Studies on Organophosphorus Compounds. I. The Reaction of O, O-Dimethyl Phosphonate with p-Benzoquinone

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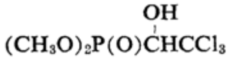
It is well known that phosphonates* having phosphorus-hydrogen linkage react with the carbonyl groups as aldol-condensation to produce α-hydroxy phosphonate⁽¹⁾:

$$C_6H_5CHO+HP(O)(OH)_2 \rightarrow C_6H_5CH(OH)P(O)(OH)_2$$

Ville⁽²⁾ and Marie⁽³⁾ studied this reaction with various ketones and aldehydes from 1889 to 1904.

Recently, it has been well known that Dipterex⁽⁴⁾ was prepared by this reaction of *O, O*-dimethyl phosphonate with chloral, which proved to be very useful as an insecticide.

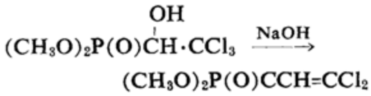
$$(CH_3O)_2P(O)H+OHC\cdot CCl_3$$



$$\rightarrow (CH_3O)_2P(O)\overset{OH}{\overset{|}{C}}HCCl_3$$

Furthermore, Sallman et al.⁽⁵⁾ have reported that *O, O*-dialkyl phosphonates react with α, α'-dihalo-ketones to produce α-hydroxy-β, β'-dihalo phosphonates which are also useful as an insecticide.

The products of this reaction, α-hydroxy-β-halo phosphonates, have not only the agricultural usefulness but also a very interesting property which is that the phosphonates are changed to vinyl phosphorates under the presence of alkaline⁽⁶⁻⁸⁾.

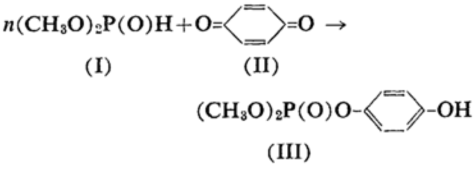


$$(CH_3O)_2P(O)\overset{OH}{\overset{|}{C}}H\cdot CCl_3 \xrightarrow{NaOH} (CH_3O)_2P(O)CCH{=}CCl_2$$

Thus, the reaction of phosphonate having the phosphorus-hydrogen linkage with carbonyl groups of aldehydes or ketones were studied widely, but the reaction with the carbonyl group of benzoquinone has not been reported yet.

During the course of an investigation of organophosphorus compounds, the present author found that the reaction of *O, O*-dimethyl phosphonate with carbonyl group of *p*-benzoquinone did not produce the usual α-hydroxy phosphonate but the phosphorate having *p*-hydroxy-phenyl group.

The reaction of two moles ratio of *O, O*-dimethyl phosphonate with one mole ratio of *p*-benzoquinone produced undistillable pale yellow oil. This product was purified by acetone and ligroin. The refractive index and the infrared absorption spectrum of this product was not changed by the purification using silica-gel column-chromatography. So, it was considered that this product was a pure substance. The microanalytical data of this product showed that this product was composed of one mole ratio of *O, O*-dimethyl phosphonate and one mole ratio of *p*-benzoquinone. Moreover, the reaction product of one mole ratio of *O, O*-dimethyl phosphonate and one mole ratio of *p*-benzoquinone showed the same refractive index, infrared absorption spectrum and microanalytical data as the above product.



$n(CH_3O)_2P(O)H$ + O= =O →

(I) (II)

$(CH_3O)_2P(O)O$- -OH

(III)

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* Phosphorus compounds in this paper were named according to the Drake Comittee's Report (*Chem. Eng. News*, **30**, 4515 (1952)).

1) G. N. Kosolapoff, "Organophosphorus Compounds", Jhon Wiley & Sons. (1950), p. 129.

2) J. Ville, *Compt. rend.*, **107**, 659 (1888); **109**, 71 (1890); **110**, 384 (1890).

3) C. Marie, ibid., **133**, 219, 818 (1901); **134**, 286, 847 (1902); **135**, 106, 1118 (1902); **136**, 48, 234, 508 (1903); **137**, 124 (1903); **138**, 1707 (1904).

4) W. Lovenz, U. S. Pat. 2701225.

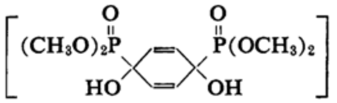
5) R. Sallman, D. R. Pat. 1000364.

6) W. F. Barthel, *J. Am. Chem. Soc.*, **77**, 2424 (1955).

7) W. Lorenz, ibid., **77**, 2554 (1955).

8) W. Perkow, D. R. Pat. 1024945.

n is 1 or 2



The infrared absorption spectrum of this product III did not show the absorption bands of the carbonyl group of *p*-benzoquinone, but strong absorption bands of phenyl group (1450, $1510\ cm^{-1}$)9), P=O ($1265\ cm^{-1}$)9) and P-O-C (Arom) linkages ($1205\ cm^{-1}$)9) were observed. (see Fig. 1).

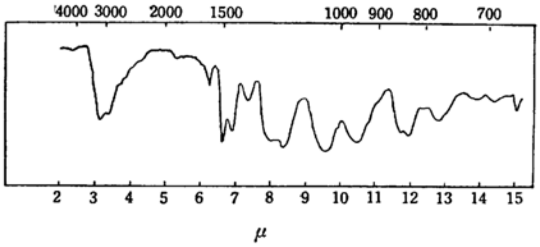


Fig. 1 The infrared spectrum of *O*, *O*-dimethyl-*O*-(*p*-hydroxy-phenyl)phosphorate (III) (liquid).

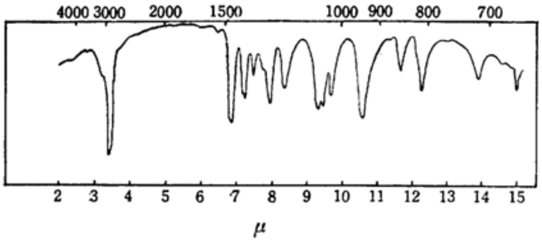


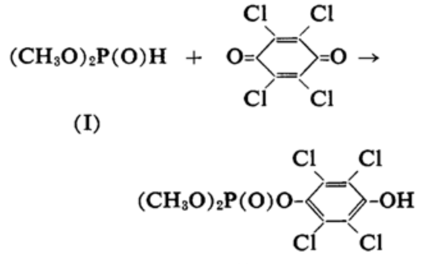
Fig. 2 The infrared spectrum of *O*, *O*-dimethyl-*O*-(4-hydroxy-2, 3, 5, 6-tetrachloro-phenyl)phosphorate (IV) (in Nujol).

Moreover, the product showed the color reaction of phenol by ferric chloride and a hydrolysis of the product produced hydroquinone.

From the above results, it was presumed that the reaction of *O*, *O*-dimethyl phosphonate with the carbonyl group of *p*-benzoquinone did not produce the usual α-hydroxy phosphonate but 4-hydroxy-phenyl phosphorate (III).

In the above experiments, there remained uncertainty whether the product is the pure material or not, because the product is an undistillable oil. However, the above presumption against the above experimental results was confirmed by the reaction of *O*, *O*-dimethyl phosphonate with chloranil. The reaction of one or two moles ratio of *O*, *O*-dimethyl phosphonate with one mole ratio of chloranil produced the same crystals which melt at 237~239°C.

The melting point of these crystals coincided with that of *O*, *O*-dimethyl-*O*-(4-hydroxy-2, 3, 5, 6-tetrachlorophenyl)phosphorate (IV) which was prepared by Ramirez's method10) and the mixed melting point did not decrease.

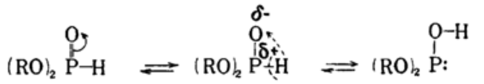


(I)

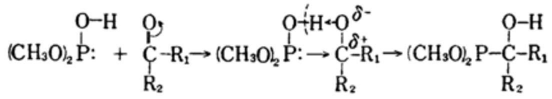
(IV)

It seems that the above reactions have different mechanism from the usual reactions of phosphonate with carbonyl groups of aldehydes and ketones.

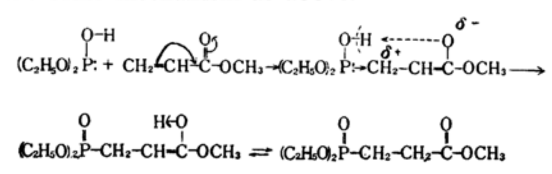
It is considered that *O*, *O*-dialkyl phosphonate have polymerized form of two or three molecules by hydrogen bonding at the free state11-13), but in aldol type reactions, the hydrogen atom is released easily as proton and the phosphonate becomes the phosphite-form14):



Therefore, when the phosphonate reacts with the aldehydes or ketones, this hydrogen atom cuts itself off as proton from phosphite molecule and the phosphite group reacts with the electrophilic carbon atom of carbonyl group just as the aldehyde group in aldol condensation does.



When the phosphonate reacts with the carbonyl group which has an ethylenic double bond in conjugated system, the phosphorus atom links the β-carbon atom of carbonyl group15). This reaction might be explained by the same mechanism as above.



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[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules"; Jhon Wiley & Sons. (1958).

[10] F. Ramirez, *J. Am. Chem. Soc.*, **81**, 587 (1959).

[11] B. A. Arbuzov, *Doklady Akad. Nauk S. S. S. R.*, **54**, 599 (1946).

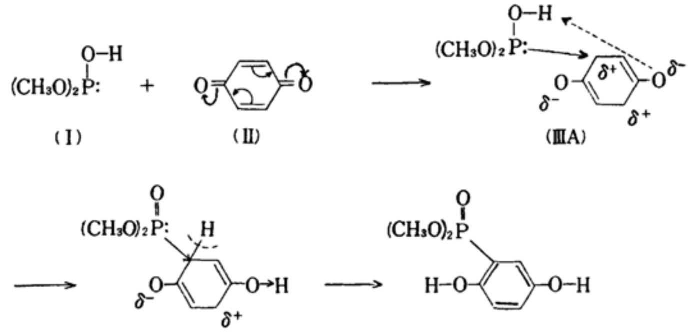
[12] B. A. Arbuzov, ibid., **54**, 787 (1946).

[13] B. A. Arbuzov, ibid., **55**, 31 (1947).

[14] M. Murakami, "Hanno-Yuukikagaku", Asakura-Syoten (1949), p. 316.

[15] E. C. Ladd, Can. Pat. 509034.

If the reaction of the phosphonate with the quinone has the same ionic mechanism, it may be considered that the quinone have the formula IIIA as excited resonance form[16]. According to this mechanism, it is normal that the phosphorus atom attacks the carbon atom of the quinone nucleus.

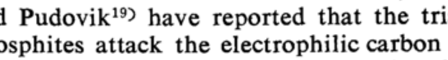


(I) (II) (IIIA)

(IIIB) (IIIC)

In fact, hydrogen halides, benzene sulfonic acids or xanthic acids react with quinone and link the carbon atom of quinone nucleus according to the above mechanism[16]. But the reaction of phosphonate can not be explained by the above mechanism, since the experimental facts show the production of the phosphorate.

On the other hand, it is well known that the reaction of trialkyl phosphites with α-halo-carbonyl compounds does not produce the phosphonates as in Arbuzov's reaction but phosphorates as in Perkow's reaction[17].



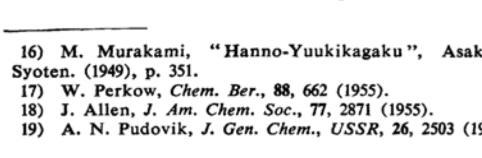
$$(RO)_3P + XR' \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}-R' + RX$$

(Arbuzov's reaction)

$$(RO)_3P + \underset{R_3}{\overset{O}{\overset{\|}{C}}}-\underset{R_2}{\overset{X}{\overset{|}{C}}}-R_1 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}-O-\underset{R_3}{C}=C\genfrac{}{}{0pt}{}{R_1}{R_2}$$

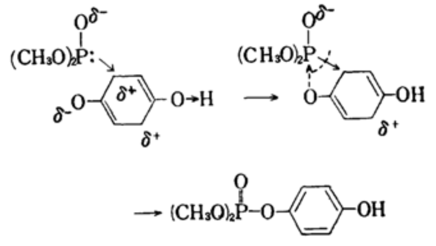
(Perkow's reaction)

On the above reaction mechanism, Allen[18] and Pudovik[19] have reported that the trialkyl phosphites attack the electrophilic carbon atom of carbonyl group and then the phosphorus atom forms the oxide ring as the intermediate:



In the reaction of *O, O*-dimethyl phosphonate with *p*-benzoquinone, it is considered that the reaction mechanism is the same as above, namely, phosphite group attacks the nucleophilic carbon atom of quinone nucleus and then the phosphorus atom forms the oxide ring as intermediate because there is a carbonyl group at α-position.

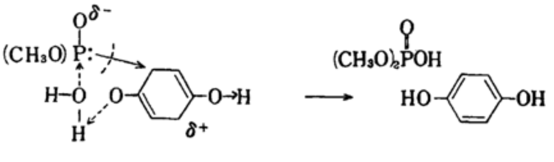
Accordingly, the phosphorus atom cuts itself off from the quinone nucleus instead of eliminating the hydrogen atom and then the phosphorate is produced.



(III)

It is well explained by this mechanism that the phosphonate reacts with *p*-benzoquinone by 1:1 mole ratio and does not produce the α-hydroxy phosphonate but produces phosphorate and, moreover, when the water is presented in this reaction, hydroquinone is produced.

Namely, in the presence of water, the phosphorus atom forms the oxide ring between the oxygen atom of water instead of the oxygen atom of quinone. So, Perkow's rearrangement occurs between the phosphonate and the water.



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[16] M. Murakami, "Hanno-Yuukikagaku", Asakura-Syoten. (1949), p. 351.
[17] W. Perkow, *Chem. Ber.*, **88**, 662 (1955).
[18] J. Allen, *J. Am. Chem. Soc.*, **77**, 2871 (1955).
[19] A. N. Pudovik, *J. Gen. Chem., USSR*, **26**, 2503 (1956).

Experimental

Reaction of *O*, *O*-Dimethyl Phosphonate with *p*-Benzoquinone.—To a solution of 15 g. of *p*-benzoquinone and 0.5 g. of triethylamine in 45 ml. of dioxane was gradually added under cooling by water 32.0 g. of *O*, *O*-dimethyl phosphonate. After the addition, the reaction mixture was stirred for 7 hr. at 70°C and then allowed to stand over night at room temperature. The reaction mixture was condensed in vacuo (0.3 mmHg) at 60°C, 30.0 g. of the pale yellow oil was obtained.

This oil was dissolved in acetone and then ligroin was added gradually. The upper layer was separated by decantation, and the lower layer was concentrated in vacuo. The viscous oil was obtained and yielded 25.0 g. (83%) n_D^{26} 1.5205.

Found: P, 14.3. Calcd. for $C_8H_{11}O_5P$: P, 14.2%.

The same reaction using 16.5 g. of *O*, *O*-dimethyl phosphonate instead of 32.0 g. of *O*, *O*-dimethyl phosphonate, produced 23.8 g. of same oil.

Hydrolysis of *O*, *O*-Dimethyl-*O*-(4-hydroxyphenyl)phosphorate (III).—The mixture of 10.0 g. of *O*, *O*-dimethyl-*O*-(4-hydroxy-phenyl)phosphorate (III) and 30 ml. of 8% hydrochloric acid was heated at 80°C for 50 hr. The water layer was extracted continuously with ether and then the ether layer was dried over anhydrous sodium sulfate. After removal of the ether, the residue was recrystallized from benzene.

Four grams of *p*-hydroquinone was obtained and melted at 170∼171°C. The melting point of a mixture of the hydroquinone and the authentic specimen did not decrease.

Reaction of *O*, *O*-Dimethyl Phosphonate with Chloranil.—To a solution of 24.6 g. of chloranil in 250 ml. of dioxane was added by drop-wise 11.0 g. of *O*, *O*-dimethyl phosphonate under cooling with ice water. After the addition, the reaction mixture was stirred for 5 hr. at 80°C and then cooled. The reaction mixture was concentrated under a reduced pressure and the crude crystals were precipitated. The crystals were recrystallized from methanol, melted at 237∼239°C. and yielded 22.0 g. (61%). A mixture of these crystals and the authentic *O*, *O*-dimethyl-*O*-(4-hydroxy-2, 3, 5, 6-tetrachloro-phenyl)-phosphorate which was prepared by Ramirez's method[10] melted at 238∼239°C.

Found: P, 9.2; Cl, 39.73. Calcd. for $C_8H_7Cl_4O_5P$: P, 8.7; Cl, 39.88%.

Reaction of *O*, *O*-Dimethyl Phosphonate with *p*-Benzoquinone under the Presence of Water.—The solution of 15 g. of *p*-benzoquinone in 100 ml. of methanol which contained 5% water was added to the solution of 16.5 g. of *O*, *O*-dimethyl phosphonate in 50 ml. of benzene. After the reaction mixture was stirred, benzene, water and alcohol were removed and then the residue was extracted continuously with ether. The ether layer was dried over anhydrous sodium sulfate. After removal of the ether, the residue was recrystallized from benzene and 10.8 g. of the hydroquinone was obtained and melted at 171∼172°C.

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