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Abstract

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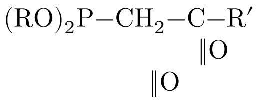
POTASSIUM AND SODIUM SALTS OF BIS-DIPHENYLPHOSPHINYL-METHANE AND THEIR REACTIONS WITH ALDEHYDES

At the present time two methods of olefin synthesis with the aid of organophosphorus compounds are widely known. These are the Wittig reaction—the action of aldehydes and ketones on methylenephosphoranes (^{1})

$$R_3P{=}CR'R'' + O{=}C< \longrightarrow R_3PO + R'R''C{=}C<$$

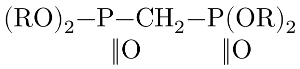
and "PO-activated olefination" according to Horner. The latter, as is known, consists in the reaction with aldehydes and ketones of sodium and other alkaline derivatives of compounds containing a methylene group activated by the neighboring $P{=}O$ group (^{2}). Horner regards this reaction as fundamentally different from the Wittig reaction and assigns the principal role in it to the true organometallic compound formed from the methylene component. The metallic derivatives of the initial methylene compounds, however, have not been isolated in pure form, and their structure as organometallic compounds has not been proved. Thus, in this part the Horner scheme has no direct experimental substantiation.

Metallic derivatives of β-ketophosphinic esters have been described in the literature, in the molecules of which the methylene group is located between a phosphoryl group and a carbonyl (I) (^{3}), and of bis-dialkylphosphorylmethanes (II) (^{4}), in which the methylene group is located between two phosphoryl groups:



$$\underset{\|O}{(RO)_2P}-CH_2-\underset{\|O}{C}-R'$$

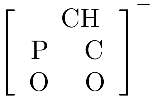
(I)

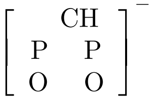


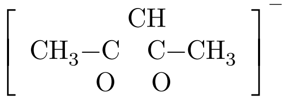
$$(RO)_2-\underset{\|O}{P}-CH_2-\underset{\|O}{P}(OR)_2$$

(II)

The structure of the metallic derivatives of these compounds has been studied by means of IR and UV spectra and by the NMR method. In this way data were obtained that made it possible to conclude that the negative charge in the anions of these compounds is delocalized between both oxygen atoms and the central carbon atom (III and IV), similarly to the distribution of bonds and of the negative charge in the acetylacetonate anion (V):





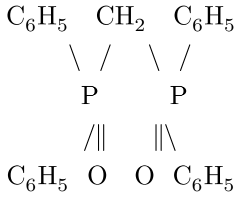


(III) (IV) (V)

Thus, these metallic derivatives have a structure analogous to acetylacetonates and, accordingly, are not true organometallic compounds. Recently, Wadsworth and Emmons reported (5) that bis-diethylphosphorylmethane reacts with benzaldehyde in the presence of sodium hydride to form esters of β-phenylvinylphosphonic acid, i.e., it undergoes a "PO-activated olefination" reaction, which in this case undoubtedly proceeds without passing through an organometallic stage. Unfortunately, in this reaction the individual sodium derivative was not isolated.

$$CH_2[P(O)(OC_2H_5)_2]_2 + C_6H_5CHO \xrightarrow{NaH} C_6H_5CH{=}CHP(O)(OC_2H_5)_2.$$

Having at our disposal bis-diphenylphosphinylmethane (tetraphenylmethylenediphosphine dioxide), hereinafter called the "dioxide" (VI) (6), we investigated its ability to form



(VI)

sodium and potassium derivatives, isolated these derivatives in analytically pure form, and studied their IR spectra and reactions with aldehydes.

The dioxide begins to react with metallic potassium already at room temperature; however, the reaction proceeds slowly. In boiling xylene it proceeds rapidly. The potassium derivative obtained in this way corresponds by analysis to the monopotassium salt. It is an infusible colorless substance distinguished by extreme hygroscopicity. In an atmosphere of dry nitrogen it can be stored unchanged for a long time. The same salt is obtained by the action of potassium tert-butoxide on a benzene solution of the dioxide under reflux for 1-2 h.

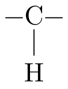
The sodium salt, like the potassium salt, can be obtained by the action of metallic sodium on the dioxide. It is also readily obtained by the action of sodium hydride. Similar in its properties to the preceding salt, it corresponds by analysis to the monosodium salt.

We investigated the infrared spectra of these salts, as well as the spectrum of the starting dioxide. The IR spectra are shown in Fig. 1*.

A number of frequencies (1587, 1482, 1434, 1371, 1188, 1173, 1117, and others) common to the spectrum of bis-diphenylphosphinylmethane and its salts are evidently associated with vibrations of phenyl rings attached to phosphorus (7), the analysis of which is not of interest here.

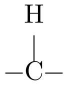
In the spectra of the salts, in comparison with the spectrum of the starting dioxide, a broad intense absorption appears in the region 1480-1400 cm^{-1}, overlapping the absorption of the phenyl rings (Fig. 1). Cotton and co-workers (3,8) point to the appearance of absorption in this region in the infrared spectra of anions of salts of diethylphosphorylacetone (I, $R = C_2H_5$, $R' = CH_3$; the structure of the salt corresponds to formula III) and acetylacetonates (V).

It is characteristic that the absorption under consideration in these salts falls precisely in the absorption region of phenyl rings (7), which corresponds to a complex vibration involving the C—C bond and the CCH angle (vibration of the structural element



$$-\underset{\displaystyle H}{\underset{|}{C}}-$$

). Since in the salts under consideration there is the same structural element



$$-\overset{\displaystyle H}{\overset{|}{C}}-$$

one may suppose that it corresponds to approximately the same distribution of bonds at the carbon atom as in the phenyl ring, i.e., the salts must correspond to a structure with equalized bonds, similar to IV.

Another interesting region for analysis is the region of “PO vibrations.” However, the absorption of the phenyl rings also falls here [7], and is superimposed on the PO-vibration band, thereby making analysis of the spectrum difficult. In the spectrum of the dioxide these are the bands at 1188 and 1174 cm^{-1}, whereas the PO vibration here corresponds to absorption at 1204 cm^{-1}. In the salts, absorption in the region of 1204 cm^{-1} is absent, and the PO vibration here is

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* The spectra were obtained for compounds in the solid state (KBr pellet) in the 2000-400 cm^{-1} region on an IKS-14 instrument.

masked by absorption of the phenyl rings. In the case of the sodium salt of bis-diethylphosphorylmethane $[(C_2H_5O)_2PO]CHNa$ [3,8], the shift of the PO band upon salt formation reaches 65 cm^{-1} [4]. A corresponding shift of the frequencies of the PO and CO vibrations is also observed in the spectra of the anions of dialkylphosphorylacetones (I; $R' = CH_3$) and acetylacetonates V.

It should be noted that in the IR spectra of the salts, in the region of 950 cm^{-1}, fairly intense absorption appears, which is difficult to assign, since it falls in a region that, as a rule, is uncharacteristic of skeletal vibrations. Preliminary results of a calculation of the vibrations of the corresponding model show that the frequency 950 cm^{-1} corresponds to a vibration involving the PC bond and the angle between the PO and PC bonds.

Fig. 1. IR spectra of bis-diphenylphosphinylmethane and its potassium and sodium salts

Thus, the changes in the IR spectrum of the dioxide upon transition to the salts correspond to the changes in the IR spectra of bis-dialkylphosphorylmethane, diethylphosphorylacetone, and acetylacetone upon transition to their salts. Hence the anion of the dioxide should be assigned a structure of type IV with delocalized PO and PC π-bonds (formation of an extended π-orbital between all atoms of the pentad).

The reactions of the salts of bis-diphenylphosphinylmethane with aldehydes were studied by us using the potassium salt as an example. They lead to the formation of phosphine oxides containing β-substituted vinyl groups, and the potassium salt

Table 1

Substituted diphenylphosphinylethylenes
$(C_6H_5)_2PCH = CHR$
$\|$
O

No.	R	m.p., °C	C, % found	C, % calcd.	H, % found	H, % calcd.	P, % found	P, % calcd.	Yield, %
1	H	114–116*	73.4; 73.4	73.7	5.6; 5.6	5.7	13.5; 13.5	13.6	49.5
2	C_2H_5	148–149	74.6; 74.8	75.0	6.9; 6.9	6.6	11.9; 12.0	12.1	35
3	iso-C_3H_7	148–150	75.4; 75.6	75.5	7.4; 7.5	7.1	11.7; 11.6	11.5	43.5
4	C_6H_5	165–167	79.2; 79.1	78.9	5.8; 5.8	5.6	10.3; 10.3	10.2	56.6
5	$NO_2C_6H_4$	162–163	68.9; 69.1	68.8	4.9; 4.8	4.6	8.9; 8.7	8.9	38.6

No.	R	m.p., °C	C, % found	C, % calcd.	H, % found	H, % calcd.	P, % found	P, % calcd.	Yield, %
6	$C_6H_5CH=CH$	175–176	79.9; 80.0	80.0	5.8; 5.7	5.8	9.4; 9.4	9.4	46.5
7	$-C_6H_4-$	354–355	76.5; 76.6	76.9	5.5; 5.4	5.3	11.7; 11.6	11.7	25

* Literature data [10]: m.p. 116–117°.

diphenylphosphinic acid. The results obtained make it possible to represent this reaction as follows:

$$[(C_6H_5)_2P-CH-P(C_6H_5)_2]^{-}+RHC=O \longrightarrow RCH=CHP(C_6H_5)_2+(C_6H_5)_2P=O$$

$$\overset{\|}{O} \qquad\qquad\qquad O^{-}$$

The reaction proceeds on heating the potassium salt of dioxie with an aldehyde in xylene. It was carried out with both aromatic and aliphatic aldehydes. The substances obtained, their melting points, analyses, and yields are presented in Table 1.

It should be noted that this reaction is a method for the synthesis of phosphine oxides containing β-substituted vinyl groups.

The question arises whether this reaction should be assigned to the Wittig type of syntheses or to "PO-activated olefination." By the manner of execution it belongs to the latter type. If, however, one considers the structure of the starting salt, in which there is a type of P–C bond characteristic of phosphinomethylenes (partial multiplicity of the P–C bond), then it should be assigned to the Wittig type of reaction. Apparently, there is not such a substantial difference between the Wittig and Horner reactions as is assumed in the literature.

Experimental Part*

Preparation of the potassium salt of bis-diphenylphosphinylmethane ("dioxie"). 0.39 g (0.01 g-at.) of potassium, dispersed according to Brühl in 200 ml of xylene, and 4.16 g (0.01 mole) of dioxie were heated in a nitrogen atmosphere for 2 hours at 115-125° with vigorous stirring. The precipitate formed was filtered off and dried to constant weight.

Found, %: P 13.3; 13.4; K 9.1; 9.2
$C_{25}H_{21}P_2O_2K$. Calculated, %: P 13.6; K 8.6

A slightly yellowish substance, strongly hygroscopic, insoluble in organic solvents. All operations were carried out in a chamber filled with thoroughly dried nitrogen.

β-Diphenylphosphinylstyrene (Table 1, substance 4). To the potassium salt in xylene, prepared as indicated above, 1.2 g (0.011 mole) of benzaldehyde was added, and the mixture was heated for one hour at 115–125°. The reaction was carried out with stirring in a nitrogen atmosphere. The precipitate formed was filtered off, dissolved in water, and the solution was acidified with hydrochloric acid until precipitation was complete. The precipitated substance was filtered off. Obtained 2 g; m.p. 191–192°. The melting point of a mixed sample with diphenylphosphinic acid was 191–192°. Literature data (9): m.p. 190–192°. The xylene filtrate was evaporated in vacuo to dryness. After two recrystallizations from acetone, 1.7 g of β-diphenylphosphinylstyrene was obtained (56.6%); m.p. 165–167°.

Similar results were obtained when the synthesis was carried out in dimethoxyethane, and also in tert-butyl alcohol in the presence of potassium tert-butylate.

Reactions with the other aldehydes listed in Table 1 were carried out in an analogous manner.

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* With the participation of G. F. Dmitrieva.

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

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