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Abstract

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Photochemical Reaction of Arylation of Triphenylphosphine with Diaryliodonium Borofluorides

Several methods for obtaining tetraarylphosphonium salts are known in the literature; however, the most general and convenient preparatively is the so-called diazo method, discovered by Horner and Hoffmann (1). To carry out the reaction, triphenylphosphine in ethyl acetate is added to an equimolecular amount of an aqueous solution of a diazonium salt containing sodium acetate buffer. The formation of the phosphonium salt can be represented by the following equation:

$$(C_6H_5)_3P + ArN_2X \rightarrow (C_6H_5)_3ArPX + N_2.$$

By this method, bromides and iodides of triphenylarylphosphonium with various substituents in Ar were obtained in yields of 40–80%.

In recent years, phosphonium salts of the type $(C_6H_5)_3ArPJ$, also with various Ar, have been obtained by arylation of triphenylphosphine with aryliodides under irradiation with an Hg lamp at 65° (2):

$$(C_6H_5)_3P + ArJ \xrightarrow[65^\circ]{h\nu} (C_6H_5)_3ArPJ.$$

The yield of triphenylarylphosphonium iodides in this case is 9–42%. A substantial drawback of the method is the long duration of the reaction (46–346 h, depending on the nature of the substituent in ArJ) and the comparatively low yields for most $(C_6H_5)_3ArPJ$.

Recently we showed (3) that triphenylphosphine can be successfully arylated during the photochemical decomposition of diphenyliodonium chloride or borofluoride in ethyl alcohol at room temperature.

The present work describes the photochemical reaction between triphenylphosphine and the following diaryliodonium borofluorides: di-(p-anisyl)iodonium, di-(p-chlorophenyl)iodonium, di-(m-carbethoxyphenyl)iodonium, and di-(m-nitrophenyl)iodonium. The reactions we studied can be expressed by the following equation:

$$(C_6H_5)_3P + Ar_2JBF_4 \xrightarrow{h\nu} (C_6H_5)_3ArPBF_4 + ArJ.$$

We found that acetone is best used as the solvent, since the starting substances are readily soluble in it. In this case, the yield of tetraphenylphosphonium borofluoride is 85%. The photochemical reaction between triphenylphosphine and diaryliodonium salts was carried out under irradiation with a PRK-4 mercury lamp for 6–10 h. The distance between the reaction tube and the light source was 30 cm. The results of the reactions we studied are given in Table 1.

As can be seen from the data in Table 1, the borofluorides of the corresponding phosphonium salts are formed in good yield, which is only slightly inferior to that of the so-called diazo method. At the same time, the use of diaryliodonium salts, as well as diazonium salts, for the arylation of triphenylphosphine makes it possible to obtain phosphonium salts with various substituents in the aromatic ring.

Thus, the photochemical reaction between $(C_6H_5)_3P$ and diaryliodonium salts that we have studied is general and can serve as a preparative method for obtaining phosphonium salts of the type $(C_6H_5)_3ArPBF_4$,

Table 1

Photochemical reaction between triphenylphosphine and diaryliodonium salts

Starting salt	Solvent	Yield of $(C_6H_5)_3ArPBF_4$, %	M.p. of $(C_6H_5)_3ArPBF_4$, °C
$(C_6H_5)_2JBF_4$	CH_3COCH_3	85	345
$(n\text{-}CH_3OC_6H_4)_2JBF_4$	CH_3COCH_3	40	196
$(n\text{-}ClC_6H_4)_2JBF_4$	CH_3COCH_3	61	198–199
$(m\text{-}C_2H_5OC_6H_4)_2JBF_4$	CH_3OH	51	194
$(m\text{-}O_2NC_6H_4)_2JBF_4$	CH_3COCH_3	47	191

which, before the present work, had been represented by only one compound—tetraphenylphosphonium tetrafluoroborate $(C_6H_5)_4PBF_4$ (4).

Experimental Part

1. Preparation of tetraphenylphosphonium tetrafluoroborate. A mixture of 0.52 g (0.002 mole) of triphenylphosphine and 0.74 g (0.002 mole) of diphenyliodonium tetrafluoroborate is dissolved in 10 ml of absolute acetone.

The acetone solution is irradiated with a PRK-4 mercury lamp for 6 h. By this time the reaction is practically complete. The precipitated tetraphenylphosphonium tetrafluoroborate is filtered off; yield 0.48 g, m.p. 345°. Lit. (4): m.p. 350.5°.

Acetone is evaporated from the filtrate, and the residue is washed repeatedly with ether to remove iodobenzene and unreacted triphenylphosphine. To the residue, consisting of a mixture of tetraphenylphosphonium and diphenyliodonium tetrafluoroborates, a small amount of acetone is added; in this process a portion (0.16 g) of $(C_6H_5)_4PBF_4$ does not dissolve. The phosphonium salt is filtered off, and the filtrate is subjected to chromatographic separation in a thin layer on aluminum oxide (layer thickness 3-4 mm, solvent—acetone). Under these conditions diphenyliodonium tetrafluoroborate remains at the point of application, while tetraphenylphosphonium tetrafluoroborate moves with the front. After separation, $(C_6H_5)_4PBF_4$ is extracted with acetone, and the acetone is evaporated. As a result, pure tetraphenylphosphonium tetrafluoroborate is obtained (0.07 g), m.p. 343°. Lit. (4): m.p. 350°. The total yield of tetraphenylphosphonium tetrafluoroborate is 0.71 g, 85%.

2. Preparation of triphenyl-(n-anisyl)phosphonium tetrafluoroborate. A mixture of 0.21 g (0.0005 mole) of di-(n-anisyl)iodonium tetrafluoroborate and 0.13 g (0.0005 mole) of triphenylphosphine is dissolved in 10 ml of absolute acetone, and the solution is irradiated with a PRK-4 mercury lamp for 10 h. The acetone is evaporated, and the residue is treated analogously to experiment 1. As a result, 0.9 g (49%) of triphenyl-(n-anisyl)phosphonium tetrafluoroborate is obtained, m.p. 196°.

Found, %: C 65.71; 65.93; H 5.05; 5.02
$C_{25}H_{22}BF_4OP$. Calculated, %: C 65.81; H 4.82

3. Preparation of triphenyl-di(n-chlorophenyl)phosphonium tetrafluoroborate. A mixture of 0.26 g (0.001 mole) of triphenylphosphine and 0.42 g (0.001 mole) of di-(n-chlorophenyl)iodonium tetrafluoroborate in 10 ml of absolute acetone is irradiated with a PRK mercury lamp for 10 h. Further treatment of the reaction mixture is analogous to the preceding experiment. As a result, obt—

0.28 g (61%) of triphenyl-(p-chlorophenyl)phosphonium tetrafluoroborate is obtained, m.p. 198-199°.

Found, %: C 62.43, 62.29; H 4.63, 4.74
$C_{24}H_{19}ClBF_4P$. Calculated, %: C 62.57; H 4.12

4. **Preparation of triphenyl-(m-nitrophenyl)phosphonium tetrafluoroborate.** A mixture of 0.26 g (0.001 mole) of triphenylphosphine and 0.46 g (0.001 mole) of di-(m-nitrophenyl)iodonium tetrafluoroborate in 20 ml of absolute acetone is irradiated with a PRK-4 mercury lamp for 10 h. As a result of further treatment analogous to experiment 1, 0.24 g (51%) of triphenyl-(m-nitrophenyl)phosphonium tetrafluoroborate is obtained, m.p.

194°.

Found, %: C 61.11, 60.96; H 4.39, 4.37; F 15.81, 15.78; N 3.12; 2.98
$C_{24}H_{19}BF_4NO_2P$. Calculated, %: C 61.17; H 4.06; F 16.14; N 2.97

5. **Preparation of triphenyl-(m-carbethoxyphenyl)phosphonium tetrafluoroborate.** A mixture of 0.78 g (0.003 mole) of triphenylphosphine and 1.38 g (0.003 mole) of di-(m-carbethoxyphenyl)iodonium chloride in 100 ml of methyl alcohol is irradiated with a PRK-4 mercury lamp for 10 h. The reaction mixture is transferred to a porcelain dish, and the alcohol is evaporated. The residue is washed 3–4 times with small portions of cold water; during this, the readily water-soluble triphenyl-(m-carbethoxyphenyl)phosphonium chloride passes into solution. On adding a saturated aqueous solution of ammonium tetrafluoroborate to the aqueous solution, the sparingly soluble triphenyl-(m-carbethoxyphenyl)phosphonium tetrafluoroborate precipitates, m.p. 189–190°. After recrystallization from water, m.p. 191°. Yield 0.69 g (47%).

Found, %: C 65.06, 64.98; H 4.92, 4.92; F 15.08, 15.32
$C_{27}H_{24}BF_4O_2P$. Calculated, %: C 65.07; H 4.85; F 15.23

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Note: Figure translations are in progress. See original paper for figures.