characteristics were: droptime, t = 5.0 sec., m = 1.468 mg./sec., $m^{2/3}t^{1/6}$ = 1.69.

The electrolysis experiments were carried out in a thermostat at 25 ± 0.05°. All volumetric apparatus was calibrated.

Materials and Medium.—The three ketones were purified by recrystallization. Melting points (uncor.) were: anthrone 154°, fluorenone 83.5°, benzophenone 48.5°.

The cell solutions were 25% ethanol by volume in the cases of benzophenone and fluorenone, and 50% ethanol by volume in the case of anthrone. The cell solutions were also 0.1 M in potassium chloride.

To obtain the desired *p*H the following aqueous solutions were used: *p*H 1, hydrochloric acid; *p*H 2 to 8, McIlvaine's buffers (0.1 M citric acid, 0.2 M disodium phosphate); *p*H 9 and 10 Clark and Lubs' buffers (0.1 M sodium hydroxide, 0.1 M boric acid); *p*H 11, sodium carbonate; *p*H 12 and 13, sodium hyroxide. Equal volumes of aqueous buffer and alcoholic solution of the ketone were mixed to form the cell solutions. Both phthalate and acetate buffers were tried in the *p*H range 4 to 5, but the curves were not as well defined as in solutions containing citrate and phosphate. Some tests were also made with fluorenone to see if increased buffer concentration affected the number of reduction waves. No effect of this nature was found.

Assuming two electrons to be consumed in the total reduction of the carbonyl group, the diffusion current constants, $i_D/C\ m^{2/3}t^{1/6}$, were: fluorenone 2.48, anthrone, 2.54 (acid solution), and benzophenone 2.60. The diffusion currents were found to be fairly constant for all three ketones, the above constants being calculated from the average of a large number of measurements. The concentrations of ketones in the cell solutions were normally between 1×10^{-4} and 1×10^{-3} molar.

Measurements of *p*H were made using a glass electrode and a Beckman Model G *p*H meter. Measurements were recorded for both the aqueous solutions and the final cell solutions containing alcohol.

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RECEIVED DECEMBER 16, 1949

Use of the Halogen–Metal Interconversion Reaction for the Preparation of an Aromatic Iodo Compound

BY HENRY GILMAN AND LAWRENCE SUMMERS[1]

The halogen–metal interconversion reaction of organolithium compounds[2]

$$RLi + R'X \rightleftarrows R'Li + RX$$

(where R and R′ = alkyl or aryl, and X = preferably I or Br) has been applied to a variety of synthetic problems during the ten years since it was first described. In the applications recorded in the literature the interconversion has been used as a means of preparing organolithium compounds not otherwise readily available, and the RX compounds have represented simply by-products. In special cases, however, the halogen–metal interconversion may offer a convenient method for the laboratory preparation of RX compounds. In this Laboratory, in connection with studies concerned with the course of some organolead reactions, a need arose for *p*-iododimethylaniline. The present note describes its preparation from *p*-dimethylaminophenyllithium and iodobenzene.

p-Iododimethylaniline has been prepared from dimethylaniline by direct iodination, and from *p*-aminodimethylaniline by diazotization followed by treatment with potassium iodide. The direct iodination has been accomplished by various methods.[3] Yields are often not mentioned in the literature. The procedure most frequently cited is that of Baeyer,[3a] who used iodine in glacial acetic acid. By this method we obtained only 13% yield, and the crude product was very dark and difficult to decolorize.[4] The best procedure described would appear to be that of Reade and Sim,[3b] who used iodine and iodic acid in glacial acetic acid, and obtained a yield which we calculate as 48%. Ayling, Gorvin and Hinkel[5] diazotized *p*-aminodimethylaniline and obtained 33% yield of *p*-iododimethylaniline by addition of potassium iodide. They note, however, that the reaction with potassium iodide proceeds very slowly, and in our experience this is also true of the diazotization, so that this method of preparation is not convenient.

p-Dimethylaminophenyllithium is easily prepared, and reacts smoothly with iodobenzene to give 42–54% yields (after recrystallization) of *p*-iododimethylaniline. Since there is no free iodine present in this reaction, the crude product has none of the deep violet color characteristic of material prepared in the presence of excess iodine, and pure white plates are obtained by a simple recrystallization without charcoal treatment. *p*-Dimethylaminophenyllithium reacts also with iodine to yield the iodo derivative,

$$p\text{-}(CH_3)_2NC_6H_4Li + I_2 \longrightarrow p\text{-}(CH_3)_2NC_6H_4I + LiI$$

and yields up to 48% have been obtained from this reaction.

Experimental

In each experiment described below, all operations up to the hydrolysis step were conducted in an atmosphere of pure dry nitrogen.

***p*-Dimethylaminophenyllithium and Iodobenzene.**—To 2 g. of lithium metal, cut into small pieces and stirred in 45 ml. of anhydrous ether, there was added a solution of 21.8 g. (0.109 mole) of *p*-bromodimethylaniline in 45 ml. of ether at such a rate that steady refluxing was maintained. After addition was complete the mixture was stirred fifteen minutes longer, then allowed to settle and decanted under nitrogen, through glass wool, into a separatory funnel. This solution of *p*-dimethylaminophenyllithium was added rapidly (without cooling, since there is very little heating effect) to a stirred solution of 44.5 g. (0.218 mole) of iodobenzene in 50 ml. of ether, and the solution was refluxed for one hour, then cooled in an ice-bath and hydrolyzed by the addition of ice-water. The ether layer was separated, washed once with water, and then extracted with

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[1] du Pont Postgraduate Fellow, 1948–1950.

[2] Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939); Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938).

[3] (a) Baeyer, *ibid.*, **38**, 2759 (1905); (b) Reade and Sim, *J. Chem. Soc.*, **125**, 157 (1924); Sandin and Williams, THIS JOURNAL, **69**, 2747 (1947), (c) Weber, *Ber.*, **10**, 765 (1877), Merz and Weith, *ibid.*, **10**, 746 (1877); Samtleben, *ibid.*, **31**, 1141 (1898); Marsden and Sutton, *J. Chem. Soc.*, 599 (1936).

[4] Militzer, Smith and Evans, THIS JOURNAL, **63**, 436 (1941), studied the direct iodination of dimethylaniline with iodine in aqueous acetic acid, but report the yield only as "very small."

[5] Ayling, Gorvin and Hinkel, *J. Chem. Soc.*, 613 (1941).

10% hydrochloric acid (three portions, 100, 50 and 50 ml.). The hydrochloric acid extract was made basic with 10% sodium hydroxide, and the precipitate filtered out. This gave 17.8 g. (66%) of apparently reasonably pure product, m. p. 75–77°, granular, light tan but with no trace of violet color. One recrystallization from 55 ml. of 95% alcohol, without charcoal, gave 13.8 g. (51%) of glistening white plates, m. p. 79–81°. From the ether extract there was recovered 21.4 g. (0.105 mole) of iodobenzene.

A check experiment, carried out in exactly the same manner, gave 68% yield of crude product and 42% of recrystallized material. Another preparation in which 87.2 g. (0.44 mole) of *p*-bromodimethylaniline was used gave 54% of recrystallized product in the first crop; by taking a second crop from the mother liquor the yield was raised to 64%.

The halogen–metal interconversion is a reversible reaction,[6] and the yield will depend on the relative concentrations of the reactants used. Another experiment was performed exactly as above except that 0.15 mole of *p*-bromodimethylaniline and 0.15 mole of iodobenzene were used. The yield of crude *p*-iododimethylaniline was 54%; of recrystallized material, 33%.

***p*-Dimethylaminophenyllithium and Iodine.**[7]—A solution of *p*-dimethylaminophenyllithium, prepared as above from 0.109 mole of *p*-bromodimethylaniline, was stirred in a 3-neck flask while a solution containing 28 g. of iodine in 200 ml. of ether was added. An ice-bath was used for cooling. As soon as the mixture became colored brown from excess iodine the addition was stopped. Color Test I[8] was negative. The mixture was hydrolyzed by addition of water, and the ether layer was separated and washed with 2% sodium sulfite solution and then with water. The product was thereafter isolated as above. The yield after the first recrystallization was 12.9 g. (48%) of material with only a light brownish color, m. p. 79–80°. Another recrystallization gave 8.5 g. (32%) of nearly white product.

In another experiment a solution of *p*-dimethylaminophenyllithium, prepared from 0.109 mole of *p*-bromodimethylaniline, was added at room temperature over a period of forty-five minutes to 55.8 g. (0.220 mole) of iodine stirred in 400 ml. of ether. The mixture was refluxed for fifteen minutes, after which Color Test I[8] was negative. The mixture was cooled and hydrolyzed, and the ether layer was separated and washed with sodium sulfite solution. The product was isolated as before. The yield of crude material was 13.9 g., m. p. 67–73°, very dark in color. Two recrystallizations, including a charcoal treatment, were necessary in order to obtain a white product, and the final yield was 19%.

These two experiments represent two sets of conditions under which the reaction with iodine may be carried out. The first experiment, in which the organolithium compound remained in excess throughout the reaction, gave the better result. No attempt was made, however, to establish the optimal conditions for this reaction.

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(6) Gilman and Jones, This Journal, **63**, 1441 (1941).

(7) See Datta and Mitter, *ibid.*, **41**, 287 (1919); Gilman and Meyers, *Rec. trav. chim.*, **45**, 314 (1926); Gilman and Thirtle, This Journal, **66**, 858 (1944).

(8) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

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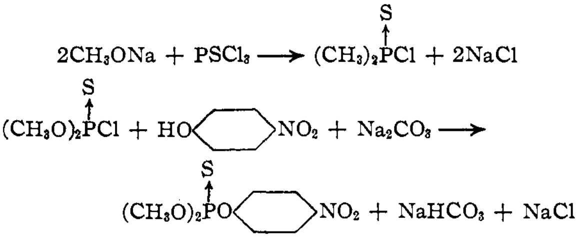
RECEIVED OCTOBER 17, 1949

Methyl Homolog of Parathion

BY S. A. HALL

O,O-Dimethyl O-*p*-nitrophenyl thiophosphate is a white crystalline compound melting at 35°. This is the methyl homolog of the new insecticide parathion, the chemical name of which is O,O-diethyl O-*p*-nitrophenyl thiophosphate.[1] The methyl homolog is insecticidal, although somewhat less potent than parathion. It has recently attracted interest, as it is being produced in Germany for insecticide formulations. It is not possible to distinguish between parathion and its methyl homolog by the analytical method of Averell and Norris,[2] since both esters gave a magenta color of nearly identical absorption peak (555 to 560 mμ). The preparation of O,O-dimethyl O-*p*-nitrophenyl thiophosphate and also a procedure of obtaining the pure crystalline ester from the technical product, a dark odorous liquid, are reported here. The reactions in its preparation are



$$2CH_3ONa + PSCl_3 \longrightarrow (CH_3)_2\overset{\overset{S}{\uparrow}}{P}Cl + 2NaCl$$

O,O-Dimethyl Chlorothiophosphate.[1]—Powdered sodium methylate 31.8 g., dissolved in 250 ml. of absolute methanol contained in a dropping funnel was added with stirring during one hour to 47.7 g. of freshly distilled thiophosphoryl chloride mixed with 100 ml. of benzene and contained in a 1-liter three-necked flask fitted with a mercury-sealed stirrer and thermometer. During the addition the reaction temperature was maintained at 0 to 5° by an ice–salt-bath. The reaction mixture was allowed to stand at room temperature for 1.5 hours and then concentrated to a thick slurry on a warm water-bath under a vacuum of 100 mm. The slurry was taken up in a mixture of 50 ml. of cold water and 150 ml. of benzene and transferred to a separatory funnel. The benzene extract was washed with cold water and then with cold saturated sodium chloride solution, dried over anhydrous sodium sulfate and filtered. Solvent was removed at the water pump at a bath temperature of 75°, and the residual oil distilled. A colorless fraction, b. p. 63–66° at 15 mm., n^{25}_D 1.4799, weighed 12.6 g., yield 28%.

Anal. Calcd. for $C_2H_6ClO_2PS$: Cl, 22.1. Found: Cl, 22.2.

O,O-Dimethyl O-*p*-nitrophenyl Thiophosphate.—*p*-Nitrophenol recrystallized from benzene 6.8 g., anhydrous sodium carbonate 5.2 g., and dried methyl ethyl ketone 25 ml. were placed in a 100 ml. two-necked flask fitted with a reflux condenser protected from atmospheric moisture, a magnetic stirrer and a dropping funnel containing 7.9 g. of dimethyl chlorothiophosphate. The acid chloride was added during 30 minutes with vigorous stirring and sufficient heating for gentle refluxing. Heating was continued for 2.5 hours after carbon dioxide evolution had ceased. Solvent was then removed under vacuum, and the residue taken up in ether and transferred to a separatory funnel. The extract was washed with water and with saturated sodium bicarbonate solution until the washings were no longer yellow, and then with saturated sodium chloride solution. In order to remove colored and odorous by-products of the reaction, the ether extract was passed through a 3-cm. column containing an adsorbent mixture, previously made wet with ether, of 2 parts Attaclay (an attapulgite clay) and 1 part Hyflo-Supercel (a diatomaceous earth) between plugs of dried cotton. Finally, the column was washed with 50 ml. of ether.

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(1) Fletcher, *et al.*, This Journal, **70**, 3943 (1948).

(2) Averell and Norris, *Anal. Chem.*, **20**, 753 (1948).