

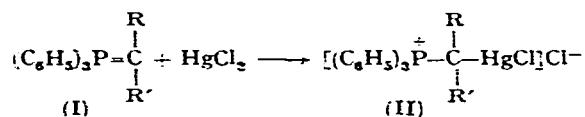
## PROPERTIES OF MERCURATED PHOSPHONIUM SALTS\*

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Wittig reagents readily add  $\text{HgCl}_2$ \*\* to form mercurated phosphonium salts<sup>†</sup>.



- (a)  $\text{R}=\text{H}$ ,  $\text{R}'=\text{COOCH}_3$     (c)  $\text{R}=\text{H}$ ,  $\text{R}'=\text{COC}_6\text{H}_5$   
 (b)  $\text{R}=\text{H}$ ,  $\text{R}'=\text{COCH}_3$     (d)  $\text{R}=\text{H}$ ,  $\text{R}'=\text{COC}_6\text{H}_4\text{C}_6\text{H}_5$   
 (e)  $\text{R}=\text{C}_6\text{H}_5$ ,  $\text{R}'=\text{COOCH}_3$

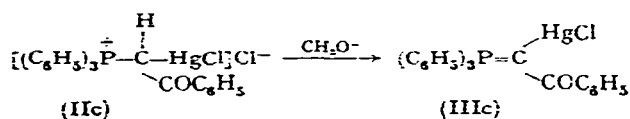
The only difficulty in preparing these compounds lies in the formation of the salt of the same cation with the complex anion  $\text{HgCl}_3^-$ , which is not readily removed.

Mercurated phosphonium salts, (II), are colourless crystalline substances, which are fairly stable on prolonged storage. They do not dissolve in non-polar organic solvents and are usually slightly soluble in methanol and chloroform but dissolve in nitromethane and dimethylformamide.

We have studied more thoroughly the properties of (IIa)–(IIc) which have at the central carbon atom two electron-accepting substituents (triphenylphosphonio and carbonyl), a labile hydrogen atom and a mercury atom. The infrared spectra of these compounds reveal a shift in the carbonyl peak to the low frequency range, accounted for by the conjugation of  $\text{Hg}-\text{C}$  and  $\text{C}=\text{O}$  bonds [absorption bands for (IIa),  $1697\text{ cm}^{-1}$ ; (IIb),  $1675\text{ cm}^{-1}$ ; (IIc),  $1645\text{ cm}^{-1}$ ; and (IIe),  $1650\text{ cm}^{-1}$ ]. A similar shift is found in the spectra of  $\alpha$ -mercurated aldehydes and ketones<sup>2a</sup>. The compounds obtained exhibit a triple reactivity.

## I. PREPARATION OF PHOSPHORYLIDES CONTAINING MERCURY

When reacted with sodium methoxide, (IIc) loses a molecule of hydrogen chloride to yield a mercurated phosphorylide.

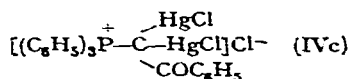


\* Translated by A. L. Pumpiansky, Moscow.

\*\* Seyferth and Grim<sup>2</sup> have reported that addition of  $\text{HgBr}_2$  to methylenetriphenylphosphorane results in  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2]_2\text{Hg} \cdot 2\text{HgBr}_3^-$ , but the substance has not been further investigated.

The structure of the latter is proved by the analysis for C, H, Cl, P, and Hg, by infrared evidence and by some of the properties. The infrared spectrum of (IIIc) shows no carbonyl peak but an absorption band at  $\sim 1520 \text{ cm}^{-1}$  observed by Ramirez<sup>3</sup> is characteristic of the conjugated-bond system  $\text{P}=\text{C}-\text{C}=\text{O}$ . We have found a rather similar peak in our corresponding synthetic arsenic ylides<sup>4</sup>.

Unlike its starting salt (but like phosphorylides), (IIIc) is readily soluble in alcohol and chloroform and crystallises from benzene. It adds hydrogen chloride to form the initial phosphonium salt, or a molecule of  $\text{HgCl}_2$  to give a doubly mercurated phosphonium salt:

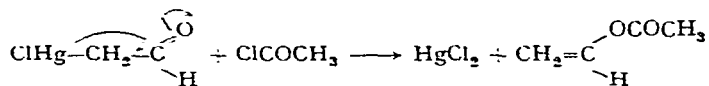


Heating phosphorylide, (IIIc), in tetrahydrofuran or dimethylformamide leads to the ready evolution of metallic mercury. On storage, the melting point of (IIIc) is gradually lowered. Phosphonium salts, (IIa) and (IIb), did not give similar phosphorylides.

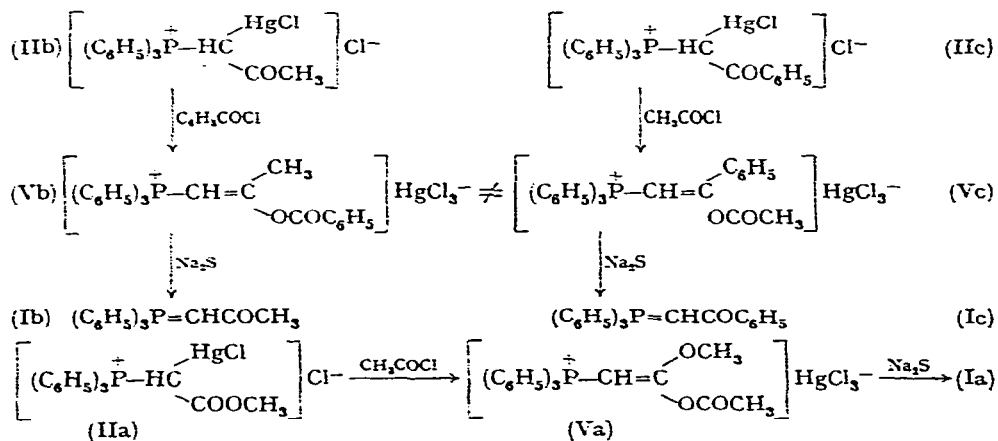
We consider that the formation of a mercury-containing ylide from (IIc) is chemical evidence for these salts being true organometallic compounds rather than complexes (*e.g.*  $\pi$ -complexes). This is substantiated by the infrared spectra of salts (II) revealing a carbonyl absorption band but no band at  $1520 \text{ cm}^{-1}$ .

## 2. REACTIONS OF (II) WITH ACID CHLORIDES

Nesmeyanov and Lutsenko *et al.*<sup>5-7</sup> have shown that the reaction of  $\alpha$ -mercurated aldehydes and ketones with acid chlorides involves the transfer of the reaction centre, that is on oxygen, for instance:



Mercurated phosphonium salts of the type (II) have been found to behave similarly to form *O*-acylated phosphonium salts with a complex anion.

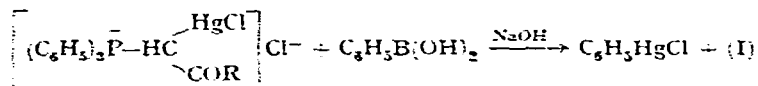


The structure of the reaction products was deduced from the following. First, if acylation had proceeded on the carbon, the reaction products of (IIb) with benzoyl chloride and (IIc) with acetyl chloride would have been identical, *i.e.*,  $[(C_6H_5)_3P^+-CH(COCH_3)(COOC_6H_5)]HgCl_3^-$ . This, however, is not the case. Secondly, the action of sodium sulphide on (Va-c) results in the initial phosphorylides, (Ia-c). Had the acyl been bound to carbon, one would have expected the formation of a new ylide  $(C_6H_5)_3P=C(COCH_3)(COOC_6H_5)$ . Thirdly, the comparison of the authentic  $[(C_6H_5)_3P^+-CH(COCH_3)(COOCH_3)]HgCl_3^-$  with (Va) showed them to be different substances.

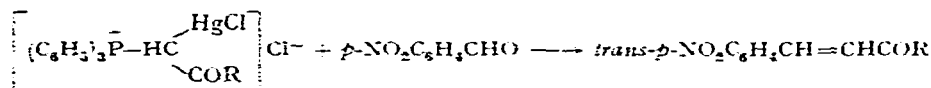
### 3. QUASI-COMPLEX PROPERTIES OF (II)

In many reactions, mercurated phosphonium salts behave as if they were complexes of phosphorylide and mercury chloride, or even mixtures. By passing ammonia into the solution of (II) in dimethylformamide the starting phosphorylide is obtained. A similar result is obtained by the action of sodium thiosulphate or sodium sulphide.

The reaction of (II) with benzeneboronic acid gives rise to phenylmercury chloride and phosphorylide

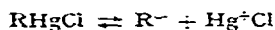


whereas with *p*-nitrobenzaldehyde (II) gives an olefin:

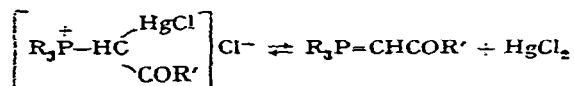


It has been shown above that (II) are true organomercury compounds. It is, however, likely that in some solvents there is a slight dissociation of (II) into the starting components: mercuric chloride and phosphorylide. If this is indeed the case, it is easy to interpret all these reactions. The reagent interacts with one of the dissociation products carrying it away from the reaction sphere and the equilibrium is shifted (mechanism  $S_{E1}$ ). On the other hand, there are difficulties in interpreting some reactions in terms of the mechanism  $S_{E2}$ . Thus, the reaction of (II) with aldehyde by mechanism  $S_{E2}$  would involve the attack of the carbon atom of carbonyl on the electron-depleted carbon atom of the phosphonium salt; this is unlikely.

It has been shown in this laboratory, that some organo-mercury compounds of the benzyl type (with electron-accepting substituents) react in polar solvents by mechanism  $S_{E1}$  or with the preliminary dissociation<sup>8,9</sup>:

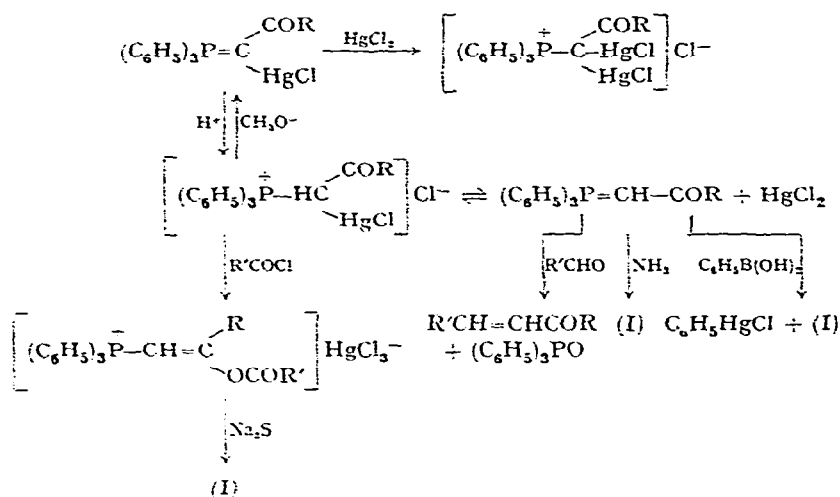


This type of dissociation is more likely for the compounds under study, because it leads to two stable molecules, phosphorylide and mercuric chloride (instead of the energetically unfavourable carbonium ion):



We, therefore, consider that the reaction most likely follow a unimolecular mechanism. Nevertheless, some of them (*e.g.*, with ammonia) might, of course, be bimolecular, depending on the solvent, etc. The reaction of (II) with acid chlorides in tetrahydrofuran seems to be bimolecular (mechanism *S<sub>E</sub>i*). In the case of a monomolecular reaction, the products of the reaction of phosphorylide (I) with acyl chloride and those of the salt (II) with the same reagent should be identical. In a special experiment we have shown that (Ic) is acylated by acetyl chloride on the oxygen. However, (carbomethoxymethylene)triphenylphosphorane, (Ia), adds acyl to carbon<sup>10</sup> whereas in the case of the mercurated salt (IIa), acyl is directed to oxygen as already noted above. The latter reaction cannot, therefore, be unimolecular.

The reactivity of mercurated phosphonium salts of the type (IIa-c) may be summarised by the following scheme:



The term "quasi-complex" compounds was proposed by Nesmeyanov<sup>11</sup> for the adducts of unsaturated compounds and mercury salts,  $\text{XHgCH}_2\text{CH}_2\text{X}$ ,  $\text{XHgCH}=\text{CHX}$ , and for compounds of other elements of a similar structure. In general, it is possible to denote by this term those organometallic (organoelement) compounds that behave in a number of reactions as complexes notwithstanding the covalent character of the carbon-metal bond. In this respect the adducts of mercury salts and unsaturated compounds have a great deal in common with the adducts of mercuric chloride and phosphorylides. In the latter case phosphorylide acts as an olefin. The mercurated phosphonium salts resemble complexes to an even greater extent because of their labile C-Hg bond and the probability of their dissociation in polar solvents. On the other hand, these compounds of the type (IIa-c) behave on acylation like  $\alpha$ -mercurated ketones.

#### EXPERIMENTAL

All reactions were carried out in anhydrous solvents and after recrystallisation the products were dried at 100° and 5 mm.

*Synthesis of mercurated phosphonium salts*

1. [ $\alpha$ -(Chloromercuri)phenacyl]triphenylphosphonium chloride (IIc). A solution of  $\text{HgCl}_2$  (2.7 g, 0.01 mole) in methanol (10 ml) was added to phenacylidetriphenylphosphorane (3.2 g,  $\sim$  0.01 mole) in methanol (15–20 ml) during 10 min with stirring. After an hour the precipitate was isolated and washed with methanol and ether, (IIc) being obtained in a quantitative yield (5.6 g). The crystals were reprecipitated with ether from a solution in a mixture of nitromethane and chloroform, m.p. 199–200° (dried at 90–100°, pressure 5 mm). After recrystallisation from nitromethane, m.p. 208–210°,  $\nu_{\text{C}=\text{O}}$  1645  $\text{cm}^{-1}$ . (Found: C, 47.73, 47.61; H, 3.43, 3.60; Hg, 30.36, 30.47; P, 4.74, 4.64.  $\text{C}_{28}\text{H}_{21}\text{Cl}_2\text{HgOP}$  calcd.: C, 47.87; H, 3.33; Hg, 30.80; P, 4.75%.)

2. [(Chloromercuri)carbomethoxymethyl]triphenylphosphonium chloride (IIa). In a similar way, (carbomethoxymethylene)triphenylphosphorane (1.67 g, 0.005 mole) and  $\text{HgCl}_2$  (1.36 g, 0.005 mole) gave (IIa) in a 69% yield (2.12 g). It was recrystallised from a mixture of nitromethane and ether (cooled to  $-70^\circ$ ), m.p. 190–191°,  $\nu_{\text{C}=\text{O}}$  1697  $\text{cm}^{-1}$ . (Found: C, 41.24, 41.42; H, 3.47, 3.36; Hg, 33.10, 32.90; P, 4.79; 5.11;  $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{HgO}_2\text{P}$  calcd.: C, 41.63; H, 3.14; Hg, 33.11; P, 5.11%.)

3. [1-(Chloromercuri)acetonyl]triphenylphosphonium chloride (IIb). Similarly, 0.005 mole of acetonylidetriphenylphosphorane and  $\text{HgCl}_2$  gave (IIb) in a 95% yield,  $\nu_{\text{C}=\text{O}}$  1680  $\text{cm}^{-1}$ . After recrystallisation from nitromethane the product was dried *in vacuo* at 20°. (Found: C, 41.68, 41.76; H, 3.25, 3.35; Hg, 33.62, 33.64; P, 5.24, 5.18.  $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{HgOP}$  calcd.: C, 42.76; H, 3.22; Hg, 34.01; P, 5.25%.) After drying at 100° and 5 mm the sample, m.p. 208–210° (decomp.), had the following analysis. (Found: C, 42.49, 42.31; H, 3.63, 3.57. Calcd.: C, 42.76; H, 3.25%.)

4. [ $\alpha$ -(Chloromercuri)-*p*-phenylphenacyl]triphenylphosphonium chloride (IId). To ylide (Id) (4.56 g, 0.01 mole) in methanol (50 ml) was added dropwise an equivalent amount of  $\text{HgCl}_2$  (2.71 g) dissolved in the minimum amount of methanol. After 30 min the precipitate, (IIId), was isolated in 70% yield (5.1 g). After recrystallisation from tetrahydrofuran it had no sharp melting point (150–220°).  $\nu_{\text{C}=\text{O}}$  1650  $\text{cm}^{-1}$ . (Found: C, 51.14, 51.29; H, 3.87, 3.89; Cl, 9.42, 9.41; Hg, 27.86, 27.75; P, 4.01, 3.73.  $\text{C}_{32}\text{H}_{25}\text{Cl}_2\text{HgOP}$  calcd.: C, 52.80; H, 3.43; Cl, 9.70; Hg, 27.6; P, 4.21%.)

5. [ $\alpha$ -(Chloromercuri)- $\alpha$ -carbomethoxybenzyl]triphenylphosphonium chloride (IIe). This compound was obtained in a similar manner to (IIc), in 64% yield, m.p. 168–169°. (Found: C, 46.79, 46.85; H, 3.44, 3.55; Hg, 30.21, 30.31; P, 4.37, 4.39.  $\text{C}_{27}\text{H}_{23}\text{Cl}_2\text{HgO}_2\text{P}$  calcd.: C, 47.28; H, 3.35; Hg, 29.25; P, 4.51%.)

*Synthesis of mercurated phosphorylide (IIIc) and the properties of this compound*

6. [ $\alpha$ -(Chloromercuri)phenacylidene]triphenylphosphorane (IIIc). Sodium methoxide (0.03 g, 0.013 mole, of sodium and 10 ml of methanol) was added to (IIc) (6.51 g, 0.01 mole) dissolved at 60° in dimethylformamide (10 ml) during 10 min. After an hour the product was precipitated by water, m.p. 222–225°, yield  $\sim$  90%. After recrystallisation from benzene the product melted at 226–228°. (Found: C, 50.97, 50.82; H, 3.40, 3.45; Cl, 5.65, 5.65; Hg, 32.85, 33.06; P, 5.07, 4.94;  $\text{C}_{26}\text{H}_{20}\text{ClHgOP}$  calcd.: C, 51.06; H, 3.28; Cl, 5.80; Hg, 32.80; P, 5.08%.)

7. Mercuric chloride addition to phosphorylide (IIIc): synthesis of (IVc). To a solution of 2.4 g (0.004 mole) of (IIIc) in the minimum amount of methanol was added dropwise  $\text{HgCl}_2$  (1.08 g, 0.004 mole) in methanol (10 ml) at 60°. After 12 h the precipitate was isolated, washed with ether and dried. The yield was about 95% of

theory, m.p. 200–208°; after a double recrystallisation from dimethylformamide the melting point was 205–208°;  $\nu_{C=O} = 1605 \text{ cm}^{-1}$ . (Found: C, 35.30, 35.47; H, 2.36, 2.46; Cl, 11.98, 11.97; Hg, 44.18, 44.12; P, 3.79, 3.63.  $C_{26}H_{30}Cl_3Hg_2OP$  calcd.: C, 35.20; H, 2.26; Cl, 12.00; P, 3.49; Hg, 45.20 %.)

8. *Reaction of phosphorylide (IIc) with hydrochloric acid.* To (IIc) in dimethylformamide was added an excess of 1 % hydrochloric acid and the precipitate isolated. The yield of (IIc) was 80 % of theory, m.p. 190–192°. A mixed melting point with an authentic sample showed no depression.

#### Miscellaneous reactions of mercurated phosphonium salts

9. *Reaction of (IIc) with *p*-nitrobenzaldehyde.* To a solution of (IIc) (3.26 g, 0.005 mole) in the minimum amount of dimethylformamide, was added *p*-nitrobenzaldehyde (1.21 g, 0.008 mole). The mixture was left to stand for two days, poured into water and the precipitate isolated; it was washed with cold methanol and then repeatedly with ether to give a 70 % yield of *trans*- $\alpha$ -(*p*-nitrobenzylidene)acetophenone, m.p. 152–154°. After a double recrystallisation from methanol the m.p. was 161.5–162° (lit.<sup>12</sup> 162.5°). (Found: C, 70.66, 70.66; H, 4.28, 4.36; N, 5.79, 5.59.  $C_{15}H_{11}NO_3$  calcd.: C, 71.15; H, 4.31; N, 5.53 %.)

10. *Reaction of (IIa) with *p*-nitrobenzaldehyde.* A mixture of (IIa) (2.8 g, 0.084 mole) and *p*-nitrobenzaldehyde (1.5 g, 0.01 mole) in dimethylformamide was heated on a water bath for 1 h, left to stand for a day and then poured into water. The precipitate was collected and recrystallised from nitromethane. The yield of methyl *trans*-*p*-nitrocinnamate was 95 % (1.6 g), m.p. 157–157.5° (lit.<sup>13</sup> 161°). (Found: C, 57.79, 57.50; H, 4.37, 4.40; N, 7.07, 7.10.  $C_{10}H_9NO_4$  calcd.: C, 57.63; H, 4.34; N, 6.87 %.)

11. *Reaction of (IIc) with benzenboronic acid.* To (IIc) (1.3 g, 0.002 mole) in dimethylformamide (20 ml) was added benzenboronic acid (0.3 g, 0.0025 mole) in 1 ml of dimethylformamide and 0.11 g of NaOH in 1 ml of water. After an hour the reaction mixture was poured into a four-fold volume of water and the precipitate filtered off and dried. The precipitate consisted of a mixture of phenylmercury chloride and ylide (Ic). It was washed repeatedly with small amounts of cold benzene and cold methanol and the filtrates collected together. The undissolved precipitate (0.69 g), having a wide m.p. of 165–215°, was recrystallised twice from methanol, m.p. 245–251°. The mixed melting point with an authentic sample of phenylmercury chloride (m.p., 250–252°) showed no depression. The solvent was removed from the filtrate *in vacuo* and the residue recrystallised from a mixture of petroleum ether and benzene to give 0.60 g of phenacylidenetriphenylphosphorane, (Ic), m.p., 165–170°. The mixed melting point with an authentic sample (m.p. 178–180°) showed no depression. Since the m.p. of our ylide was low the compound was also characterised as a  $HgCl_2$  adduct (see expt. 1) yielding (IIc), m.p. 203–205°; m.p. of the authentic sample 208–210° and of the mixed sample 207–209°.

12. *Reaction of (IIb) with benzenboronic acid.* To 1.0 g (0.0017 mole) of (IIb) in dimethylformamide was added benzenboronic acid (0.3 g, 0.0025 mole); the solution was heated to 70° and 10 % sodium hydroxide (0.3 ml) introduced. After 15 min a three-fold volume of water was added, the precipitate was isolated and washed with cold methanol. The precipitate remaining on the filter was recrystallised from nitromethane to give 0.20 g of  $C_6H_5HgCl$ . The melting points of authentic phenylmercuric

chloride, and the reaction product and their mixed melting point were found to be the same: 249–251°.

Acetonylidenetriphenylphosphorane (0.3 g) was isolated from the methanol solution. It was recrystallised from benzene, m.p. 187–190°; m.p. of authentic sample 190–191°, m.p. of mixed sample 188–190°.

13. *Reaction of (II) with complexing compounds.* When ammonia was passed into solutions of (II) in dimethylformamide or chloroform and the mixture left to stand for a short time, the original phosphorylides, (I), were formed. A similar result was achieved by pouring solutions of (II) in dimethylformamide into an aqueous solution of sodium thiosulphate.

14. *Reaction of (IIc) with acetyl chloride.* To a stirred suspension of (IIc) (1.84 g, 0.003 mole) in tetrahydrofuran (15 ml) was added, dropwise, acetyl chloride (0.30 ml, 0.0037 mole). The reaction proceeded exothermally and eventually resulted in the dissolution of the precipitate. A precipitate was obtained by the addition of a three-fold excess of ether, the solvent was decanted and the viscous precipitate stirred in ether until crystalline, giving 1.86 g of (Vc) (88 %); m.p. 185–187° (from nitromethane). (Found: C, 45.21, 45.26; H, 3.31, 3.33; Hg, 28.37, 28.32; P, 4.88, 4.23.  $C_{23}H_{24}Cl_3HgO_2P$  calcd.: C, 45.80; H, 3.28; Hg, 27.50; P, 4.23 %.)

To prove the structure of the product, (Vc) (0.36 g) in dimethylformamide (2 ml) was added to a solution of sodium sulphide (1 ml), in water (8 ml) and the mixture carefully stirred. The black precipitate was filtered off, dried and repeatedly washed with benzene, to give phenacylidenetriphenylphosphorane (Ic); yield 0.185 g. (~100 %), m.p. 179–180° (from benzene); the mixed melting point determination with the authentic sample showed no depression. For further identification mercuric chloride was added to the ylide obtained (see expt. 1). The reaction resulted in (IIc), m.p. 208–210°. A mixed melting point determination with the authentic sample showed no depression.

15. *Interaction of (IIb) with benzoyl chloride.* To a suspension of (IIb) (1.6 g, 0.0027 mole) in tetrahydrofuran (5 ml) was added with stirring benzoyl chloride (0.80 g, 0.0057 mole) in 2 ml of tetrahydrofuran. The precipitate dissolved and then began to reappear. After 30 min it was isolated, washed with benzene and ether to yield (Vc) (95 %, 1.80 g) after two recrystallisations from nitromethane, m.p. 183–186°. The mixed melting point determination with (Vc) showed a considerable depression. (Found: C, 45.92, 45.90; H, 3.30, 3.33; Cl, 14.35, 14.42; Hg, 26.99, 26.12; P, 4.52, 4.48.  $C_{23}H_{24}Cl_3HgO_2P$  calcd.: C, 46.13; H, 3.32; Cl, 14.58; Hg, 27.51; P, 4.25 %.) As with (Vc) (expt. 14), (Vb) was reacted with sodium sulphide to give 0.65 g of acetonylidenetriphenylphosphorane, (Ib), m.p. 193–198° (from benzene), lit.<sup>3</sup> 191–192°. The mixed melting point determination with an authentic sample showed no depression.

16. *Reaction of (IIa) with acetyl chloride.* The reaction was carried out as in expt. 14 to resulting in 83 % of (Va), m.p. 110–111° (from methanol). (Found: C, 39.58, 39.73; H, 3.46, 3.50.  $C_{23}H_{22}Cl_3HgO_3P$  calcd.: C, 40.35; H, 3.24 %.) The mixed melting point of determination with the authentic  $[(C_6H_5)_3P^+CH(COCH_3)(COOCH_3)]^-HgCl_2^-$  showed depression. This compound was prepared by the action of  $HgCl_2$  on the solution of ylide  $(C_6H_5)_3P=C(COCH_3)(COOCH_3)$  in diluted hydrochloric acid, m.p. 140° (the ylide was prepared following Märkl<sup>10</sup>). The structure of the compound (Va) was further substantiated by the reaction of (Va) with sodium sulphide, as described above which yielded 61 % of ylide, m.p. 167–168.5° (from benzene), lit.<sup>14</sup>

167–168°. The mixed melting point determination with an authentic sample showed no depression.

17. *Acylation of phenacylidetriphenylphosphorane.* To a suspension of ylide, (Ic), (1.90 g, 0.0050 mole) in tetrahydrofuran (10 ml) was added, dropwise, acetyl chloride (0.50 ml, 0.0064 mole). After 30 min the solution was decanted. The precipitate was carefully stirred in ether and recrystallised from tetrahydrofuran, yield 52% (1.16 g), m.p. 260–263°. (Found: C, 73.52, 73.50; H, 5.51, 5.40; P, 6.51, 6.56.  $C_{25}H_{24}ClO_2P$  calcd.: C, 73.20; H, 5.22; P, 6.75%.) The action of ammonia or alkali gives the initial phosphorylide, thus proving that acyl is bound to oxygen.

#### Synthesis of starting compounds

Phosphorylides were synthesised by procedures given in the literature as follows: (Ia)<sup>14</sup>, (Ib)<sup>3</sup>, (Ic)<sup>3</sup>, (Ie)<sup>14</sup>. (Id) is described below for the first time.

18. *Synthesis of (p-phenylphenacylidene)triphenylphosphorane (Id).* A mixture of 9.5 g (0.035 mole) of *p*-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>Br and 9.05 g (0.035 mole) of triphenylphosphine in 40 ml of chloroform was left to stand for two days and then diluted with 350 ml of ether. The precipitated oil was crystallised by stirring carefully in ether to yield 15 g of crystals. Reprecipitation from chloroform with ether yielded 72% (13.4 g) of the product. To 13.4 g (0.025 mole) of phosphonium salt in 20 ml of methanol was added sodium methoxide solution (sodium, 1.15 g, 0.050 mole and ethanol 12 ml). After one hour the solvent was removed and benzene (30 ml) added, the solution heated to boiling and filtered when hot. The filtrate was treated with petroleum ether to yield about 60% of phosphorane (7.5 g), m.p. 228–230°; after recrystallisation from benzene, m.p. 229–230°. (Found: C, 84.15, 84.07; H, 5.54, 5.64.  $C_{32}H_{25}OP$  calcd.: C, 84.44; H, 5.52%.)

#### SUMMARY

The addition of HgCl<sub>2</sub> to stable Wittig reagents has resulted in mercurated phosphonium salts of the type:  $[R_3P^+-C(HgCl)(R'')-C(O)R']Cl^-$ . These compounds were found to exhibit triple reactivity. First, they react with aldehydes, benzenboronic acid and reagents binding HgCl<sub>2</sub>, as if they were complexes of HgCl<sub>2</sub> and phosphorylide. Secondly, with acid chlorides they react with the reaction centre transfer on oxygen. Thirdly, at least in one case, it proved possible to prepare a mercury-containing phosphorylide by the action of sodium methoxide on the mercurated phosphonium salt. The substances prepared have been proved to be true organometallic compounds. The possible mechanisms of the reactions studied have been discussed.

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