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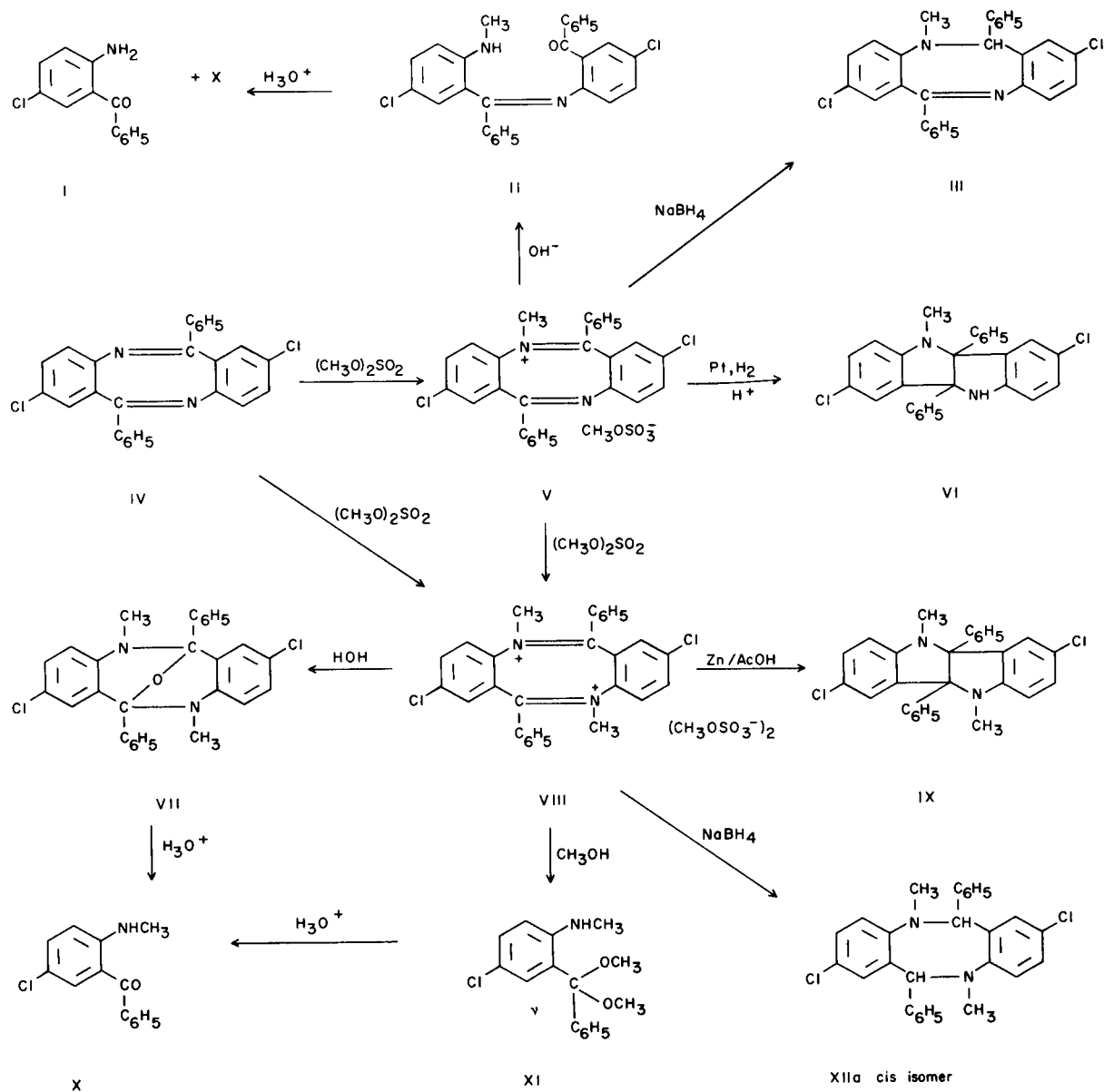
Transannular Reactions of Imonium Salts of  
2,8-Dichloro-6,12-diphenyl[*b,f*] [1,5] dibenzodiazocine

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The observation of transannular reactions (1) of the 1,5-dibenzodiazocine (IV) (2) led us to study the quaternization of this compound and the reduction of the resulting imonium salts.

The methosulfate (V) was obtained from the reaction of IV and dimethylsulfate in over 70% yield. This product

was found to be stable under anhydrous conditions and showed the expected reactions. Aqueous base caused instantaneous hydrolysis to the Schiff base (II) which on further acidic hydrolysis gave 2-amino-5-chlorobenzophenone (I) and its *N*-methyl derivative (X) in a ratio of 1:1. Reduction of V with sodium borohydride resulted in the



formation of the partially hydrogenated dibenzodiazocine (III) which had formerly been prepared by a different method (3). The latter compound has previously been rearranged to the indoloindole (VI) which was now found to be the major product obtained by catalytic hydrogenation of V using platinum in acetic acid.

Further methylation of V with dimethylsulfate or treatment of IV with a large excess of dimethylsulfate gave the diquaternary compound (VIII). This product was obtained in crystalline form, but was extremely sensitive to moisture and was, therefore, used without purification for further reactions. With zinc in acetic acid the dimethylated indoloindole derivative (IX) was obtained which had formerly been prepared by further methylation of VI (3). Reduction of VIII with sodium borohydride in tetrahydrofuran gave a mixture of the *cis* and *trans*-tetrahydrodimethyldiphenyldibenzodiazocines (XIIa and XIIb). The ratio of the two isomers was determined as *cis:trans* 6:1 by vapor phase chromatography. Preparation and proof of stereochemistry of these two products has been described previously (3).

On hydrolyzing VIII in aqueous methanol the main crop was not the expected 5-chloro-2-methylaminobenzophenone (X) but a higher melting compound VII which was recognized as the product of a transannular addition of water (4). Further hydrolysis of VII with hydrochloric acid gave a quantitative yield of X. Solvolysis of VIII in methanol gave the unstable ketal (XI) which was very readily hydrolyzed to the ketone (X).

#### EXPERIMENTAL (5)

5-Chloro-2-[1(5-chloro-2-methylaminophenyl)-1-phenylmethyl]benzophenone (II).

To a stirred, ice cold solution of 500 ml. of aqueous 1 *N* sodium hydroxide was added 80 g. (0.14 mole) of V in small portions. After 2 hours stirring the suspension was extracted with methylene chloride, the extract was washed with water, dried and concentrated after addition of ethanol. Yellow needles (64.5 g., 97%) were obtained which melted at 148-151°. Ultraviolet maxima (propanol-2) at 247  $m\mu$  ( $\epsilon = 48,000$ ), 325  $m\mu$  ( $\epsilon = 4,500$ ) and 407  $m\mu$  ( $\epsilon = 7,000$ ); infrared absorption (chloroform) at 1660  $cm^{-1}$  (C=O).

*Anal.* Calcd. for  $C_{27}H_{20}Cl_2N_2O$ : C, 70.59; H, 4.39. Found: C, 70.41; H, 4.25.

Compound II (2 g.) was hydrolyzed by refluxing for 5 hours with a mixture of 30 ml. of methanol and 10 ml. of 20% aqueous hydrochloric acid. A mixture of 2-amino-5-chlorobenzophenone (I) (6) and 5-chloro-2-methylaminobenzophenone (X) (7) was isolated melting at 68-72°. The mixture melting point between this sample and an artificial mixture of I and X was undepressed. Vapor phase chromatography showed the hydrolysis product to contain I and X in the ratio of 1:1.

2,8-Dichloro-5,6-dihydro-5-methyl-6,12-diphenyldibenzo[*b,f*]-[1,5]diazocine (III).

To a stirred, ice cold suspension of 82.3 g. (0.149 mole) of V in 800 ml. of ethanol was added 8.2 g. (0.22 mole) of sodium boro-

hydride. After stirring for 1 hour at 25°, 750 ml. of water was added slowly and the mixture was left at 25° for 16 hours. A yellow precipitate was collected and dissolved in methylene chloride. Addition of ethanol and concentration gave 36.7 g. (55.5%) of pale yellow prisms of III melting at 181-184° (3).

2,8-Dichloro-5-methyl-6,12-diphenyldibenzo[*b,f*][1,5]diazocinium Methosulfate (V).

A solution of 86 g. (0.2 mole) of IV (2) in 450 ml. of benzene and 50 ml. (0.54 mole) of dimethyl sulfate was refluxed for 16 hours. On cooling yellow prisms precipitated which were collected and washed with benzene. Recrystallization from a mixture of methylene chloride and ether gave 82.3 g. (74%) of tan prisms melting at *ca.* 190-205° (dec.); ultraviolet maximum (methylene chloride) at 269  $m\mu$  ( $\epsilon = 27,000$ ).

*Anal.* Calcd. for  $C_{28}H_{22}Cl_2N_2O_4S$ : C, 60.76; H, 4.01; OCH<sub>3</sub>, 5.61. Found: C, 60.97; H, 4.25; OCH<sub>3</sub>, 5.43.

3,8-Dichloro-4b,5,9b,10-tetrahydro-5-methyl-4b,9b-diphenyldibenzo[3,2-*b*]indole (VI).

A solution of 81.7 g. (0.147 mole) of V in 700 ml. of acetic acid containing *ca.* 25 g. of hydrogen chloride was hydrogenated at 25° and 1 atm. using 2 g. of platinum oxide as catalyst. During the reaction a white salt precipitated from the solution and the uptake of hydrogen stopped at *ca.* 4,900 ml. The precipitate was filtered from the solution and washed with acetic acid. The filter cake was suspended in ice water, made alkaline with ammonia and extracted with methylene chloride. The extract was dried, concentrated and on addition of ether gave 46.2 g. (70%) of white prisms (VI) melting at 229-231° (3).

2,8-Dichloro-5,11-dimethyl-6,12-epoxy-5,6,11,12-tetrahydro-6,12-diphenyldibenzo[*b,f*][1,5]diazocine (VII).

A solution of 5.1 g. (0.0075 mole) of VIII in 40 ml. of methanol containing 0.14 ml. (0.0078 mole) of water was stirred for 5 hours at 25°. A crystalline precipitate was collected and after recrystallization from a mixture of methylene chloride and methanol gave 2.5 g. (70%) of pale yellow prisms melting at 256-258°. Ultraviolet maxima (propanol-2) at 253  $m\mu$  ( $\epsilon = 21,800$ ) and 311  $m\mu$  ( $\epsilon = 3,800$ ).

*Anal.* Calcd. for  $C_{28}H_{22}Cl_2N_2O$ : C, 71.04; H, 4.68. Found: C, 71.22; H, 4.68.

This product (0.8 g.) was hydrolyzed in a refluxing mixture of 25 ml. of ethanol and 25 ml. of 20% aqueous hydrochloric acid. The usual work-up gave 0.8 g. of X (96%) (7).

2,8-Dichloro-5,11-dimethyl-6,12-diphenyldibenzo[*b,f*][1,5]diazocinium Dimethosulfate (VIII).

A solution of 43 g. (0.1 mole) of IV was refluxed in a mixture of 100 ml. of dimethylsulfate and 20 ml. of benzene for 10 minutes. Another 80 ml. of benzene was added and the refluxing was continued for 2 hours. On cooling a crystalline precipitate was obtained. The dark supernatant solution was removed under exclusion of moisture and the precipitate was washed twice with dry benzene to yield 9.6 g. (14%) of tan prisms melting at 146° (dec.) Owing to the extreme sensitivity to moisture this compound was used for further reactions without recrystallization.

*Anal.* Calcd. for  $C_{30}H_{28}Cl_2N_2O_8S_2$ : S, 9.44. Found: S, 9.68.

The same product was obtained on refluxing V in 2:1 mixture of dimethylsulfate and benzene.

3,8-Dichloro-4b,5,9b,10-tetrahydro-5,10-dimethyl-4b,9b-diphenyldibenzo[3,2-*b*]indole (IX).

To a suspension of 10 g. of zinc dust in 50 ml. of acetic acid was added 2.5 g. of VIII. The mixture was stirred for 2 hours at 25°, poured into ice water, made alkaline and extracted with ether. The

extract was concentrated to give a crystalline crop which after recrystallization from a mixture of methylene chloride and methanol yielded 1.2 g. (68%) of white prisms of IX melting at 261-263° (3).

#### 5-Chloro-2-methylaminobenzophenone Dimethylacetal (XI).

A solution of 1.4 g. of VIII in 50 ml. of methanol was refluxed for 1 hour. The red solution was poured into aqueous sodium carbonate solution. Extraction with ether gave colorless crystals which after recrystallization from a mixture of methylene chloride and methanol melted at 132-134°; yield 0.4 g. (30%); ultraviolet maxima (propanol-2) at 255  $m\mu$  ( $\epsilon = 14,600$ ) and 317  $m\mu$  ( $\epsilon = 3,500$ ).

*Anal.* Calcd. for  $C_{16}H_{18}ClNO_2$ : C, 65.86; H, 6.22. Found: C, 65.65; H, 6.45.

A sample of XI was heated in 20% aqueous hydrochloric acid on a steam bath for 5 minutes and gave a quantitative yield of X (7).

*cis* and *trans*-2,8-Dichloro-5,6,11,12-tetrahydro-6,12-diphenyldibenzo[*b,f*][1,5]diazocine (XIIa, XIIb).

A stirred solution of 0.5 g. of sodium borohydride in 25 ml. of tetrahydrofuran was cooled in an ice bath and 2.5 g. of VIII was added. The solution was kept at 25° for 1 hour and poured into water. A crystalline precipitate (1.3 g., 77%) was obtained which was shown by vapor phase chromatography (1% polyethylene glycol 20 M on Chromosorb W at 250°,  $N_2$  at 100 ml./min.) to be a mixture of XIIa and XIIb (3) in a ratio of ca. 6:1.

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