# Phosphonic Acids and Esters. XVI. Formation of Dialkyl Phenylphosphonates by the Photoinitiated Phenylation of Trialkyl Phosphites[1,2]

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The photolysis of iodobenzene (5) in the presence of trialkyl phosphites (1) has been shown to yield dialkyl phenylphosphonates (8) and alkyl iodides in essentially equivalent quantities. The only important competing reaction is the ionic Michaelis–Arbuzov isomerization of 1 initiated by the attack of the alkyl iodide. Variations in reaction temperature and reactant ratio have shown that the use of excess phosphite (methyl, ethyl, *n*-butyl) at low temperatures effectively retards the ionic isomerization and allows high yields of 8 to be obtained. Thus, the photolysis of 5 in a three- to fivefold excess of trimethyl phosphite at −3° yields dimethyl phenylphosphonate in quantitative yield. The isomerization is also retarded by the use of phosphites with branched (isopropyl) alkyl groups. Bromobenzene may also be used in the photolytic phenylation of 1, although the yields are significantly lower than with 5. A mechanism has been proposed for the reaction which involves the attack of phenyl radicals on 1 to yield a phosphoranyl radical (6); a one-electron transfer from 6 to an iodine atom yields a quasi-phosphonium salt which collapses to 8 and alkyl iodide. The phosphonium salt formed by photolysis of 5 in the presence of triphenyl phosphite has been isolated. The only complicating side reaction observed in these studies is the photolytic decomposition of 8, this decomposition limits the yield of 8, but is only important in the cases of diethyl and diisopropyl phenylphosphonates at higher temperatures.

The Michaelis–Arbuzov reaction (1 → 3) constitutes one of the most general and widely applicable approaches to the formation of the esters of phosphonic acids (3) and of carbon–phosphorus bonds in general.[3]

$$P(OR)_3 + R'X + [R'P(OR)_3]^+ X^- \longrightarrow$$
$$\phantom{xxx} 1 \phantom{xxxxxxxx} 2$$
$$R'P(O)(OR)_2 + RX$$
$$\phantom{xxxxxxxxx} 3$$

However, the reaction does suffer from certain serious synthetic limitations since the halide (R'X) employed must be capable of undergoing the ionic displacement required in the first step of the reaction, *i.e.*, formation of the quasi-phosphonium intermediate (2). This limitation applies to the formation of aryl- and vinylphosphonates (3, R' = aryl, vinyl), since in the absence of an accumulation of electron acceptor groups, aryl and vinyl halides fail to undergo either SN1 or SN2 displacements. A number of methods are available for the preparation of arylphosphonates,[3,4] but none of these procedures possesses the generality of the Michaelis–Arbuzov reaction. The most critical limitations on these methods are the formation of mixtures of positional isomers in direct aromatic substitution reactions and the formation of diarylphosphinates and triarylphosphine oxides in the reactions of organometallics and diazonium salts with phosphorus halides.[4] Additionally, certain substituent groups are incompatible with the latter processes, the most useful of these synthetic procedures.

The physical properties, particularly the proton magnetic resonance[5] and ultraviolet[6] spectra, of a variety of arylphosphonyl compounds have been a primary subject of investigation in this laboratory.

As a prerequisite for certain of these studies, the development of a simple method for the preparation of a variety of nuclear substituted arylphosphonates was necessary. The basic requirements for this method were that no isomers or higher arylated products be formed and that a wide variety of nuclear substituents be tolerated.

The most promising area for investigation appeared to be the free-radical modification of the Michaelis–Arbuzov reaction. Kamai, Griffin, Crofts, and Cadogan and their co-workers[7] have shown that free radicals derived from polyhalomethanes attack trialkyl phosphites (1) to yield phosphoranyl radicals (4); these radicals react with the halomethane to yield a quasi-phosphonium salt and the halomethyl free radical in a chain propagation step. Decomposition of the salt in the normal manner yields an alkyl halide and the dialkyl halomethylphosphonate. Such a procedure

$$\cdot CX_3 + 1 \longrightarrow CX_3\dot{P}(OR)_3$$
$$4 + CX_4 \longrightarrow [CX_3P(OR)_3]^+X^- + \cdot CX_3$$

appeared to possess potential for the synthesis of arylphosphonates since it would avoid the lack of reactivity of aryl halides toward nucleophilic attack. However, certain of the conventional procedures for the generation of aryl radicals, *e.g.*, thermal decomposition of diaroyl peroxides, could not be employed in reactions with trialkyl phosphites (1) because of the susceptibility of 1 to oxidation.[7b] The most suitable method for the generation of aryl radicals in the presence of 1 appeared to be the procedure developed by Kharasch and co-workers[8] who have shown that the photolysis of aryl iodides leads to homolysis of the carbon–iodine bond; the aryl radicals formed by this procedure are effectively trapped by aromatics with the formation of biaryls in good yield. A wide range of nuclear substituted aryl iodides have been used effectively and no isomerizations have been observed.

Accordingly, an investigation of the photolysis of iodobenzene (5) in the presence of 1 has been carried out. Based on previous studies of the attack of free

(1) Part XV: W. M. Daniewski, M. Gordon, and C. E. Griffin, *J. Org. Chem.*, **31**, 2083 (1966).

(2) Preliminary communication: J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962).

(3) R. G. Harvey and E. R. De Sombre, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 57 ff.

(4) L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

(5) (a) C. E. Griffin, *Tetrahedron*, **20**, 2399 (1964); (b) C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935, 2829 (1965); (c) C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, **22**, 561 (1966); (d) M. Gordon and C. E. Griffin, *J. Org. Chem.*, **31**, 333 (1966).

(6) C. E. Griffin, R. P. Peller, K. R. Martin, and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).

(7) For a summary of these studies, see (a) ref 3, p 69–70; (b) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).

(8) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965), and earlier references.

$$C_6H_5I \xrightarrow{h\nu} C_6H_5\cdot + I\cdot$$
$$5$$

$$C_6H_5\cdot + 1 \longrightarrow C_6H_5\dot{P}(OR)_3$$
$$6$$

$$6 + I\cdot \longrightarrow [C_6H_5P(OR)_3]^+I^-$$
$$7$$

$$7 \longrightarrow C_6H_5P(O)(OR)_2 + RI$$
$$8$$

radicals on 1, the above sequence might be anticipated. In contrast to the chain process postulated for the reactions of polyhalomethanes with 1, a nonchain reaction would be anticipated for 5 since it is unlikely that 5 would function very effectively as a chain-transfer agent.[9] The postulation of formation of the quasi-phosphonium salt (7) by a one-electron transfer from 6 to the iodine atom is supported by the results of recent studies of the photolyses of triarylphosphines and arylphosphonium salts.[10] These studies have provided evidence that analogous one-electron transfers occur between polyarylphosphoranyl radicals [Ar$_4$P·, Ar$_3$(R)P·] and halogen atoms to yield phosphonium salts.

This postulated reaction sequence requires the formation of 1 equiv of alkyl iodide for each equivalent of dialkyl phenylphosphonate (8). Since the Michaelis–Arbuzov reaction is known to occur readily between 1 and RI,[3] isomerization of 1 to the corresponding dialkyl alkylphosphonate (3, R = R' = alkyl) could be anticipated to be competitive with the free-radical phenylation of 1. Additionally, it has been shown that the ultraviolet irradiation of trialkyl phosphites in the absence of added species results in a relatively slow isomerization of the phosphite to the corresponding 3.[11] Consequently, any reaction between 1 and 5 would have to be conducted in a manner to minimize these side reactions since such reactions would consume 1 and decrease the probability of formation of 8. In this respect, the reaction of 1 and 5 should be sensitive to (a) variations in the structure of 1, (b) reaction temperature, and (c) reactant ratio.

Initial experiments were conducted with 1:1 ratios of reactants in order to determine reaction feasibility and to examine the effects of variables a and b. Irradiations were carried out in a quartz apparatus using a 450-w high pressure mercury lamp; the reaction mixtures were maintained at constant temperature under an atmosphere of nitrogen.[12] The results of these experiments are presented in Table I and indicate that the basic premise on which this study was founded is correct. The products obtained in the reaction are those anticipated on the basis of the postulated

(9) In support of this postulation, evidence has been obtained (J. B. Plumb and C. E. Griffin, unpublished results) that the analogous reaction of 5 and triphenylphosphine[2] is nonchain in character and proceeds by attack of the phosphine on the radical pair [C$_6$H$_5$·I·]. Studies of the mechanism of the reaction of 5 and 1 are in progress and preliminary results support the mechanistic sequence outlined above.

(10) L. Horner and J. Dörges, *Tetrahedron Letters*, 763 (1965); M. L. Kaufman and C. E. Griffin, *ibid.*, 769 (1965); C. E. Griffin and M. L. Kaufman, *ibid.*, 773 (1965).

(11) R. B. LaCount and C. E. Griffin, *ibid.*, 3071 (1965).

(12) Reactions carried out in the presence of air resulted in a significant degree of oxidation of 1 to the corresponding phosphate. The photoinitiated oxidation of 1 has been reported [J. I. G. Cadogan, M. Cameron-Wood and W. G. Foster, *J. Chem. Soc.*, 2549 (1963); J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, 28, 2908 (1963)]. The formation of the phosphate has relatively little effect on the over-all yield of 8, but does complicate the isolation procedure.

$$\underset{5}{C_6H_5I} + \underset{1}{P(OR)_3} \xrightarrow{h\nu} \underset{8}{C_6H_5P(O)(OR)_2} + \underset{3}{RP(O)(OR)_2} + RI$$

| Expt no. | R | Temp, °C | Reaction time, hr. | % products[b] | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | 8 | 3 | RI | 5 | C$_6$H$_6$[c] |
| 1 | CH$_3$ | -3 | 24 | 40.5 | 55.2 | ...[d] | 40.5 | 81.0 |
| 2 | | -3 | 13 | 40.2 | 50.0 | ... | 42.0 | 82.2 |
| 3 | | 25 | 13 | 26.0 | 66.5 | ... | 46.5 | 72.5 |
| 4 | | 99 | 24 | 0.4 | 99.6 | ... | ... | ... |
| 5 | C$_2$H$_5$ | -3 | 24 | 35.3 | 0 | ...[d] | 56.7 | 92.0 |
| 6 | | 25 | 24 | 37.5 | 0 | ... | 52.0 | 89.5 |
| 7 | | 38 | 25 | 37.5 | 0 | ... | 50.1 | 87.6 |
| 8 | | 43 | 24 | 38.0 | 0 | ... | 44.0 | 82.0 |
| 9 | | 58 | 24 | 28.5 | 1.8 | ... | 51.1 | 79.6 |
| 10 | | 90 | 24 | 20.0 | 4.5 | ... | 57.3 | 77.3 |
| 11 | n-C$_4$H$_9$ | 0 | 18 | 31.0 | 0.1 | 18.4 | 65.0 | 96.0 |
| 12 | | 25 | 18 | 36.0 | <0.1 | 31.3 | 60.4 | 96.4 |
| 13 | | 57 | 25 | 37.5 | 3.3 | 38.1 | 58.0 | 95.5 |
| 14 | | 87 | 24 | 31.0 | 29.5 | 35.0 | 66.2 | 97.2 |
| 15 | i-C$_3$H$_7$ | -3 | 19 | 29.2 | 0 | 21.2 | 62.5 | 91.7 |
| 16 | | 8 | 24 | 22.7 | 0 | 28.8 | 68.3 | 91.1 |
| 17 | | 23 | 19 | 18.8 | 0 | 30.0 | 61.0 | 79.8 |
| 18 | | 50 | 19 | 11.6 | 0 | 38.2 | 56.3 | 67.9 |

reaction sequence and, under appropriate conditions (expt 1, 2, 5–8, 12, 13, and 15), moderate yields of the dialkyl phenylphosphonate (8) can be obtained. Only trace amounts of products other than those listed in Table I were observed during glpc analyses, indicating that 1 is a very effective trap for phenyl radicals generated under these conditions.[13] The effects on the yield of 8 of changes in reaction temperature and nature of the trialkyl phosphite are readily rationalized on the basis of the probable mechanism of the reaction. Lowering the reaction temperature produces a retardation of the rate of the ionic Michaelis–Arbuzov process leading to the formation of 3 (e.g., expt 1–4, 8–10, and 11–14) and allows the free-radical phenylation of 1 to complete more effectively. It would be anticipated that the ionic reaction would be the more susceptible to thermal effects.[3] This interpretation is supported by the results of control experiments. Both photoinitiated and dark reactions of (RO)$_3$P and RI (R = C$_2$H$_5$, n-C$_4$H$_9$, i-C$_3$H$_7$) at 0–50° for 18–24 hr gave only trace amounts of the dialkyl alkylphosphonate (3). The analogous control reaction of methyl iodide and trimethyl phosphite gave dimethyl methylphosphonate in yields comparable with those listed in Table I under the conditions of expt 1–4.[14] Lastly, the results obtained by changes in

(13) The photolysis of neat iodobenzene under the conditions of the reaction of 1 and 5 was carried out as a control; trace amounts (0.05–0.15%) of benzene, biphenyl and the isomeric iodobiphenyls were detected [see J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 1788 (1960)]. Of these products, only biphenyl could be detected in even trace amounts in the reactions of 1 and 5. No evidence for the formation of products arising from the attack of phenyl radicals on 8 was ever obtained.

(14) The irradiated reactions of methyl iodide and trimethyl phosphite at low temperatures (0–25°) gave somewhat higher yields of dimethyl methylphosphonate than did dark reactions. This observation suggests that either the Michaelis–Arbuzov reaction of these reagents is capable of photoinitiation or that the photoinitiated isomerization[11] of trimethyl phosphite is proceeding at an appreciable rate under these conditions. For the other phosphites of Table I, photoinitiated isomerization does not constitute a side reaction of any apparent importance.

the nature of the alkyl group of 1 (e.g., expt 1, 5, 11 and 9, 13, 18) reflect the well-known degree of susceptibility of the corresponding alkyl iodides to SN2 displacement.[3,15] For triisopropyl phosphite, the Michaelis–Arbuzov isomerization is not an important competing process even at 50°; this isomerization remains an important competitive reaction even at −3° for trimethyl phosphite.

In general, the material balances and correspondences between yields of products (e.g., 8 and RI in expt 12–14) are good and in accord with expectation. However, in certain of the higher temperature reactions (e.g., expt 17 and 18) the mass balance is poor and the observed yield of 8 is lower than would be anticipated on the basis of the yield of RI. These observations suggested that 8 may possess some degree of photolytic instability under the conditions of these reactions. In order to substantiate this explanation, a sample of diisopropyl phenylphosphonate (8, R = i-C₃H₇) was irradiated at 70° for 19 hr; 47% of the phosphonate was converted to other products in this reaction. Similarly, irradiation of a 30% solution of this phosphonate in triisopropyl phosphite for 19 hr at 80° led to 43% decomposition. The nature of the photolysis products has not been determined. A similar photochemical instability of dimethyl methylphosphonate has been reported;[11] carbon dioxide, methane, ethane, propane, and a complex mixture of high molecular weight products were observed. These findings indicate that the reaction times of Table I are not optimal (i.e., expt 1 and 2). However, the results obtained from use of higher [1]/[5] ratios (Table II) partially obviate the necessity for determination of optimum reaction times.

A number of control reactions of 1 and 5 were carried out. No detectable formation of 8 was observed in either dark reactions or in irradiation reactions using Pyrex apparatus. Results comparable with those cited in Table I were obtained by irradiation using Vycor filters.

Since the yields of 8 which were obtained employing 1:1 ratios of 1 and 5 were modest, a series of experiments (Table II) were conducted employing excess amounts of 1. For each of the phosphites examined, an increase in the ratio [1]/[5] from 1.0 to 2.0 produced a significant (46–93%) increase in the yield of 8; for trimethyl phosphite, quantitative yields of 8 could be obtained by the use of three- to fivefold excesses of phosphite. These results illustrate in a convincing manner the synthetic potential of this reaction. In preparative reactions carried out subsequent to this study, three- to fivefold excesses of trialkyl phosphites have been employed routinely and high isolated yields of the appropriate 8 have been obtained. Nuclear substituted (carboxy, carboalkoxy, formyl, alkyl, alkoxy, amino, hydroxy, halo)[5c,16] phenyl and other aryl (naphthyl, thienyl, furyl)[16c] phosphonates have been prepared satisfactorily. Vinyl iodides have also been shown to undergo photolysis with the formation of dialkyl vinylphosphonates.[17]

In a number of cases, aryl bromides are more readily available than the corresponding iodides and, consequently, the synthetic potential of this reaction would be increased if phenylation of 1 with bromobenzene (9) proved to be feasible. Although no convincing demonstration of the formation of phenyl radicals from 9 by ultraviolet photolysis has been reported, the initiation of this process by γ irradiation has been demonstrated.[18] Accordingly, a 1:1 mixture of 9 and triethyl phosphite was irradiated at −3° for 24 hr to give diethyl phenylphosphonate (23%) and ethyl bromide (27%); a 61% recovery of 9 was achieved. The comparable reaction (Table I, expt 5) with 5 gave a 35% yield of the phenylphosphonate. Under identical reaction conditions, a 1:1:1 mixture of 9, 5 and triethyl phosphite gave the phenylphosphonate (35.5%), 9 (86%), and 5 (52%). These results indicate that aryl bromides may be used effectively for the phenylation of 1, but that their order of reactivity is appreciably lower than that of the aryl iodides.

In addition to the results of temperature, reactant ratio and phosphite structure variations, the postulated mechanism for the reaction of 1 and 5 is further supported by the isolation of a quasi-phosphonium salt (7) in one instance. Such salts have been isolated previously in Michaelis–Arbuzov reactions by the use of triphenyl phosphite; salts derived from this phosphite cannot undergo the displacement reaction (7 → 8) and are, consequently, relatively stable.[3] Irradiation of a 1:1 mixture of 5 and triphenyl phosphite for 24 hr at 60° gave 7 (R = C₆H₅) in 8.1% yield. The salt was extremely hygroscopic, but satisfactory elemental analyses were obtained; alkaline hydrolysis gave diphenyl phenylphosphonate and phenol. The yield of phenylation product in this reaction is considerably lower than that obtained from triethyl phosphite under similar conditions. Walling and Pearson[19] have shown triphenyl phosphite to be significantly less susceptible to attack by thiyl and alkoxyl radicals than is triethyl phosphite.

(15) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 12.

(16) (a) M. Gordon, V. A. Notaro, and C. E. Griffin, J. Am. Chem. Soc. 86, 1898 (1964); (b) V. A. Notaro, Ph.D. Thesis, University of Pittsburgh, 1965; (c) R. Obrycki and C. E. Griffin, unpublished results.

(17) W. M. Daniewski, M. Gordon and C. E. Griffin, J. Org. Chem., submitted.

(18) A. F. Everard, J. D. Parrack, G. A. Swan and P. S. Timmons, J. Chem. Soc., 905 (1962); S. U. Choi and J. E. Willard, J. Phys. Chem., 66, 1041 (1962).

(19) C. Walling and M. S. Pearson, J. Am. Chem. Soc., 86, 2262 (1964).

## Experimental Section

**General Procedure for Photoinitiated Phenylation of Trialkyl Phosphites.**—A weighed solution of iodobenzene (0.2–0.6 mole) in a 1.0–5.0 $M$ excess of the appropriate trialkyl phosphite (total volume of solution 5–15 ml) was flushed with dry nitrogen and placed in the inner tube of the photolysis vessel. This vessel consisted of a flat-bottomed inner tube (2.7 × 13.0 cm) fitted with a 24–40 outer joint with a jacket (3.5 × 14.5 cm) for circulating coolant; the entire vessel was fabricated of silica. A constant temperature ($\pm 1°$ at $T < 50°$; $\pm 2°$ at $T > 50°$) was maintained during the irradiation by circulation of 95% ethanol from a thermostatically controlled refrigeration unit through the outer jacket. The inner tube was fitted with a water-cooled condenser protected with a calcium chloride drying tube. An atmosphere of nitrogen was maintained above the reaction mixture and the mixture was stirred continuously with a magnetic stirrer. The radiation source was a 450-w Hanovia (Model 679A-10) high pressure quartz mercury vapor lamp fitted with an aluminum reflector head; the lamp was placed 5 cm from the inside tube. On completion of reaction, mixtures were analyzed directly without prior treatment by gas–liquid chromatography. All other photolytic reactions were carried out employing the same apparatus and procedure.

**Gas–Liquid Chromatographic Analyses.**—All analyses were carried out on an F & M Model 300 chromatograph using the following columns and conditions: (A) 6-ft stainless steel column of 20% silicone oil 710 on 60–80 mesh Chromosorb P, injection port temperature 160°, helium flow rate 50 ml/min; (B) 6-ft copper column of 15% Carbowax 20M and 5% Carbowax 1500 on the same support, injection port temperature 245°, helium flow rate 50 ml/min. Column temperatures were programmed manually. Biphenyl was used as an internal standard for quantitative determination of yields; standard normalization techniques were employed in quantitative determinations. Typical retention times for products and reactants are listed in Table III. All peaks were identified by "spiking" with an authentic sample of the given material. Authentic samples of the dialkyl phenyl and dialkyl alkylphosphonates were prepared by standard literature methods.

**Photoinitiated Phenylation of Triphenyl Phosphite. Formation of Triphenoxy(phenyl)phosphonium Iodide.**—A solution of freshly redistilled triphenyl phosphite (10.0 g, 32.2 mmoles) and iodobenzene (6.7 g, 32.2 mmoles) was placed in a 20-ml Vycor tube; the tube was cooled to −78°, evacuated, and sealed. The tube was allowed to warm to room temperature and irradiated for 24 hr at 60° with the 450-w lamp; the tube was shaken mechanically throughout the irradiation period. The tube was cooled to room temperature and the crystals which had formed during the irradiation were removed by rapid filtration from the dark red reaction mixture. The crystalline quasi-phosphonium salt was washed with anhydrous ether and stored in a vacuum desiccator over phosphorus pentoxide. The salt must be handled rapidly since it is extremely hygroscopic; on exposure to moist air, the crystals darken rapidly and change to a brown oil. An 8.1% yield (135 mg) of the salt was obtained. The salt darkens at

#### TABLE III
GAS–LIQUID PARTITION CHROMATOGRAPHIC ANALYSES OF
IODOBENZENE–TRIALKYL PHOSPHITE PHOTOLYSIS MIXTURES[a]

| | R | | | | | |
|---|---|---|---|---|---|---|
| | CH₃ | | C₂H₅ | | $i$-C₃H₇ | $n$-C₄H₉ |
| RI | 1[b] | 1[b] | 1[b] | 1[b] | 2 | 4 |
| P(OR)₃ | 1[b] | 1[b] | 1[b] | 1[b] | 6 | 38 |
| C₆H₅I | 9 | 19 | 10 | 16 | 13 | 10 |
| RP(O)(OR)₂ | 20 | 14 | ...[c] | 17 | 21 | 55 |
| C₆H₅C₆H₅ | 36 | 46 | 30 | 40 | 32 | 42 |
| C₆H₅P(O)(OR)₂ | 40 | 82 | 42 | 66 | 38 | 77 |
| Column[a] | A | B | A | B | A | A |
| Column temp,[d] | 105 (0) | 130 (0) | 130 (0) | 125 (0) | 100 (0) | 100 (0) |
| Time, min | 175 (22) | 165 (20) | 175 (20) | 130 (9) | 170 (24) | 175 (28) |
| | | | | 170 (20) | | 200 (31) |

[a] For conditions and column descriptions, see Experimental Section. [b] Peaks inseparable under these conditions. [c] No diethyl ethylphosphonate was detected in reaction mixtures analyzed with column A. [d] Times of column temperature (°C) changes indicated in parentheses.

temperatures above 60°; the melting point is not sharp and is dependent on rate of heating, 80–88° (slow), 98–131° (rapid).

*Anal.* Calcd for $C_{24}H_{20}IO_3P$: C, 56.04; H, 3.93; I, 24.68; P, 6.02. Found: C, 56.35, 56.14; H, 4.09, 3.70; I, 24.91, 24.80; P, 6.51, 6.40.

Infrared and pmr spectra of the filtrate from the above reaction showed it to consist of essentially unchanged starting materials. This reaction was also carried out in similar fashion using a 100-w lamp and the following yields of salt were obtained: 4.0% (111.5-hr irradiation), 13.8% (236 hr).

**Hydrolysis of Triphenoxy(phenyl)phosphonium Iodide.**—A mixture of 1.0 g (1.95 mmoles) of the salt and 20 ml of 10% aqueous sodium hydroxide was refluxed for 30 min and allowed to stand at room temperature overnight. The solid was removed by filtration, ground under water, washed with warm water, and dried in air to give 0.32 g (53%) of diphenyl phenylphosphonate, mp 66.5–69.5°. Recrystallization of a sample from petroleum ether (30–60°) gave material of mp 72.5–73.5°; a mixture melting point with an authentic sample of the phosphonate was not depressed. The alkaline filtrate was treated with benzoyl chloride (1.5 ml) and the mixture was shaken until a solid crystallized. The solid was removed by filtration, washed with water, and dried in air to give 0.33 g (85.5%) of phenyl benzoate, which was identical with an authentic sample.