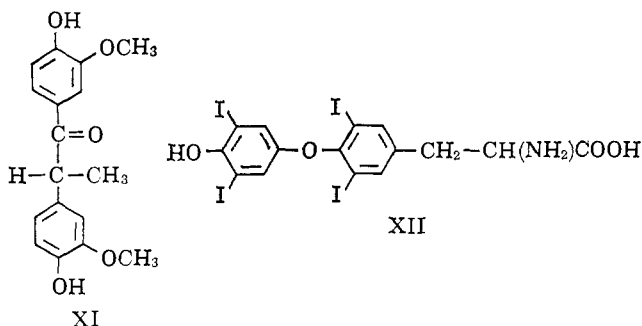
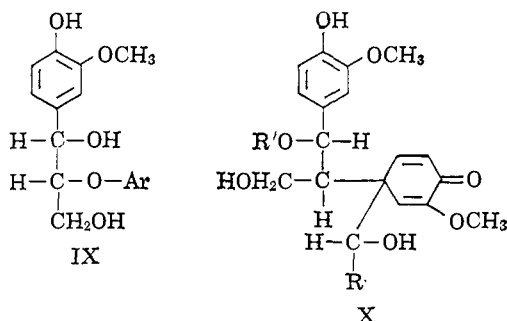


system<sup>1</sup> and mildly acidic persulfate system,<sup>3</sup> it is not in keeping with the nonacidic reaction conditions of the lead dioxide<sup>3</sup> and manganese dioxide systems and the reactivity of III with the latter oxidant.

This oxidative dealkylation mechanism ought to be applicable to certain phenolic natural products. It provides a possible dealkylation pathway for many lignin oligomers such as IX (AR denotes any polyconiferyl alcohol oligomer) to aldehydic fragments which may serve to bond lignins to the carbohydrates of the plant cell wall. Recently, Lundquist and Miksche<sup>13</sup> have postulated structure X as an intermediate in order to explain product XI in Bjoerkman lignin oligomers. This reaction scheme also pro-



vides an extension to a proposed mode<sup>14</sup> of oxidative dealkylation of 3,5-diiodotyrosine to thyroxine (XII).

(13) K. Lundquist and G. E. Miksche, *Tetrahedron Letters*, 2131 (1965).

(14) T. Matsuura and H. J. Cahnmann, *J. Am. Chem. Soc.*, **82**, 2055 (1960).

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### Precipitation of Sodium Chloride from Aqueous Solution by Compound Formation with an Organic Amine

Sir:

We wish to report the first example of the precipitation of simple sodium salts such as sodium chloride from aqueous solution by compound formation with a nonionic organic substance. The compound capable of precipitating these salts is racemic *p,p'*-diamino-2,3-diphenylbutane (I). Equally unique is that the compound, II, which results from combination of I with sodium chloride, is best described as a solid coordination compound of sodium with a nitrogen donor ligand.

Of the alkali metals only lithium salts are known to form isolable coordination compounds with nitrogen-donor ligands.<sup>1</sup> The more stable are those where the ligand is ammonia. Replacement of ammonia by amines decreases their stability. It is therefore very surprising that I, which is a weakly basic and bulky aromatic amine, can exhibit bonding with sodium. Furthermore, the previously reported ammonium compounds are decomposed upon addition to water. Not only is II prepared by precipitation from aqueous solution, but it does so without incorporation of any detectable quantity of water. The hydrolytic stability of II is also evidenced by the fact that when a quantity of it sufficient to give a 6.1 g/l. solution of sodium chloride was shaken with water for 1 week at 30°, the amount of sodium chloride found in solution was only 1.03 g/l.

Compound II can be simply obtained by agitating an ether solution of I with saturated aqueous sodium chloride. A more convenient method was to add 0.288 g (5 mmoles) of sodium chloride dissolved in 8 ml of water to 2.40 g (10 mmoles) of I dissolved in 24 ml of ethanol. Recrystallization from 25 ml of 1:3 aqueous alcohol gave 1.91 g of II. Although the melting point of I is 84–85° and that of sodium chloride is 800°, II fuses to a clear melt at 200°. There is no apparent phase separation when II is kept at or above its melting point for an extended period of time.

Assignment of a coordination structure rather than a clathrate or inclusion compound not only requires that II be stoichiometric, but that it also have constant composition. This was found to be the case. Elemental analysis of II was that for a substance consisting of three molecules of I per sodium chloride. *Anal.* Found: C, 74.23; H, 7.78; N, 10.92; Na, 3.15; Cl, 4.53. X-Ray data provide supporting evidence for a 3 to 1 stoichiometry for II. Diffraction analysis and density measurements were those for a unit cell containing 12 formula units of I and 4 units of sodium chloride. The property of constant composition was demonstrated by the fact that unrecrystallized II prepared from 2:1 and 18:1 molar ratios of I to sodium chloride contained 3.12 and 3.15% sodium, respectively.

The infrared spectrum of II provides compelling evidence for assigning it a coordination structure. The infrared spectrum (hexachlorobutadiene mull) of II is very similar to that of I except that the two sharp N–H stretching vibrations have each shifted 53 cm<sup>-1</sup> to lower frequency and have become more intense. This is important for two reasons. The magnitude of this shift offers good evidence for *sodium to nitrogen bonding*, since for Pt(en)Br<sub>2</sub> the shift in N–H stretching frequency from that of ethylenediamine is 70 cm<sup>-1</sup>.<sup>2</sup> Also the fact that only two sharp N–H stretching frequencies are observed means that there continues to be *only one kind of amino group in II*. This, in conjunc-

(1) For a discussion of coordination compounds of the alkali metals, see M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964; and N. V. Sidwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, London, 1950. For some recent work on weak alkali metal complexes in solution, see G. A. Rechnitz and J. Brauner, *Talanta*, **11**, 617 (1964); G. A. Rechnitz and S. B. Zamochnic, *ibid.*, **11**, 1061 (1964); L. E. Erickson and J. A. Denbo, *J. Phys. Chem.*, **67**, 707 (1963); O. Jardetsky and J. E. Wertz, *J. Am. Chem. Soc.*, **82**, 318 (1960); L. Erickson and R. A. Alberty, *J. Phys. Chem.*, **66**, 1702 (1962).

(2) G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).

tion with the composition data, is consistent with a structure in which all six of the amino groups from three molecules of I are octahedrally coordinated with sodium.

Finally, it is significant that the *meso* isomer of I does not precipitate sodium chloride. A coordination structure in which I acts as a bidentate requires that it be in an eclipsed conformation. The apparent inability of the *meso* isomer to coordinate may be due to the higher energy of its eclipsed conformer compared to that of the racemate.

We have also found that good yields of crystalline adducts are formed with sodium bromide, iodide, nitrate, and azide, but not with sodium carbonate, sulfate, sulfide, or acetate. Certain halides of potassium, rubidium, and cesium, but not calcium or barium, also form adducts with I and will be discussed elsewhere.

**Acknowledgment.** We wish to thank the Research Corporation for a Frederick Gardner Cottrell Grant in support of this work and Professor D. P. Miller for the X-ray examination.

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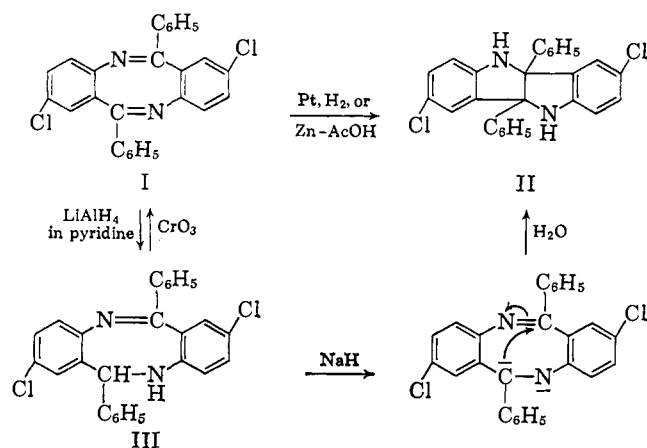
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Received December 4, 1965

### Transannular Reactions in the Dibenzodiazocine Series

Sir:

We wish to report the formation of compounds of the indoloindole type II from the dibenzodiazocine I. Compound I, mp 217–219° (Anal. Calcd for  $C_{26}H_{18}Cl_2N_2$ : C, 73.08; H, 3.77; N, 6.56; mol wt, 427.3. Found: C, 73.37; H, 3.86; N, 6.75; mol wt, 445, by thermoosmosis),  $\lambda_{max}$  (2-propanol) 260 ( $\epsilon$  38,000), shoulder at approximately 320  $m\mu$  ( $\epsilon$  6,000), was obtained from the corresponding *o*-aminobenzophenone in almost 90% yield on treatment with Lewis acids in inert solvents.<sup>1</sup>



When compound I was hydrogenated (Pt, 25°, 1 atm) in acetic acid containing hydrogen chloride, only 1 mole of hydrogen was consumed. A product (II), mp 228–230°, was isolated in 88% yield and was stable

(1) A. Sondheimer, *Chem. Ber.*, **29**, 1272 (1896), described the preparation of diphenyldibenzodiazocine by heating 2-aminobenzophenone hydrochloride. A general method for the preparation of I and various analogs in good yields will be published shortly.

to further hydrogenation. The same product was obtained on reduction of I with zinc in acetic acid. Its nmr spectrum in THF- $d_6$  showed two exchangeable protons ( $\delta = 6.23$  ppm) but no indication of aliphatic protons. It is, therefore, proposed that this product was formed by a transannular ring closure and possesses structure II,  $\lambda_{max}$  (2-propanol) 248 ( $\epsilon$  25,000) and 315  $m\mu$  ( $\epsilon$  5500). Anal. Calcd for  $C_{26}H_{18}Cl_2N_2$ : C, 72.73; H, 4.22; Cl, 16.52. Found: C, 72.62; H, 4.37; Cl, 16.30. The relative position of the phenyl groups is assumed to be *cis* because of the steric requirements for the ring junctions. As expected, a diacetyl derivative, mp 299–301°, was formed with acetic anhydride and boron fluoride.

Reduction of I with lithium aluminum hydride in pyridine gave the isomeric dihydro derivative III in 78% yield;  $\lambda_{max}$  (2-propanol) 257 ( $\epsilon$  30,000) and 320  $m\mu$  ( $\epsilon$  5000). Anal. Found: C, 72.92; H, 4.42; Cl, 16.39. This compound formed a monoacetyl derivative. The structure of III was proved by re-oxidation to the starting material I and by further reduction to a pair of diastereomeric tetrahydro derivatives of I which will be discussed in detail in a forthcoming publication.

It was found that compound III, by treatment with sodium hydride (2 equiv) in dimethylformamide and subsequent work-up, gave II in 88% yield. This transannular carbanion rearrangement constitutes an alternate route to compounds of type II and offers additional proof for the indoloindole structure. That this is a general reaction for the dihydrodibenzodiazocine ring was shown by the fact that the N-methyl derivative of III also gave the corresponding mono-N-methyl analog of II under the same conditions.

**Acknowledgments.** The authors wish to thank Professors G. Büchi and W. G. Dauben for valuable discussions.

(2) The nmr spectra were taken by Dr. E. Billeter using a Varian A-60 spectrometer at 60 Mc/sec.

(3) Originally submitted in this form on April 9, 1964.

Werner Metlesics, Leo H. Sternbach

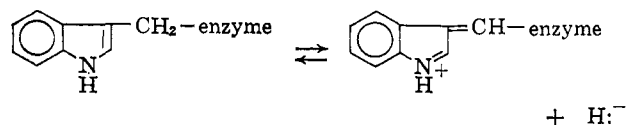
Department of Chemical Research, Research Division  
Hoffmann-La Roche, Inc., Nutley 10, New Jersey

Received February 3, 1966<sup>3</sup>

### Reactions of an Indolenine Salt as a Possible Model for Dehydrogenase Enzymes<sup>1</sup>

Sir:

Studies of the mechanism of hydrogen transfer catalyzed by yeast alcohol dehydrogenase had led to the hypothesis that a tryptophan residue participated in the enzymatic reaction by means of a reversible dehydrogenation to an indolenine salt (3H-indolylidene-methane).



The evidence for this hypothesis consisted in the finding of tritium-labeled transferred hydrogen in the meth-

(1) Supported by Research Grant GM-11799 from the National Institutes of Health.