used without further purification in the cyclization reaction.

Method B. To a mixture of 3,5-dimethoxyphenol (59 g.), solid sodium hydroxide (72 g.), and acetone (340 ml.) was slowly (45 min.) added 55 g. of chloroform. The mixture was stirred and heated under reflux on a steam bath for 3 hr. After the removal of acetone, the residue was dissolved in water. The solution was worked up as above to afford 50.4 g. (54.7%) of a viscous oil.[13] This was used as such in the cyclization reaction.

A portion (25 g.) of the above product was dissolved in 200 ml. of ether and extracted with 10% sodium bicarbonate solution. Extraction of the combined and acidified aqueous solution with ether yielded 23 g. of solid IV. After recrystallization from a mixture of hexane and toluene, the solid had a melting point of 65–68°.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.98; H, 6.71; CH_3O, 25.83; neut. equiv., 240.2. Found: C, 59.85; H, 6.64; CH_3O, 25.60; neut. equiv., 233.3.

4,6-Dimethoxy-2,2-dimethyl-3[2H]benzofuranone (VI). *Method A.* 2-(3,5-Dimethoxyphenoxy)-2-methylpropionic acid (12 g.) was mixed with trifluoroacetic anhydride (21 g.). The exothermic reaction was moderated by cooling at 40°. After the initial reaction subsided, the mixture was heated at 90° for 30 min. and concentrated under reduced pressure. The residue was recrystallized from anhydrous ethanol to afford 5.25 g. (47.3%) of VI, m.p. 123–125°.

Method B. A mixture of IV (16 g.) and polyphosphoric acid (130 g.) was stirred and heated at 90–100° for 2 hr. After being cooled, the reaction mixture was poured into 300 ml. of water and extracted with ethyl acetate. The ethyl acetate solution was washed with 10% sodium bicarbonate, then with water, dried over magnesium sulfate, and concentrated *in vacuo.* The solid was recrystallized from anhydrous ethanol to give 3.8 g. (25.5%) of VI, m.p. and mixture m.p. with above, 123–125°.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; CH_3O, 27.93. Found: C, 64.98; H, 6.39; CH_3O, 27.95.

Monobromo-4,6-dimethoxy-2,2-dimethyl-3[2H]benzofuranone (VII). Liquid bromine (2.2 g.) was added to a solution of VI (3 g.) in glacial acetic acid (10 ml.). The mixture was allowed to stand at room temperature for 15 min. and then concentrated *in vacuo.* The residue was crystallized from anhydrous ethanol to afford 3 g. (74%) of VII, m.p. 191–193°.

Anal. Calcd. for $C_{12}H_{13}BrO_4$: C, 47.86; H, 4.35. Found: C, 47.83; H, 4.37.

5,7-Dibromo-4,6-dimethoxy-2,2-dimethyl-3[2H]benzofuranone (VIII). Liquid bromine (5 g.) was slowly added to a solution of VI (1 g.) in glacial acetic acid (15 ml.). The mixture was heated under reflux on a steam bath for 30 min. and concentrated *in vacuo.* The residue was crystallized from ethanol to give 1.2 g. (70.5%) of VIII, m.p. 126–129°.

Anal. Calcd. for $C_{12}H_{12}Br_2O_4$: C, 37.91; H, 3.18; CH_3O, 16.33. Found: C, 38.30; H, 2.97; CH_3O, 16.35.

5,7-Dichloro-4,6-dimethoxy-2,2-dimethyl-3[2H]benzofuranone (IX). A mixture of VI (5 g.), chloroform (40 ml.), and sulfuryl chloride (6 g.) was allowed to stand at room temperature overnight and concentrated under reduced pressure. The residue was crystallized from ethanol to afford 4.2 g. (57.5%) of IX, m.p. 95–97°.

Anal. Calcd. for $C_{12}H_{12}Cl_2O_4$: C, 49.50; H, 4.16; Cl, 24.36; CH_3O, 21.32. Found: C, 49.64; H, 4.33; Cl, 24.41; CH_3O, 21.40.

Acknowledgment. We wish to thank Dr. R. M. Ross for his encouragement and interest in this work, Mr. C. W. Nash and his staff for chemical analyses, and Dr. H. L. Keil and his associates for fungicidal evaluation.

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[13] This oil had the correct analysis of IV. Calcd.: C, 59.98; H, 6.71; Acid No., 233.1. Found: C, 59.78; H, 6.41; Acid No., 238.7. Distillation of this material at 0.4 mm. also resulted in partial decomposition. The distillate had an acid number of 140.9 after one distillation and of 89.5 after a second distillation.

Oxidation-Reduction Concomitant with Molecular Complexing

MORTIMER M. LABES AND HANA UR

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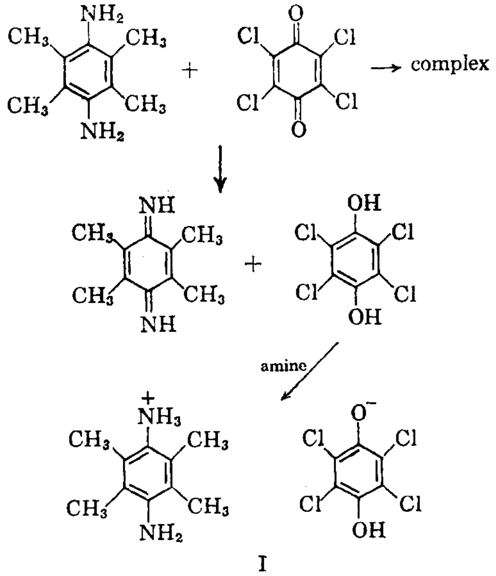
In the course of studying the electronic properties of solid molecular complexes,[1] attempts at growth of single crystals of diaminodurene-chloranil from chloroform gave well developed small crystals, $\rho \sim 10^4\ \Omega$ cm.,[1a,b] while from benzene only irregular-shaped crystals of poor quality, and duller in color could be obtained. None of our crystals were suitable for electrical measurements, but it has been reported that these benzene-grown crystals have a higher resistivity.[2] It was noted, however, that a crystalline, off-white colored solid was formed in conjunction with the complex in very dilute solution.

The reaction is apparently a case of oxidation-reduction under extremely mild conditions, followed by formation of the salt I:



I

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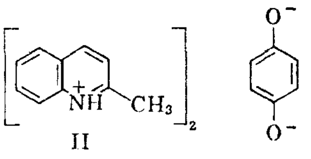
[1] (a) P. L. Kronick and M. M. Labes, *J. Chem. Phys., in press;* (b) M. M. Labes, R. Sehr, and M. Bose, *Proc. International Conference on Semiconductor Physics,* Prague, Czechoslovakia, Aug. 29–Sept. 2, 1960, *in press;* (c) R. Sehr, M. M. Labes, M. Bose, F. Wilhelm, and H. Ur, *Proc. Conference on Electronic Conductivity in Organic Solids,* Duke University, April 1960, Interscience Publishers, Inc., New York, *in press;* (d) M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.,* **33**, 868 (1960); (e) M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.,* **32**, 1570 (1960).

[2] R. G. Kepler, private communication.

The only analogous reaction we are aware of is the report by Bell[3] of the formation of a crystalline material by the reaction of benzoquinone and quinaldine in refluxing xylene, which in subsequent work by Bothner-By[4] was shown to be II. This compound is in reality formed as an adduct of the hydroquinone and quinaldine, the hydroquinone being formed by the reduction of the quinone by the amine.


II

We have not observed the reaction for any of the other diamine-quinone systems studied,[1] and believe that the driving force in this case is the comparative stability of the *diimine* of diaminodurene. This stability has been noted by Michaelis *et al.*,[5] who report that of thirty-three C- and/or *N*-alkyl substituted and unsubstituted *p*-phenylenediamines, *only* diaminodurene has a sufficiently stable diimine to allow measurement of the equilibrium involving diamine, diimine and semiquinone radical.

The salt I is an insulator (ρ powder $\sim 10^{12}$ Ω cm.), and could be present in the charge-transfer crystals grown from benzene and responsible for the higher resistivity. The possibility of this type of reaction under mild conditions should be carefully considered in relation to any study of electrical properties of these complexes.

EXPERIMENTAL

When diaminodurene[6] (1.6 g.) and chloranil (2.5 g.) separately dissolved in benzene (total volume 1700 ml.) at room temperature were mixed, material precipitated almost immediately which was a mixture of the diaminodurene-chloranil 1:1 charge-transfer complex, a black crystalline material, and a light-colored material (approximately 1.0 g. crude). The light colored material after five recrystallizations from alcohol and sublimation decomposed at 191° and was identical in its infrared spectrum and decomposition point with the reaction product of 1:1 ratios of *tetrachlorohydroquinone* and diaminodurene mixed in ethanol, the salt I.

Anal. Calcd. for $C_{16}H_{18}Cl_4N_2O_2$: C, 46.6; H, 4.4; N, 6.8; Cl, 34.4. Found: C, 46.1; H, 4.3; N, 7.3; Cl, 33.7.

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(3) F. Bell, *J. Chem. Soc.*, 348 (1953).

(4) A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 749 (1955).

(5) L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, 61, 1981 (1939).

(6) L. I. Smith, *Org. Syntheses*, Coll. Vol. II, 254 (1943).

The Preparation and Characterization of 1-Methylinosine

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The reaction of diazomethane with the weakly acidic hydrogen atom of uridine was employed by Levene and Tipson[1] to prepare 1-methyluridine. The procedure has since been applied to other pyrimidine nucleosides both with and without protecting groups[2,3] on the sugar hydroxyl groups.

Bredereck and Martini[4] treated some purine nucleosides with diazomethane and applied the the name 1-methylinosine to the product of the reaction with tri-*O*-acetylinosine. While it was not unreasonable to expect this compound to result from the reaction,[5] the structure was not proved, the homogeneity of the product was not demonstrated, and no characterization was presented which would permit the compound to be recognized. An acid hydrolysis was carried out to produce, in unspecified yield, a material which was assigned the structure 1-methylhypoxanthine. The lack of proof of structure of this hydrolysis product was pointed out by Elion,[6] who has prepared 1- and 3-methylhypoxanthine by unambiguous syntheses and reported their ultraviolet spectra and paper-chromatographic behavior. As a water-soluble 1-alkylinosine of undoubted structure was needed for infrared spectroscopic studies,[7] the reaction of diazomethane with tri-*O*-acetylinosine was reinvestigated. From the heterogeneous reaction mixture, crystalline 1-methylinosine (I) was obtained and characterized

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(1) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **104**, 385 (1934).

(2) R. E. Beltz and D. W. Visser, *J. Am. Chem. Soc.*, **77**, 736 (1955).

(3) H. T. Miles, *J. Am. Chem. Soc.*, **79**, 2565 (1957).

(4) H. Bredereck and A. Martini, *Chem. Ber.*, **80**, 401 (1947).

(5) The deacylation of esters by diazomethane has been reported [J. Herzig and J. Tichatschek, *Ber.*, **39**, 268 (1906); H. Biltz and W. Klemm, *Ann.*, **448**, 153 (1926); H. Biltz, L. Loewe, and H. Pardon, *Ber.*, **64**, 1146 (1931); H. Bredereck, R. Sieber, and L. Kamphenkel, *Angew. Chem.*, **67**, 347 (1955)] by several workers, but a careful investigation of the experimental conditions has apparently not yet been published. In the authors' experiments this aspect of the reaction appeared to be erratic, deacylation occurring in some experiments and not in others. Though this point was not specifically investigated, it appeared that prolonged contact with diazomethane (several days) would produce deacylation, whereas a few hours contact would not. Zemplen saponification of a reaction mixture in which deacylation had not occurred established that the same ring methylation products had been produced. It should be noted that the addition of ether to a methanolic solution would precipitate those compounds which had been deacetylated and leave in solution those which were still esterified.

(6) G. B. Elion, *The Chemistry and Biology of Purines*, Ciba Foundation Symposium, 1957, p. 39.

(7) H. T. Miles, *Proc. Natl. Acad. Sci.*, **47**, 791 (1961) and references there cited.