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Abstract

Full Text

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Interaction of Dialkylphosphorous Acids with Quinones

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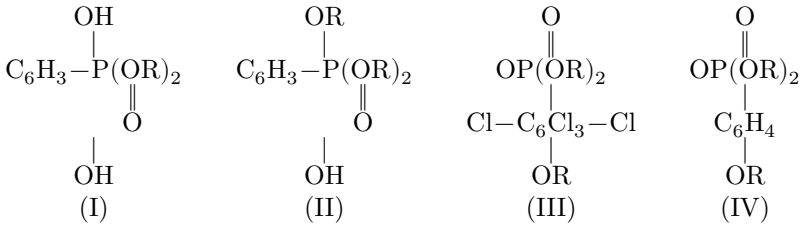
In previous works (1-3) the high activity of organophosphorus compounds as synthetic additives to lubricating oils was shown. These include, for example, certain derivatives of dithiophosphoric, phosphonic, and phosphorous acids. It seemed of considerable interest to obtain organophosphorus compounds which, in addition to other properties, would also possess the properties of antioxidants, additives that inhibit the oxidation of hydrocarbons by atmospheric oxygen.

We attempted to carry out the addition of incomplete esters of phosphorous acid, dialkylphosphorous acids, to quinones. This reaction was also of independent significance. V. S. Abramov (4,5) studied the reaction of dialkylphosphorous acids with aldehydes and ketones in the presence of alcohol. It was established that the addition of dialkylphosphorous acids occurs at the carbonyl group with the formation of esters of α-hydroxyalkylphosphonic acids. A. N. Pudovik, Yu. P. Kitaev, and G. Zametaeva (6-8) carried out the addition of dialkylphosphorous acids, also in the presence of alcoholates, to various unsaturated compounds. In this case, addition to unsaturated ketones occurs at the double carbon-carbon bond.

In the case considered by us, the interaction of dialkylphosphorous acids with *p*-benzoquinone could presumably lead to the formation of esters of dihydroxyphenylphosphonic acids (I). The possibility of such a reaction pathway was indicated by

(I) (II) (III) (IV)



the patent of Ledd and Harvey (9). In a recently published work (10), the addition of complete esters of phosphorous acid to *p*-benzoquinone was carried out, and it was shown that compounds of the same type (II) are obtained. At the same time, there are indications in the literature that the addition reaction of phosphites to *p*-benzoquinone and some of its derivatives can also proceed in another direction, namely with the formation of compounds in which phosphorus is bonded to oxygen. Thus, in work (11), in the interaction of triethyl phosphite with chloranil, a compound of structure (III) was obtained as the main reaction product. The authors (12) attri-

···ascribe to compounds obtained as a result of the reaction of trialkyl phosphites with *p*-benzoquinone (IV). Subsequent works (13,14) confirmed their conclusions.

As we have established, in the reaction of dialkylphosphorous acids with *p*-benzoquinone, dialkyl *p*-oxyphenyl phosphates are formed, and, consequently, the phosphorus group adds to the oxygen atom of benzoquinone according to the equation:

$$C_6H_4O_2 + HOP(OR)_2 \xrightarrow{RONa} HO - C_6H_4 - OP(=O)(OR)_2$$

The addition is accompanied by the usual transformation of the quinoid structure of the ring into the benzenoid one. In an analogous way the interac—

Table 1

Phosphoric acid esters	Melting temp., °C	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	OH, % found	OH, % calculated	Yield, %
HO − C_6H_4 − OP(= O)(OCH_3)$_2$	74.5 — 75.5	43.87; 43.75	44.00	5.17; 5.07	5.05	14.04; 14.28	14.26	7.76; 7.89	7.80	70
HO − C_6H_4 − OP(= O)(OC_2H_5)$_2$	38.5 — 39.0	48.06; 48.99	48.00	6.15; 6.06	6.09	12.66; 12.69	12.60	—	—	41
HO − C_6H_4 − OP(= O)(OC_3H_7-iso)$_2$	49.5 — 50.0	52.41; 52.55	52.50	7.07; 7.07	6.93	11.31	11.40	6.22	6.13	53
HO − C_6H_4 − OP(= O)(OC_4H_9-iso)$_2$	52.5 — 53.5	55.32; 55.44	55.62	7.81; 7.82	7.61	10.24; 10.31	10.26	5.57; 5.21	5.59	50
HO − C_6H_4 − OP(= O)($OC(CH_3)_2$)$_2$	—	—	—	—	—	11.57	11.40	—	—	62

Phosphoric acid esters	Melting temp., °C	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	OH, % found	OH, % calculated	Yield, %
$HO-C_6H_4-OP(=O)(OC_6H_5)_2$	93–95.0	—	—	—	—	9.30	9.06	—	—	—
$HO-C_{10}H_6-OP(=O)(OCH_3)_2$	111–99.0	—	—	—	—	11.47	11.55	—	—	62
$HO-C_{10}H_6-OP(=O)(OC_2H_5)_2$	98.5–99.0	—	—	—	—	10.60	10.45	—	—	51
$NHC_6H_5-OC_6H_4-OP(=O)(OCH_3)_2$	120–121.0	53.37; 53.45	$C_{16}H_{18}NO_5P$ 53.40	4.77; 4.79	5.04	9.16; 9.19	9.20	—	—	89
$CH_3O-C_6H_4-OP(=O)(OCH_3)_2$	153.0–156.0° (3 mm)**	—	—	—	—	13.62	13.37	—	—	42.4

* Nitrogen content, %: found 4.25; 4.35; calculated 4.15.
** n_D^{20} 1.4968; d_{20}^{20} 1.2511.

···action of dialkylphosphorous acids with α-naphthoquinone. Table 1 gives the melting points and analytical results for the compounds we obtained.

The reaction was carried out with an equimolecular ratio of *p*-benzoquinone (or α-naphthoquinone) and the dialkylphosphorous acid, in the presence of sodium alcoholate. As solvent, dry alcohol containing the same hydrocarbon radical as the alkoxy groups of the phosphite was used, or dry benzene. In the reaction of *p*-benzoquinone with tetramethylethylene glycol phosphorous acid and diphenylphosphorous acid, the solvents were dioxane and diethyl ether. As a result of the reaction, crystalline substances are formed, soluble in aqueous alkali solutions, giving the characteristic color reaction for phenolic hydroxyl with ferric chloride and showing no reactions characteristic of a carbonyl group.

On hydrolysis of the substances obtained with hydrochloric acid (1 : 1), hydroquinone is formed in yields of up to 80%. Saponification with alcoholic alkali at 40–50° also leads to the formation of hydroquinone (or the corresponding phenol) and a phosphorus compound. Quantitative determination of the hydroxyl-group content, by acetylation with acetic anhydride in the presence of pyridine, showed that all the compounds obtained contain only one hydroxyl group each. For one compound, namely that obtained from dimethylphosphorous acid and *p*-benzoquinone, the reaction with phenyl isocyanate was carried

out and the corresponding phenylurethane was isolated.

The study of the absorption spectra of the compounds in the ultraviolet region also confirms that the compounds obtained are esters of *p*-oxyphenylphosphoric acid. Indeed, if the reaction products of dialkyl phosphites with quinones were esters of hydroquinonephosphinous acid (I), then in their spectra one would expect a shift of the absorption maximum toward longer wavelengths in comparison with hydroquinone, as occurs, for example, in the case of 2,5-dioxybenzoic acid[15] or nitrohydroquinone[16]. If, however, the compounds obtained by us are constructed as esters of *p*-oxyphenylphosphoric acid (IV), then a shift of the maximum toward shorter wavelengths should be expected, as in the case of *O*-acetyl derivatives of hydroquinone[17].

Table 2

UV absorption spectra of hydroquinone derivatives

Compound	λ_{max}, mμ	lg ε
$HO-C_6H_4-OH$	290	3.4
$HO-C_6H_3(COOH)-OH$	320	–
$HO-C_6H_4-O-P(=O)(OCH_3)_2$	280	3.7
$HO-C_6H_4-O-P(=O)(OC_2H_5)_2$	280	3.67
$HO-C_6H_4-O-P(=O)(OC(CH_3)_2)_2$	280	3.69
$HO-C_6H_4-O-P(=O)(OC_6H_5)_2$	280	3.66
$CH_3O-C_6H_4-O-P(=O)(OCH_3)_2$	280	3.69

As can be seen from Table 2, the absorption maximum of the products of the interaction of dialkylphosphorous acids with quinones is shifted toward shorter wavelengths and coincides with the absorption maximum of dimethyl-*p*-methoxyphenyl phosphate. The latter was synthesized by us by a known method[18], and its structure is beyond doubt.

Thus, the results of investigation of the substances obtained by the interaction of dialkylphosphorous acids with *p*-benzoquinone (hydrolysis with formation of hydroquinone, absence of carbonyl groups, content of one phenolic hydroxyl) show that these substances are indeed···

are phosphoric acid esters, namely dialkyl-*p*-oxyphenyl phosphates

$$HO-C_6H_4-OP(OR)_2$$
$$\|$$
$$O$$

Experimental Section

Dimethyl-*p*-oxyphenyl phosphate. To a solution of 5.5 g (0.05 mole) of dimethylphosphorous acid in 40 ml of dry methyl alcohol was added about 1 ml of a solution of sodium methylate and, after cooling the resulting solution to 0°, 5.4 g (0.05 mole) of benzoquinone was added in small portions. The reaction mixture was then heated for $1\frac{1}{2}$ hours on a water bath. After the reaction was complete, the methyl alcohol was distilled off; the residue crystallized. After two recrystallizations from water, 7.3 g (70.7% of the theoretical yield) of the ester was obtained, m.p. 74.5–75.5°.

Phenylcarbamate of the acid (phenylurethane). A mixture of 2.1 g of dimethyl-*p*-oxyphenyl phosphate and 4 ml of phenyl isocyanate was heated for 10 hours on a water bath at 75–85°. The white crystalline substance formed was washed with petroleum ether and recrystallized twice from benzene, m.p. 120–121°.

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