[Contribution from the Department of Chemistry, Oregon State College]

STUDIES OF THE PHOSPHORYLATION OF DIMETHYLANILINE WITH PHOSPHORUS TRICHLORIDE AND PHOSPHORUS OXYCHLORIDE[1]

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The use of dimethylaniline has been reported by Baddiley and Topham (1) to enhance markedly the chlorinating properties of phosphorus oxychloride in reactions with barbituric acid. For this reason, uric acid which is relatively difficult to chlorinate, was treated with dimethylaniline in the presence of refluxing phosphorus oxychloride; the properties of the reaction product, however, were not those of the expected derivative. Chemical analysis confirmed this opinion and the product, $C_{16}H_{21}N_2O_2P$ (m.p. 209–211°) (I), indicated that reaction had probably occurred between dimethylaniline and phosphorus oxychloride. Repeated experiments in the absence of uric acid gave the same product, although it was noted that the yield was much greater even in the presence of only catalytic amounts of uric acid.

According to the literature Bourneuf (2) had phosphorylated dimethylaniline under pressure with phosphorus oxychloride and obtained an alkali-soluble product, $C_{16}H_{21}N_2O_2P$ [m.p. 199° (capillary), 249° (block)] together with three alkali-insoluble side products, tetramethyldiaminodiphenylmethane (m.p. 90°), oxide of hexamethyltriaminotriphenylphosphine (m.p. 262°), and its hydrate (m.p. 318°). The analytical data given for the side products were very questionable, suggesting impure samples, while the position of phosphorylation in no case was determined.

Dimethylaniline has likewise been phosphorylated with phosphorus trichloride by a number of investigators (2–4) who isolated dimethylaminophenylphosphinous acid (II) from the reaction product, but in no instance established the position of phosphorylation.

Judging by the properties and the analytical data it is apparent that the product obtained in this laboratory ($C_{16}H_{21}N_2O_2P$) and that reported by Bourneuf as resulting from phosphorylation of dimethylaniline with phosphorus oxychloride were identical. However, in view of the uncertainty regarding the position of phosphorylation with both phosphorus trichloride and phosphorus oxychloride and the discrepancies in the melting point in what appears to be the same product, this problem was subjected to further investigation.

Bis(*p*-chlorophenyl)phosphinic acid was prepared by the method of Kosolapoff (5), and in turn converted to the amino derivative by well-established procedures described by Bauer (6); however conversion to the dimethylamino derivative was unsuccessful.

Attempts to prepare a Grignard reagent from *p*-bromodimethylaniline, to be

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[1] All melting points are corrected.

used as an intermediate in the preparation of I, failed. In view of these experiments, *p*-dimethylaminophenyllithium was prepared and used according to the directions of Kosolapoff (5). This intermediate reacted readily with phosphorus oxychloride to yield an alkali-soluble bis(*p*-dimethylaminophenyl)phosphinic acid (m.p. 208–210°) (Figure 1) which was judged to be identical with the original

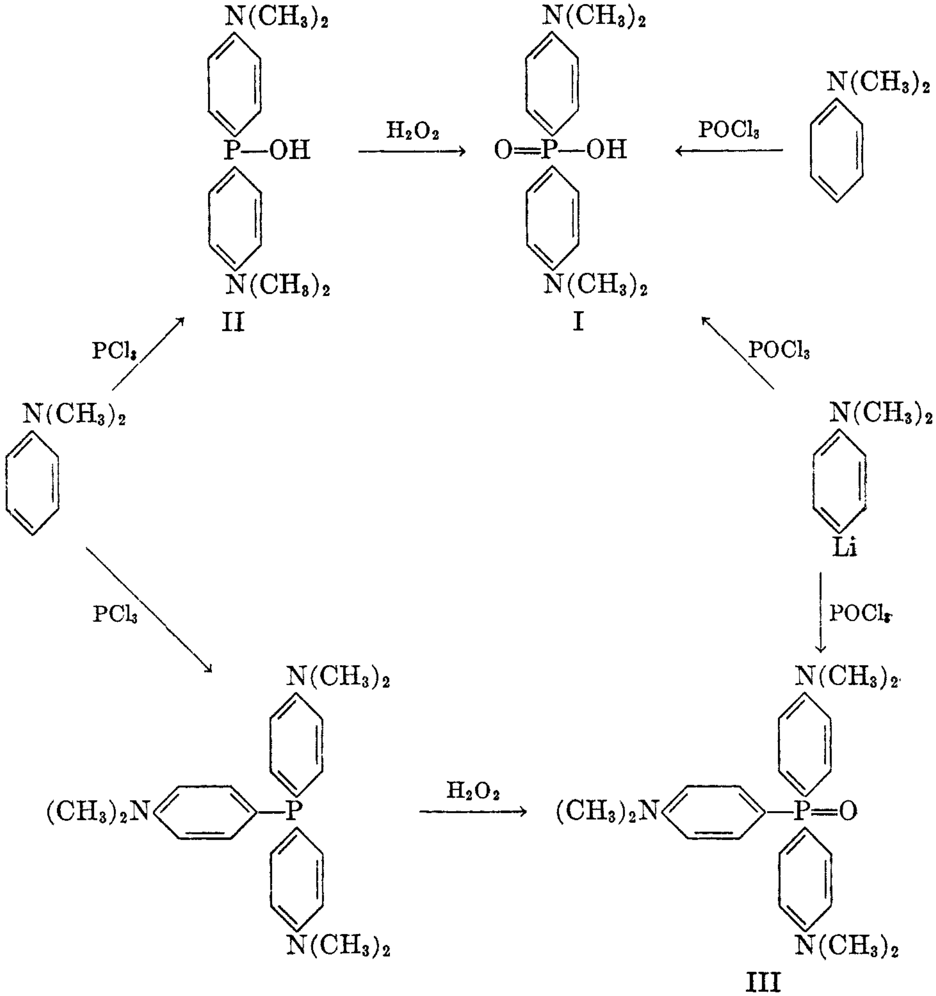

FIGURE 1. REACTION SCHEME

reaction product (I) on the basis of mixture melting points. An alkali-insoluble by-product was also isolated which on basis of synthetic and analytical data was found to be tris(*p*-dimethylaminophenyl)phosphine oxide (III), which was probably the same as the hexamethyltriaminotriphenylphosphine oxide described by Bourneuf. A similar compound had been reported by Michaelis and Soden (7), who nitrated triphenylphosphine oxide and then reduced and methylated the product to obtain a compound apparently isomeric with III as judged by its melting point.

The reaction of phosphorus trichloride and dimethylaniline as described by Bourneuf and Raudnitz was repeated. The two products bis(dimethylaminophenyl)phosphinous acid and tris(dimethylaminophenyl)phosphine were oxidized with 3% hydrogen peroxide. The two oxidation products were found to be identical with I and III respectively, thus proving that phosphorylation had again taken place in the *para* position (Figure 1).

EXPERIMENTAL[2]

Bis(p-dimethylaminophenylphosphinic acid. Redistilled phosphorus oxychloride (80 g.) and 40 g. of dimethylaniline were refluxed in the absence of moisture for 36 hours. The excess phosphorus oxychloride was removed under reduced pressure, the residue treated with 150–200 ml. of water, made alkaline with 6 *N* sodium hydroxide, and extracted with two 200-ml. portions of ether to remove unreacted dimethylaniline. The aqueous fraction was acidified with glacial acetic acid; crystallization was completed in approximately 12 hours; yield, 8.6 g. (17.1%), m.p. 206–208°. The crude product was treated with a small amount of Norit in a hot ethanol-water mixture, cooled, and recrystallized; yield, 8.1 g. of colorless plates, m.p. 209–211°.

When the above operations were repeated under identical conditions except for the addition of 0.2 g. of uric acid and a reaction time of 20 hours, the yield was 16.1 g. (32%), m.p. 209–211°.

Anal. Calc'd for $C_{16}H_{21}N_2O_2P$: C, 63.2; H, 6.96; N, 9.20, P, 10.2.
Found: C, 63.0; H, 6.83; N, 9.27; P, 10.15.

Method two. One gram of lithium shot was placed in a three-necked 500-ml. flask containing 50 ml. of anhydrous ether and equipped with a separatory-funnel, stirrer, and a reflux condenser having a moisture-protected outlet. The ether was brought to a gentle reflux and 60 ml. of an anhydrous ethereal solution containing 12 g. of *p*-bromodimethylaniline was slowly added over a period of two hours. The solution was refluxed two additional hours and transferred to a separatory-funnel.

An ice-cold solution (200 ml.) containing 9.0 g. of phosphorus oxychloride in ether was placed in the reaction flask which was now maintained at 0°. The solution of *p*-dimethylaminophenyllithium was added dropwise with stirring over a period of one hour. After two more hours of stirring at 0°, 125 ml. of 3 *N* sodium hydroxide was slowly added; the solid matter was removed and *set aside.* After separation of the ether layer, the aqueous basic solution was acidified with glacial acetic acid and set aside in a refrigerator. A crude precipitate of 1.07 g. (11.7%) of bis(*p*-dimethylaminophenyl)phosphinic acid was obtained; m.p. 207–209°. Recrystallization from isopropyl alcohol gave m.p. 208–210°. Mixture melting point of this compound and I gave no depression.

Tris(p-dimethylaminophenyl)phosphine oxide. The alkali-insoluble material obtained in the previous experiment was repeatedly washed with small portions of cold water and then recrystallized from ethanol-water mixtures; yield, 4.1 g. (50.4%), m.p. 301–306°. Recrystallization from ethanol gave m.p. 305–306° which could not be raised.

Anal. Calc'd for $C_{24}H_{30}N_3OP$: N, 10.31. Found: N, 10.52, 10.27.

Oxidation of bis(p-dimethylaminophenyl)phosphinous acid. One gram of the acid (2) was suspended in 40 ml. of 3% hydrogen peroxide and sufficient sulfuric acid was added to effect solution. The solution was then heated just below the boiling point for five minutes,

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cooled, and treated with 6 *N* sodium hydroxide until the precipitate which *first formed* was dissolved. An alkali-insoluble fraction was removed; yield, 0.1 g. m.p. 294–296° [probably impure tris(*p*-dimethylaminophenyl)phosphine oxide]. The filtrate was acidified with glacial acetic acid, cooled, and filtered; yield, 0.72 g., 68.2%. Recrystallization from an ethanol-water mixture gave a white product, bis(*p*-dimethylaminophenyl)phosphinic acid, m.p. 209–211°. Mixture melting point with I gave no depression.

Oxidation of tris(p-dimethylaminophenyl)phosphine. The phosphine (2) (0.8 g.) was oxidized under the identical conditions used for the bis compound; yield of tris(*p*-dimethylaminophenyl)phosphine oxide, 0.8 g. (95.8%); m.p. 300–301°. After several recrystallizations from ethanol-water mixtures and then ethanol this product melted at 302–303°. Mixture melting point of this compound with III (m.p. 305–306°), 305–306°.

Anal. Calc'd for $C_{24}H_{30}N_3OP$: N, 10.31. Found: N, 10.26.

Bis(p-aminophenyl)phosphinic acid. A mixture composed of 3.0 g. of bis(*p*-chlorophenyl)-phosphinic acid, 40 ml. of 28% ammonia, and 5 g. of freshly prepared cuprous oxide was placed in a high pressure bomb and heated at 155°. After 12 hours the bomb was cooled and the contents removed and filtered. The excess ammonia in the filtrate was removed by gentle heating *in vacuo.* Glacial acetic acid (5 ml.) was added to dissolve the precipitated copper hydroxides; the solution was diluted to 40 ml. and heated to boiling and the copper precipitated with hydrogen sulfide. The brown filtrate was clarified with Norit and placed in a refrigerator. An almost colorless precipitate was obtained; yield, 0.83 g. (32.4%), m.p. 233–236°. Recrystallization from glacial acetic acid gave m.p. 242–243°.

Anal. Calc'd for $C_{12}H_{13}N_2O_2P$: N, 11.75. Found: N, 11.66.

SUMMARY

The structure of bis(*p*-dimethylaminophenyl)phosphinic acid, tris(*p*-dimethylaminophenyl)phosphine oxide, bis(*p*-dimethylaminophenyl)phosphonous acid, and tris(*p*-dimethylaminophenyl)phosphine was established.

Bis(*p*-aminophenyl)phosphinic acid was prepared.

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