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.

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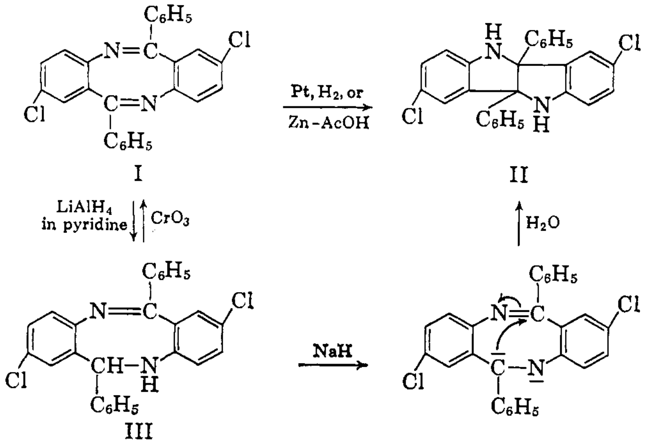
Transannular Reactions in the Dibenzodiazocine Series

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 $C_{26}H_{16}Cl_2N_2$: 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), λ_{max} (2-propanol) 260 (ϵ 38,000), shoulder at approximately 320 mμ (ϵ 6,000), was obtained from the corresponding *o*-aminobenzophenone in almost 90% yield on treatment with Lewis acids in inert solvents.[1]



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 to further hydrogenation. The same product was obtained on reduction of I with zinc in acetic acid. Its nmr spectrum in THF-d_8[2] showed two exchangeable protons (δ = 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, λ_{max} (2-propanol) 248 (ϵ 25,000) and 315 mμ (ϵ 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; λ_{max} (2-propanol) 257 (ϵ 30,000) and 320 mμ (ϵ 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 reoxidation 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.

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[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.

[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.

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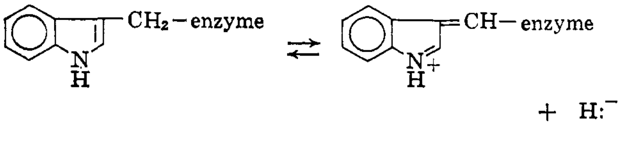
Reactions of an Indolenine Salt as a Possible Model for Dehydrogenase Enzymes[1]

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-indolylidenemethane).



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

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[1] Supported by Research Grant GM-11799 from the National Institutes of Health.