

360. 2 : 3-Bis-*p*-dimethylaminophenylbutane-2 : 3-diol.

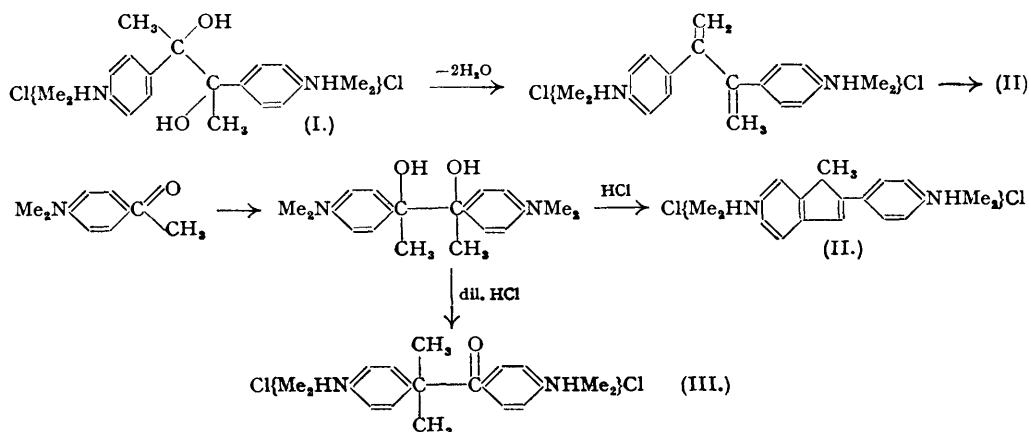
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The pinacol from *p*-dimethylaminoacetophenone was prepared by electrolytic reduction, in two forms. Treatment of either form with very dilute hydrochloric acid yielded the pinacone 1 : 2-di-*p*-dimethylaminophenyl-2-methylpropan-1-one dihydrochloride, and a more concentrated acid gave 6-dimethylamino-2-*p*-dimethylaminophenyl-3-methylindene.

RECENTLY Allen and Corwin (*J. Amer. Chem. Soc.*, 1950, **72**, 117) described the formation of 6-amino-2-*p*-aminophenyl-3-methylindene from 2 : 3-bis-*p*-aminophenylbutane-2 : 3-diol and of 6-amino-2-*p*-aminophenyl-3-ethyl-1-methylindene from 3 : 4-di-*p*-aminophenylhexane-3 : 4-diol. Indene formation occurred when the diols were treated with an excess of hydrochloric acid. In addition, the respective pinacones, 1 : 2-di-*p*-aminophenyl-2-methylpropan-1-one and 1 : 2-di-*p*-aminophenyl-2-ethylbutan-1-one were also isolated from the reaction mixtures. Attempts to obtain indenenes without pinacones by varying the concentration of acid proved unsuccessful.

In the preparation of 2 : 3-bis-*p*-dimethylaminophenylbutane-2 : 3-diol by electrolytic reduction at constant reference potential with the apparatus and cells previously described (Allen, *Analyt. Chem.*, 1950, **22**, 804; *J. Org. Chem.*, 1950, **15**, 435), an acidic medium and a reference potential of -1.5 volts gave the high-melting form of the pinacol, whereas a basic medium and a reference potential of -2.2 volts gave a low-melting form.

Treatment of either of the two stereoisomeric pinacols (I) with a quantity of dilute hydrochloric acid comparable to that which converted the pinacols of *p*-aminoacetophenone and *p*-aminopropiophenone into the respective pinacones exclusively gave in this case only the



indene (II) and in very good yield. A much smaller quantity of acid was sufficient to cause the pinacol to undergo a pinacol-pinacone rearrangement to the ketone (III). Apparently

dimethylamino-groups exert a greater influence on ring closure than do amino-groups themselves.

Application of the mechanism previously described by Allen and Corwin serves as a strict structural analogy for the formation of (II) from (I).

The ketone formed is 1 : 2-bis-*p*-dimethylaminophenyl-2-methylpropan-1-one (as III), by analogy with the ketones obtained by pinacol-pinacolone rearrangement of the aforementioned amino-pinacols, and this is confirmed by a comparison of its infra-red spectrum with that of 1 : 2-di-*p*-aminophenyl-2-methylpropan-1-one. This shift of the methyl group is consistent with previous work on symmetrical pinacols (Bachmann and Sternberger, *J. Amer. Chem. Soc.*, 1934, 56, 170; Price and Mueller, *ibid.*, 1944, 66, 634) in which it was demonstrated that the strongest electron-donating group migrates: in this case the methyl group is the strongest electron-donating group owing to the deactivating influence of the dimethylammonium substituents on the benzene ring.

EXPERIMENTAL.

M. p.s were taken on a Kofler hot stage and are corrected.

2 : 3-Bis-*p*-dimethylaminophenylbutane-2 : 3-diol.—The catholyte consisted of *p*-dimethylaminoacetophenone (8 g.) in concentrated hydrochloric acid (7.2 ml.) and distilled water (42.8 ml.). A solution of concentrated hydrochloric acid (2.8 ml.) and distilled water (17.1 ml.) served as the anolyte. At a reference potential of -1.5 v. and 27° the initial current was 4.3 amps. After 22 minutes of electrolysis a current plateau of 2.5 amps. was reached, accompanied by the evolution of hydrogen at the cathode. The catholyte was filtered, made basic to litmus with dilute aqueous sodium hydroxide, and chilled. The precipitate was filtered off, washed with water, triturated with hot 70% acetone, and refrigerated overnight. The *butanediol* was filtered off and dried (6.8 g.). Recrystallization from acetone yielded white prisms, m. p. $186.1-187^\circ$ (Found: C, 73.25; H, 8.8. $C_{20}H_{28}O_2N_2$ requires C, 73.1; H, 8.6%).

The lower-melting form of the pinacol was obtained in the following manner: *p*-Dimethylaminoacetophenone (3 g.) was dissolved in warm ethanol (48 ml.). To this was added 10% aqueous potassium hydroxide (24 ml.). The anolyte consisted of 2 : 1 ethanol-10% aqueous potassium hydroxide. At a reference potential of -2.2 v. and 32° the initial current was 3.0 amps. After 12 minutes of electrolysis a current plateau of 1.1 amps. was reached. During the reduction a precipitate formed in the catholyte, increasing in quantity as the reduction progressed. The catholyte was diluted with water (24 ml.) and refrigerated overnight. The precipitate was filtered off and dried (2.3 g.). Recrystallization from 50% ethanol yielded a *form*, m. p. $163.3-164.3^\circ$ (Found: C, 73.3; H, 8.6%).

6-Dimethylamino-2-*p*-dimethylaminophenyl-3-methylindene.—The pinacol (2 g.) was refluxed ($1\frac{1}{2}$ hours) with concentrated hydrochloric acid (7 ml.) and water (14 ml.). The solution was evaporated to dryness and the residue triturated with a small amount of absolute ethanol. The oily residue began to solidify and after addition of an equal quantity of ethyl acetate the mixture was refrigerated. The white solid was filtered off, washed with ethyl acetate-ethanol (7 : 3) and then ether, and dried (1.8 g.). The *indene* decomposed at $212-214^\circ$. Recrystallization from anhydrous *n*-propyl alcohol gave a white crystalline solid decomposing at $212-214^\circ$ (Found: C, 65.95; H, 7.2; N, 7.4. $C_{20}H_{26}N_2Cl_2$ requires C, 65.75; H, 7.2; N, 7.7%). The mother-liquors from the crystallization yielded only unidentifiable tars.

The free base was prepared from the *dihydrochloride* by neutralization of an aqueous solution. The precipitate, on crystallization from absolute methanol, yielded light yellow rosettes, m. p. $112-113^\circ$ (Found: C, 81.9; H, 8.5. $C_{20}H_{24}N_2$ requires C, 82.1; H, 8.3%).

• 2-Di-*p*-dimethylaminophenyl-2-methylpropan-1-one *Dihydrochloride*.—A sample of the pinacol (1.85 g.) was dissolved in concentrated hydrochloric acid (1.38 ml.) and water (27.75 ml.) and refluxed for 1 hour. The solution was evaporated to dryness and the solid residue triturated with absolute ethanol (5 ml.) to which was added ethyl acetate (5 ml.). The chilled solution was filtered and the precipitate washed with ether. Recrystallization from ethanol-ether yielded the *ketone* (1.65 g.), m. p. $118-119^\circ$ (Found: C, 62.9; H, 7.6. $C_{20}H_{28}ON_2Cl_2$ requires C, 62.7; H, 7.4%).

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[Received, February 19th, 1951.]