction, carried out in moist ether, gives the *trans*

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(1) Taken in part from the doctoral thesis of P. L. Ferrarini.

(2) For a complete review, see A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 1.

(3) (a) J. H. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956); (b) D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *ibid.*, **78**, 4064 (1956); (c) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957); (d) G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960); (e) G. Berti, F. Bottari, and B. Macchia, *Gazz. chim. ital.*, **90**, 1783 (1960); (f) *Tetrahedron*, **20**, 545 (1964).

(4) D. Reulos and C. Collin, *Compt. rend.*, **218**, 795 (1944).