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Abstract

Full Text

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CHEMISTRY

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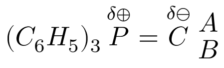
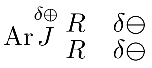
PHENYLIODONATION OF SOME TRIPHENYLPHOSPHORANES

In the last decade, triphenylphosphoranes (I) have found broad application in organic synthesis (1,2). The limits of their applicability are determined by the possibility of varying substituents A and B in I.



$$(C_6H_5)_3\overset{\delta\oplus}{P}=\overset{\delta\ominus}{C}\begin{matrix}A\\B\end{matrix}$$

(I)

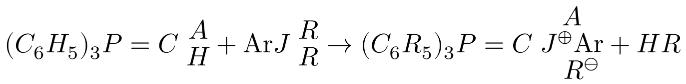


$$\text{Ar}\overset{\delta\oplus}{J}\begin{matrix}R & \delta\ominus\\R & \delta\ominus\end{matrix}$$

(II)

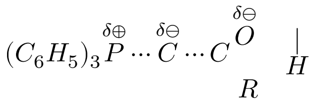
The starting substances for the synthesis of disubstituted I may be I, $B=H$, subjected to electrophilic substitution at the carbon atom, which in I has a strongly nucleophilic character. This has been demonstrated in practice by reactions of halogenation (3–5), sulfuration (6), alkylation (7), acylation (8–10), mercuration (11), and azo coupling (12).

Aryliodoso compounds II are typical electrophilic reagents with an electrophilic center on the iodine atom (13,14). It may be assumed that, upon interaction of II with I, iodonium compounds will be formed according to the general scheme (provided that the process of electron removal from I, i.e. oxidation, does not predominate):



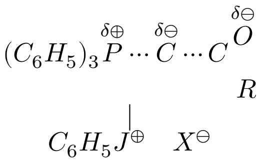
$$(C_6H_5)_3P=C\begin{matrix}A\\H\end{matrix}+\text{Ar}J\begin{matrix}R\\R\end{matrix}\rightarrow(C_6R_5)_3P=C\begin{matrix}A\\J^{\oplus}\text{Ar}\\R^{\ominus}\end{matrix}+HR$$

We studied the reactions of phenyliodosoacetate ($II,\ Ar=C_6H_5,\ R=OOCCH_3$) with carbethoxymethylenetriphenylphosphorane ($III,\ R=OC_2H_5$) and benzoylmethylenetriphenylphosphorane ($III,\ R=C_6H_5$). Phenyliodosoacetate



$$(C_6H_5)_3\overset{\delta\oplus}{P}\cdots\overset{\delta\ominus}{C}\cdots C\genfrac{}{}{0pt}{}{\overset{\delta\ominus}{O}}{R}\quad\overset{|}{H}$$

(III)



$$(C_6H_5)_3\overset{\delta\oplus}{P}\cdots\overset{\delta\ominus}{C}\cdots C\genfrac{}{}{0pt}{}{\overset{\delta\ominus}{O}}{R}\qquad \overset{|}{C_6H_5J^{\oplus}}\quad X^{\ominus}$$

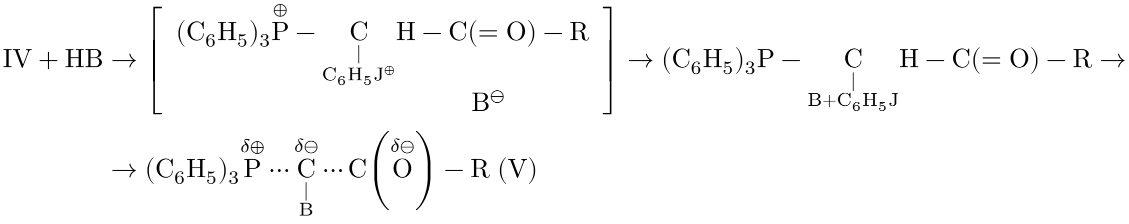
(IV)

reacts very readily with III in methanol solution, forming substances readily soluble in water, evidently acetates of phenyliodonated phosphoranes ($IV,\ X = OOCCH_3$), which were not isolated; instead their aqueous solution was diluted with a solution of sodium bromide. Bromides poorly soluble in water precipitated, i.e. the bromide of phenyliodoniocarbethoxymethylenetriphenylphosphorane ($IV,\ R = OC_2H_5,\ X = Br$) and the bromide of phenyliodoniobenzoylmethylenetriphenylphosphorane ($IV,\ R = C_6H_5,\ X = Br$), which are colorless, rather unstable (especially IV, $R = C_6H_5$,

X = Br) substances. Phenyliodonation of III with phenyliodosoacetate in the presence of fluoroboric acid gives the corresponding fluoroborates (IV, X = $\mathrm{BF_4}$), colorless, stable, readily crystallizing substances. The fluoroborates are somewhat soluble in 20% alcohol; from solutions of the aforementioned bromides they can be precipitated by saturating the solution with sodium bromide.

These experiments indicate the presence in triphenylphosphoranes of a particularly nucleophilic carbon atom, since they react with phenyliodosoacetate without the presence of acid. Usually phenyliodonation is carried out in the presence of strong acids—sulfuric, trifluoroacetic, fluoroboric ([14,15])—and only especially nucleophilic species are capable of reacting directly with phenyliodosoacetate or iodosobenzene ([13]).

IV are readily cleaved by strong acids (HCl, HBr) with formation of iodobenzene and the corresponding phosphonium salt, which were isolated in the form of halomethylenetriphenylphosphoranes V.



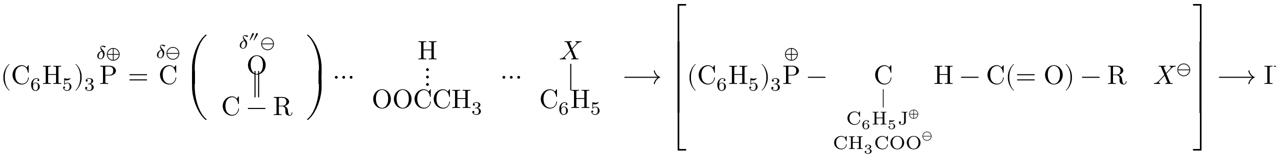
$$\mathrm{IV + HB \rightarrow \left[(C_6H_5)_3\overset{\oplus}{P}-\underset{\underset{C_6H_5J^{\oplus}}{|}}{C}\ H-C(=O)-R \quad B^{\ominus}\right] \rightarrow (C_6H_5)_3P-\underset{\underset{B+C_6H_5J}{|}}{C}\ H-C(=O)-R \rightarrow}$$

$$\mathrm{\rightarrow (C_6H_5)_3\overset{\delta\oplus}{P}\cdots\underset{\underset{B}{|}}{\overset{\delta\ominus}{C}}\cdots C\left(\overset{\delta\ominus}{O}\right)-R\ (V)}$$

1) $X = \mathrm{Br},\quad B = \mathrm{Br},\quad R = \mathrm{OC_2H_5}$,
2) $X = \mathrm{BF_4},\quad B = \mathrm{Cl},\quad R = \mathrm{C_6H_5}$.

Such cleavage of IV in the presence of acids, first, confirms the iodonium structure of IV and, second, may open a convenient route to the preparation of new, difficultly accessible triphenylphosphoranes. The use of various acids HB can be limited only by insufficient nucleophilicity of the anion B and insufficient acidity of HB. IV are evidently very weak bases ($pK_B > 11$), owing to the strong acceptor influence of the phenyliodonium group. For V, $X = \mathrm{Cl}, R = \mathrm{OC_2H_5}$, $pK_B = 7.7$ was found, and for V, $X = \mathrm{Cl}, R = \mathrm{C_6H_5}$, $pK_B = 9.7$ was found (^{3}).

The low basicity of IV (i.e., the high acidity of the conjugate acid VI) is evidently the reason for the stability of IV in the presence of acetic acid and even small amounts of fluoroboric acid



$$(C_6H_5)_3\overset{\delta\oplus}{P}=\overset{\delta\ominus}{C}\left(\begin{matrix}\overset{\delta''\ominus}{O}\\ \|\\ C-R\end{matrix}\right)\cdots\begin{matrix}H\\ \vdots\\ OOCCH_3\end{matrix}\cdots\begin{matrix}X\\ |\\ C_6H_5\end{matrix}\longrightarrow\left[(C_6H_5)_3\overset{\oplus}{P}-\begin{matrix}C\\ |\\ C_6H_5J^{\oplus}\\ CH_3COO^{\ominus}\end{matrix}\quad H-C(=O)-R\quad X^{\ominus}\right]\longrightarrow I$$

(VI) $X = CH_3COO$
BF_4

under the conditions of synthesis of IV. It may be thought that phenyliodonation of more basic triphenylphosphoranes than III should be carried out in the presence of equimolar amounts of bases, in order to promote rapid protolysis of VI, i.e., to forestall cleavage of VI with liberation of iodobenzene.

Infrared absorption spectra were taken in the region 1800—1460 $\mathrm{cm^{-1}}$ for suspensions of the substances in paraffin oil of the triphenylphosphoranes obtained. In the spectra there is observed not the characteristic absorption of ester or ketone carbonyl groups, but strongly lowered frequencies, which indicates the formation of systems with nonintegral bonds and agrees with the literature data (^{3,5}). Attention should be drawn to the large

difference in absorption of IV, R = $\mathrm{OC_2H_5}$, X = $\mathrm{BF_4}$ and X = Br. For carbethoxymethylenetriphenylphosphoranes such a low value (about 1600 $\mathrm{cm^{-1}}$) is characteristic only in solutions. But the question of the influence of the state of aggregation and of substituents on the absorption frequency of triphenylphosphoranes has not yet been studied at all.

The C–I bond in unprotonated IV, X = $\mathrm{BF_4}$, possesses considerable stability, and in the presence of pyridine thermal decomposition does not proceed in the desired direction (formation of pyridinium triphenylphosphoranes), but a slow, though deep, decomposition in an unknown direction occurs. IV, X = Br, decomposes rapidly on storage, especially when R = $\mathrm{C_6H_5}$, and it could not be recrystallized even by reprecipitation from acetone with ether. The reason for such an enormous difference in the stability of IV, X = Br and X = $\mathrm{BF_4}$, is not yet clear.

Table 1

Triphenylphosphoranes obtained

Compound	M.p., °C	IR absorption spectrum, cm^{-1} (absorp., %)	Found, %	Calculated, %
IV, R=OC_2H_5X=BF_4	189–191°(methanol)	1600 (83), 1570 (30)1486 (23)	I 20.20	$C_{28}H_{25}BF_4IO_2P$I 19.89
IV, R=OC_2H_5X=Br	125–127°(acetone/ether)	1657 (80), 1580 (31)1480 (31)	I 19.86;P 4.81	$C_{28}H_{25}BrIO_2P$I 20.10; P 4.91
IV, R=C_6H_5X=BF_4	148–149°(methanol/ether)	1573 (11), 1511 (41)1483 (42)	I 20.01	$C_{32}H_{25}BF_4IOP$I 18.93
IV, R=C_6H_5X=Br	75–80°(not recryst.)	1578 (34), 1523 (58),1484 (62)	I 18.03;P 4.87	$C_{32}H_{25}BrIOP$I 19.13; P 4.67
V, R=OC_2H_5B=Br	154–156°	1650 (80), 1585 (74),1486 (46)	Br 18.65;P 7.30	$C_{22}H_{20}BrO_2P$Br 18.70; P 7.25
V, R=C_6H_5B=Cl	Lit. (4) 157–158°152–153°	Lit. (3) 1625 ($CHCl_3$)1609 (42), 1473 (72)	Cl 8.15;P 7.13	$C_{26}H_{20}ClOP$Cl 8.54; P 7.47
B=Cl	Lit. (5) 134–156°	Lit. (5) 1492, 1475		

Experimental part

Phenylidoniumcarbethoxymethylenetriphenylphosphorane borofluoride (IV, R = OC_2H_5, X = BF_4). A solution of 0.01 mole of phenyliodosoacetate in 10 ml of 1 N hydrofluoroboric acid (from 1.9 g of 41.5% HF, 0.6 g of boric acid, and methanol to 10 ml) is added at 0° to a solution of 0.01 mole of carbethoxymethylenetriphenylphosphorane in 15 ml of methanol. Crystallization of the borofluoride soon begins. Then 15 ml of ether is added; after an hour the colorless crystals are filtered off with suction. Yield up to 72%. It can be crystallized from methanol, but the melting point does not increase.

Phenylidoniumbenzoylmethylenetriphenylphosphorane borofluoride (IV, R = C_6H_5, X = BF_4). Under conditions analogous to those described above, from 0.01 mole of phenyliodosoacetate, 10 ml of 1 N HBF_4 in methanol, and 0.01 mole of benzoylmethylenetriphenylphosphorane in 30 ml of methanol, with addition of 30 ml of ether at the end of the reaction, up to 60% of the borofluoride is obtained. Crystallization from methanol—ether does not raise the melting point.

Cleavage of IV, R = OC_2H_5, X = Br, with hydrobromic acid. 0.0005 mole of the bromide is shaken with 5 ml of water, 0.5 ml of 47% HBr, and 5 ml of ether until dissolution. The aqueous layer is made alkaline and the carbethoxybromomethylenetriphenylphosphorane is separated. Yield 80%, m.p. of the crude product 147—153°.

Cleavage of IV, R = C_6H_5, X = BF_4, with hydrochloric acid. 0.0005 mole of the borofluoride is dissolved in 5 ml of ethanol and 0.5 ml of conc. HCl is added. The mixture is heated to boiling, cooled,

diluted with water and made alkaline. The yield of crude benzoylchloromethylenetriphenylphosphorane is up to 100%, but with m.p. 90-120°. After purification by crystallization from cyclohexane, the yield is below 50%.

Phosphorus analyses were carried out by combustion of the substance according to the Schöniger method; the phosphate ion was determined by method (16). The presence of fluorine interferes with the determination of phosphorus. For introducing the phosphorus-determination procedure and for carrying out the analyses, the authors express their sincere gratitude to Dz. Bite.

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