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).

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

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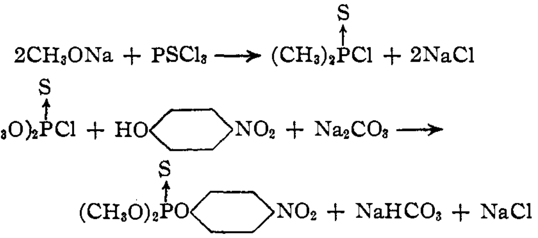
Methyl Homolog of Parathion

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



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

$$(CH_3O)_2\overset{\overset{S}{\uparrow}}{P}Cl + HO\bigcirc NO_2 + Na_2CO_3 \longrightarrow$$

$$(CH_3O)_2\overset{\overset{S}{\uparrow}}{P}O\bigcirc NO_2 + NaHCO_3 + NaCl$$

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).

The ether was removed on a warm water-bath under a stream of dried nitrogen. The pale yellow residual oil obtained weighed 8.9 g. (70% yield). The oil was cooled in a bath of dry ice and acetone. About 5 ml. of methanol was added. Scratching with a stirring rod soon induced crystallization. The white crystalline mass thus obtained was filtered at once, while cold from the yellow mother liquor. It was then recrystallized twice by dissolving in a mixture containing 40% of a petroleum ether (Skellysolve A) and 60% of methanol at room temperature and cooling to 0°. The yield was 2.3 g. of fine white odorless prisms of irregular shape, m. p. 35.3–35.6° (cor.). An additional 5 g. of crystals melting slightly lower was recovered from the mother liquors.

Anal. Calcd. for $C_8H_{10}O_5NPS$: C, 36.50; H, 3.83; N, 5.32; P, 11.8; S, 12.2. Found: C, 36.43; H, 3.79; N, 5.70; P, 11.4; S, 12.2.

Purification of Crude O,O-Dimethyl O-*p*-Nitrophenyl Thiophosphate.—A mixture of 95 g. of a crude commercial-grade product[3] in the form of a dark viscous liquid of unpleasant odor was placed in a separatory funnel and shaken with two 50-ml. portions of Skellysolve A, which separated as an upper yellow layer and was removed by pipet (toxic substance, use vacuum line) and discarded. The oil was dissolved in 150 ml. of ether and shaken repeatedly with 20-ml. portions of saturated sodium bicarbonate solution until the washings were no longer yellow. It was then washed with water and twice with saturated sodium chloride solution. When the aqueous layer was drawn off, a quantity of suspended sludge was also removed. The dark red ethereal solution was then passed, with the aid of gentle suction, through a column 5 cm. long containing an adsorbent exactly like that described above for the preparation of the synthesized ester. The column was finally washed with 75 ml. of ether. Ether was removed on a warm water (75°)-bath by use of a stream of dried nitrogen to hasten the evaporation. Avoidance of heating is important, since it was found, in a parallel experiment, that heating on the steam-bath caused the residual oil to darken. The orange-red oil, which weighed 77 g., was dissolved in an equal volume of a 40–60 mixture of Skellysolve A and methanol and chilled in the refrigerator at 0°. It was then seeded with a crystal of the pure ester and left to stand in the refrigerator overnight. A bottle of the mixed solvent was placed in the freezing compartment (−20°) of the refrigerator and used the following morning for washing the crystals. Two recrystallizations carried out in this manner yielded fine white irregular prisms melting at 35.0–35.5°. The mother liquors were worked up thus for recovery of additional material. The total yield of crystalline compound melting at 35° or slightly below from the crude starting material was about 40%.

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[3] Sample kindly supplied by R. J. Geary, Geary Chemical Corp., New York, N. Y.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND

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The Solvolysis of Triphenylmethyl Benzoate[1]

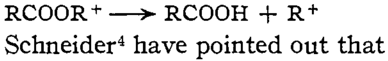
BY GEORGE S. HAMMOND AND JAMES T. RUDESILL

In their 1941 review of the mechanisms of the solvolytic reactions of carboxylic acids and their esters, Day and Ingold[1a] discussed the possibility that the rate controlling step in the reactions of certain esters might be the ionization of the neutral ester.

$$\mathrm{RCOOR} \longrightarrow \mathrm{RCOO^-} + \mathrm{R^+} \qquad (1)$$

At the time of their review there were no unambiguous examples of reactions involving this mechanism, which they designated as type B″1. It seemed possible, but not certain, that the hydrolysis of the acid phthalates of α-substituted allylic alcohols[2] with dilute base proceeded in this manner. A more clear-cut example was subsequently studied by Kenyon and his co-workers[3] who showed that the solvolysis of the esters of the optically active *p*-methoxybenzhydrols resulted in extensive racemization under all conditions studied. The results are best interpreted in terms of the B″1 mechanism.

The importance of the analogous reaction of the conjugate acids of esters is well established, and


(2)

$$\overset{\mathrm{H}}{\mathrm{RCOOR^+}} \longrightarrow \mathrm{RCOOH} + \mathrm{R^+} \qquad (2)$$

Cohen and Schneider[4] have pointed out that such a step is probably generally involved in the acid-catalyzed reactions of the esters of tertiary alcohols. They also predicted that reaction (1) would prove to be of importance in the solvolysis of the esters of polyaryl alcohols in neutral and alkaline solution.

In connection with another problem, we have had occasion to investigate the alcoholysis of triphenylmethyl benzoate. Since the stereochemical criterion used by Kenyon is not applicable in this case we have utilized a familiar kinetic approach to the study of the reaction mechanism.

In anhydrous fifty per cent. methyl ethyl ketone–ethanol solution at 55° the ester reacts at an easily measurable rate to produce benzoic acid and ethyl trityl ether. The nature of the products establishes the alkyl–oxygen bond as the point of cleavage, and the reaction is strictly unimolecular with respect to the ester, showing that catalysis by the weak acid produced in the reaction is unimportant. The rate is increased by the addition of sodium ethoxide but is increased even more by the addition of an equimolar amount of sodium perchlorate. We therefore conclude that the influence of sodium ethoxide may be attributed to a positive salt effect rather than to the incursion of a B″2 reaction between the ester and ethoxide ion.

We wished to analyze benzene solutions which contained both trityl chloride and trityl benzoate by differential alcoholysis. Therefore we solvolyzed mixtures of the two compounds in fifty per cent. benzene–ethanol. The reaction of both compounds was immeasurably rapid unless sufficient base was added to neutralize the hydrogen chloride produced in the alcoholysis of the chloride. This indicates, as would be expected, that in the presence of a strong acid a rapid reaction occurs by mechanism (2). In the presence of excess base the rate of alcoholysis of the

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[1] This research was carried out under contract number NR-056-197 with the Office of Naval Research.

[1a] Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

[2] Kenyon, *et al.*, *J. Chem. Soc.*, 85 (1936); 207 (1937); see also Balfe, Hills, Kenyon, Phillips and Platte, *ibid.*, 556 (1942).

[3] Balfe, Doughty, Kenyon and Poplett, *ibid.*, 605 (1942).

[4] Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).