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Mercurated Phosphonium Salts–a New Type of Quasicomplex Compounds

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Seyferth and Grim described the addition of certain salts to phosphorylides ([1]). By the interaction of sulema with Wittig reagents ([2]), we have obtained mercurated phosphonium salts–colorless crystalline substances insoluble in water and in low-polarity organic solvents.

$$(C_6H_5)_3P=CHR' + HgCl_2 \rightarrow [(C_6H_5)_3P^{\oplus} - \overset{R}{\underset{|}{C}}R' - HgCl]Cl^{\ominus} \qquad \text{(I)}$$

(II)

a) R = H, R′ = $COOCH_3$; b) R = H, R′ = $COCH_3$; c) R = H, R′ = COC_6H_5; d) R = H, R′ = $COC_6H_4C_6H_5$; e) R = C_6H_5, R′ = $COOCH_3$.

On treatment of these salts with ammonia or aqueous sodium thiosulfate, the starting phosphorylide is formed.

$$[(C_6H_5)_3P^{\oplus} - CH(R)HgCl]Cl^{\ominus} + nNH_3 \rightarrow (C_6H_5)_3P=CHR + nNH_3[HgCl_2].$$

Reactions with aldehydes lead to an olefin containing no mercury:

$$[(C_6H_5)_3P^{\oplus}CH(R)HgCl]Cl^{\ominus} + R'CHO \rightarrow RCH=CHR' + (C_6H_5)_3PO$$

a) R = $COOCH_3$, R′ = n-$NO_2C_6H_4$; b) R = COC_6H_5, R′ = n-$NO_2C_6H_4$.

On interaction of II with phenylboric acid, phenylmercuric chloride and a phosphorylide are obtained:

$$[(C_6H_5)_3P^{\oplus}CH(R)HgCl]Cl^{\ominus}+C_6H_5B(OH)_2 \xrightarrow{NaOH} (C_6H_5)_3P=CHR+C_6H_5HgCl$$

$$(R = COCH_3,\ R = COC_6H_5).$$

A. N. Nesmeyanov and I. F. Lutsenko with co-workers showed that α-mercurated aldehydes and ketones react with acid chlorohydrides at the oxygen of the carbonyl group with transfer of the reaction center ([3,5]). Analogously behave IIb and IIc and IIa.

Scheme 1

$$\begin{array}{ccc} [R_3P^{\oplus}-CH(HgCl)COR]Cl^{\ominus}\ (IIc) & & [R_3P^{\oplus}-CH(HgCl)COCH_3]Cl^{\ominus}\ (IIb) \\ \downarrow\ CH_3COCl & & \downarrow\ RCOCl \\ \left[R_3P^{\oplus}-CH=C\begin{matrix}R\\OCOCH_3\end{matrix}\right]HgCl_3{}^{\ominus}\ (IIIc) & \neq & \left[R_3P^{\oplus}-CH=C\begin{matrix}CH_3\\OCOR\end{matrix}\right]HgCl_3{}^{\ominus}\ (IIIb) \\ \downarrow\ Na_2S & & \downarrow\ Na_2S \\ R_3P=CHCOR\ (Ic) & & R_3P=CHCOCH_3\ (Ib) \end{array}$$

$$[R_3P^{\oplus}-CH(HgCl)COOCH_3]Cl^{\ominus} \rightarrow \left[R_3P^{\oplus}CH=C\begin{matrix}OCH_3\\OCOCH_3\end{matrix}\right]HgCl_3{}^{\ominus} \xrightarrow{Na_2S} Ia$$

(IIa) R-phenyl (IIIa)

The structure of the reaction products of IIb and IIc with acid chlorides is evident from the following. If the acyl group had taken the place of mercury (at carbon), then the products

the reactions of IIb with benzoyl chloride and IIb with acetyl chloride would be identical; namely, in both cases the salt $[R_3P^{\oplus}—CH(COCH_3)COC_6H_5]HgCl_3^{\ominus}$ would be formed. On addition of the acyl group to oxygen, different products, IIIb and IIIc, should be formed, which is in fact observed (depression of the melting point on mixing the samples). Further, treatment of IIIb and IIIc with sodium sulfide leads to the starting phosphoranes Ib and Ic; whereas a C-acylated compound should have given, under these conditions, a new phosphorane with two acyl groups at the central carbon atom: $R_3P=C(COCH_3)COR$. IIa is likewise acylated at oxygen. This is evidenced by the reaction of the acylated product (IIIa) with sodium sulfide.

On the basis of the reactions given, the mercurated phosphonium salts give the impression of having a complex character. However, some of their properties prove that they are true organometallic compounds.

In the IR spectra of IIb-g there is a carbonyl peak* and, at the same time, the absorption band in the region of 1520 cm^{-1}, characteristic of phosphoranes of type Ib-g ([6]), is absent. Approximately the same band is also characteristic of arsenic ylides of the corresponding structure ([7]). Thus, the spectra of II are more reminiscent of the spectra of phosphonium salts than of the spectra of phosphoranes. Chemical proof of the covalent character of the C–Hg bond in II is, in our opinion, the formation of the mercurated phosphorane IV upon the action of sodium methylate on IIb:

$$\left[\begin{array}{c}(C_6H_5)_3P^{\oplus}\text{—}C\text{—}COC_6H_5\\ H\\ HgCl\end{array}\right]Cl^{\ominus}\xrightarrow{NaOCH_3}(C_6H_5)_3P=C\begin{array}{c}COC_6H_5\\ HgCl\end{array}$$

(IIb) IV

The structure of the mercurated ylide IV is evident from elemental analysis for C, H, Cl, P, and Hg; from the IR spectrum of IV, in which the carbonyl peak is absent and there is an absorption band at 1525 cm^{-1}, characteristic of ylides of type Ib, c; and, finally, from the reactions of IV with hydrogen chloride and with sublimate:

$$(C_6H_5)_3P=C\begin{array}{c}COC_6H_5\\ HgCl\end{array}$$

(IV)

$$\xrightarrow{HCl}\left[(C_6H_5)_3P^{\oplus}\text{—}CH\begin{array}{c}COC_6H_5\\ HgCl\end{array}\right]Cl^{\ominus}\quad\text{(IIb)}$$

$$\xrightarrow{HgCl_2}\left[(C_6H_5)_3P^{\oplus}\text{—}C\begin{array}{c}COC_6H_5\\ \text{—}HgCl\\ HgCl\end{array}\right]Cl^{\ominus}\quad\text{(V)}$$

In our laboratory it has been shown ([8,9]) that certain benzyl-type organomercury compounds are capable of electrophilic substitution reactions by a monomolecular S_E1 mechanism.

$$RHgX\rightleftarrows R^{\ominus}+{}^{\oplus}HgX.$$

All the more should this mechanism operate in reactions of compounds of type IIa-g.

$$[(C_6H_5)_3P^{\oplus}\text{—}CHCOR\quad HgCl\ ]Cl^{\ominus}\rightleftarrows(C_6H_5)_3P=CHCOR+HgCl_2$$

Indeed, if usually as a result of such dissociation an unstable carbonium cation is formed, then analogous dissociation of mercuri-

* The carbonyl band in the IR spectrum (IIa 1700 cm^{-1}, IIb 1680 cm^{-1}, IIc 1640 cm^{-1}) is shifted to the low-frequency region owing to conjugation of the Hg–C and C=O bonds.

rated phosphonium salts leads to two stable compounds–sulene and phosphorylide*.

Scheme 2 ($R = C_6H_5$)

$$R_3P{=}C\begin{pmatrix} HgCl \\ COR' \end{pmatrix} \xrightarrow{HgCl_2} \left[R_3P^{\oplus}{-}C\begin{pmatrix} HgCl \\ COR' \\ HgCl \end{pmatrix}\right] Cl^{\ominus}$$

(IV) (V)

$$[\ R_3P^{\oplus}{-}C(H)(HgCl){-}COR'\ ]\,Cl^{\ominus} \underset{A}{\overset{\text{DMFA}}{\rightleftharpoons}} [\,R_3P{=}CHCOR' + HgCl_2\,]$$

(II)

$$\left[\ R_3P^{\oplus}{-}CH{=}C\begin{pmatrix} R' \\ O{-}COR'' \end{pmatrix}\ \right] HgCl_3^{\ominus}$$

$$[\,R_3P{=}CHCOR' + HgCl_2\,] \xrightarrow{RCHO} RCH{=}CHCOR' + R_3PO,$$

$$[\,R_3P{=}CHCOR' + HgCl_2\,] \xrightarrow{NH_3 \text{ or } Na_2S_2O_3} (I),$$

$$[\,R_3P{=}CHCOR' + HgCl_2\,] \xrightarrow{Rb(OH)_2} RHgCl + I.$$

DMFA–dimethylformamide; THF–tetrahydrofuran

Table 1

Constants and elemental analyses for the compounds described for the first time

Compound and empirical formula	m.p., °C	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	Hg, % found	Hg, % calculated
IIa $C_{21}H_{19}OPHgCl_2$	190–191	41,42	41,63	3,47	3,36	3,14	4,79	5,11	33,10	32,93	33,11
IIb $C_{21}H_{18}OPHgCl_2$	208–210	42,49	42,32	3,63	3,57	3,25	5,24	5,18	33,62	33,63	34,01

Compound and empirical formula	m.p., °C	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	Hg, % found	Hg, % calculated
IIv $C_{25}H_{21}PHgCl_2$	199–200	47,73	47,61	3,43	3,33	4,74	4,75	30,36	30,80
IIg $C_{32}H_{25}PHgCl_2$	150–220	51,10	51,29	3,87	3,43	4,01	4,21	27,75	27,60
IId $C_{27}H_{23}PO_2HgCl_2$	166–169	46,79	46,85	3,44	3,35	4,37	4,51	30,21	29,25
IIIa $C_{23}H_{22}PHgCl_3$	110–113	39,58	39,73	3,46	3,24				
IIIb $C_{28}H_{24}PHgCl_3$	183–186	45,92	45,96	3,30	3,32	4,52	4,25	26,99	27,51
IIIv $C_{28}H_{24}PHgCl_3$	185–187	45,72	45,96	3,32	3,28	4,88	4,25	28,37	27,55
IV* $C_{26}H_{25}PHgCl_2$	225–227	50,87	50,82	3,40	3,28	5,07	5,08	32,85	32,80
V** $C_{26}H_{25}PHgCl_2$	205–208	50,35	50,45	3,92	3,28	3,79	3,49	44,18	45,20
IV $C_{28}H_{26}PO_2Cl$	260–263	73,52	73,58	5,51	5,22	6,51	6,75		

* Found Cl 5,55; 5,65%; calculated 5,80%.
** Found Cl 11,97; 11,97%; calculated 12,00%.

The reactions we investigated are understandable from this point of view, whereas difficulties arise when a bimolecular mechanism is applied.

* The solvent in most cases is dimethylformamide.

For example, reaction II with an aldehyde by a bimolecular mechanism would imply attack on the carbonyl carbon atom by the electron-rich carbon atom of the phosphonium salt, which is hardly possible.

The monomolecular mechanism of reactions II includes dissociation of II into a phosphor ylide and sulema and interaction of one of the dissociation products with the reagent. For example, phenylboronic acid reacts with sulema to form phenylmercuric chloride, as a result of which the sulema is removed from the reaction sphere and the equilibrium is shifted. The aldehyde reacts with another dissociation product—the phosphor ylide. At first glance, reactions II with acid chlorides may be explained analogously. Indeed, by a special experiment we showed that phenacetylidene-triphenylphosphorane (Ib) is acylated by acetyl

chloride at oxygen, i.e., in the same way as IIb.

$$\underset{\text{(Ib)}}{(C_6H_5)_3P{=}CH{-}C(=O){-}C_6H_5} + ClCOCH_3 \longrightarrow \underset{\text{(VI)}}{\left[(C_6H_5)_3\overset{\oplus}{P}{-}CH{=}C\begin{matrix}-C_6H_5\\ -OCOCH_3\end{matrix}\right]Cl^{\ominus}} \xrightarrow{NH_3} \text{Ib}.$$

However, it is known from the literature that carbomethoxymethylene-triphenylphosphorane (Ia) is acylated at carbon [10], whereas IIa reacts with acetyl chloride (as we showed above) with transfer of the reaction center, i.e., similarly to IIb, c. It follows from this that at least IIa reacts by the bimolecular mechanism S_{Ei} (otherwise a C-acylated product would have been formed).

Thus, mercurated phosphonium salts of type IIa–d exhibit a threefold reactivity. Under the action of bases they (at least Ib) are capable of giving up a proton, being converted into mercurated phosphor ylides, i.e., they behave as ordinary phosphonium salts. They can react with transfer of the reaction center similarly to α-mercurated ketones (path B, Scheme 2). Finally, in a number of cases they react with elimination of sulema, exhibiting quasi-complex properties (path A, Scheme 2).

By calling the mercurated phosphonium salts quasi-complex compounds, we wish to emphasize their analogy with ordinary quasi-complex mercury compounds [11], for example, with adducts of sulema with olefins. The analogy lies both in the method of preparation and in a number of reactions; moreover, the phosphor ylide (phosphorylene) formally acts as an unsaturated compound. It should be borne in mind, however, that the mechanism of these reactions is apparently different.

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