Russian Journal of General Chemistry, Vol. 71, No. 10, 2001, pp. 1545–1546. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 10, 2001, pp. 1632–1633.
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Reaction of Triphenylphosphine Oxide with *ortho*-Dihydroxyaromatic Compounds

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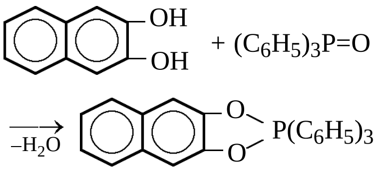
Received May 22, 2000

Abstract — Triphenylphosphine oxide was first reacted with 2,3-dihydroxynaphthalene, as well as with halo- and alkyl-substituted 1,2-dihydroxybenzenes to obtain the corresponding (*ortho*-naphthylenedioxy)- or (*ortho*-phenylenedioxy)triphenylphosphoranes.

It is known that pyrocathechol (1,2-dihydroxybenzene) reacts with dichlorotriphenoxyphosphorane to form triphenoxy(1,2-phenylenedioxy)phosphorane [1]. The reaction of pyrocathechol with phosphonites in the presence of bases gives phosphoranes and hydrogen [2]. The reaction of pyrocatechol with phosphorus trichloride affors three products [3], while with phosphorus pentachloride several compounds are formed [1]. These examples include almost all known reactions of *ortho*-dihydroxyaromatic compounds with phosphorus halides and organophosphorus compounds. Evidently, the reactivity of the P=O group in phosphine oxides toward *ortho*-dihydroxyaromatic compounds has not yet been studied.

The present communication presents the results of first performed reactions of triphenylphosphine **I** with *ortho*-dihydroxynaphthalenes and halo- and alkyl-substituted *ortho*-dihydroxybenzenes.

Whereas the phosphoryl group was previously considered rather inert, at present a great number of reactions with its participation are known. The reaction of phosphine **I** with *ortho*-dihydroxyaromatic compounds which are acidic in nature most probably begins with protonation of the oxygen atom of the electron-donor phosphoryl group. The resulting intermediate complex contains three oxygen atoms surrounding the phosphorus atom, and it is stabilized by elimination of one water molecule. Hence, the reaction of 2,3-dihydroxynaphthalene with phosphine **I** yields (2,3-naphthylenedioxy)triphenylphosphorane **V**.



Alkyl- and halo-substituted 1,2-dihydroxybenzenes presented in the table react analogously. The reactions proceed quantitatively, as evidenced by the absence of the absorption band at 1190 cm^{-1} (P=O) and of the starting compound in the IR spectra of the reaction products. The latter spectra also show no OH stretching vibration bands of the starting dihydroxy compound at 3470 and 3350 cm^{-1} in KBr pellets or at 3620 and 3570 cm^{-1} in CCl_4 solutions. The IR spectra of all the phosphoranes obtained contain bands at 1240 and 1450 cm^{-1} assignable to P–O–C and $P–C_6H_5$ stretching vibrations, respectively, but with compounds containing alkyl-substituted benzene rings such assignment is complicated by the presence of deformation and skeletal vibration bands of these substituents in the same spectral region. Note that the new reaction studied provides a preparative route to prosphoranes containing a dioxaphospholene heteroring.

EXPERIMENTAL

The IR spectra were recorded on an IKS-22 spectrometer in KBr pellets in the range 4000–400 cm^{-1}.

The starting 4-bromo-1,2-dihydroxybenzene and 3-bromo-5-*tert*-butyl-1,2-dihydroxybenzene were prepared by the bromination of 1,2-dihydroxybenzene and 4-*tert*-butyl-1,2- dihydroxybenzene according to [4]. 4-*tert*-Butyl-1,2-dihydroxybenzene and 4-cyclohexyl-1,2-dihydroxybenzene were prepared by the alkylation of pyrocatechol with corresponding alcohol according to [5] or [6]. Commercial 1,2-dihydroxybenzene and 2,3-dihydroxynaphthalene were purified by sublimation.

Reaction of triphenylphosphine oxide with *ortho*-dihydroxyaromatic compounds. A mixture of 0.005 mol of triphenylphosphine oxide and 0.005 mol

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Melting points and elemental analyses of phosphoranes prepared from triphenylphosphine oxide and 1,2-dihydroxyaromatic compounds

Compound	Initial dihydroxy compound	mp, °C (hexane)	Found, %		Formula	Calculated, %	
			C	H		C	H
Triphenyl(1,2-phenylenedioxy)phosphorane	1,2-Dihydroxybenzene	61–62	77.65	5.24	$C_{24}H_{19}O_2P$	77.83	5.17
(4-Bromo-1,2-phenylenedioxy)triphenylphosphorane	4-Bromo-1,2-dihydroxybenzene	84–85	63.97	3.82	$C_{24}H_{18}BrO_2P$	64.16	4.04
(3-Bromo-5-*tert*-butyl-1,2-phenylenedioxy)triphenylphosphorane	3-Bromo-5-*tret*-butyl-1,2-dihydroxybenzene	102–103	66.33	5.02	$C_{28}H_{26}BrO_2P$	66.54	5.19
(4-Cyclohexyl-1,2-phenylenedioxy)triphenylphosphorane	4-Cyclohexyl-1,2-dihydroxybenzene	53–54	79.49	6.28	$C_{30}H_{29}O_2P$	79.63	6.46
(2,3-Naphthylenedioxy)-triphenylphosphorane	2,3-Dihydroxy-naphthalene	141–142	79.62	4.84	$C_{28}H_{21}O_2P$	79.99	5.03

of dihydroxy compound was thoroughly mixed, triturated, and placed in a porcelain dish which was was heated on a sand bath for 2 h at 100–110°C with 2,3-dihydroxynaphthalene and at 70–80°C with the rest compounds. The temperature should be maintained within these ranges to prevent sublimation of the starting dihydroxy compounds and partial tarring of the melts. After cooling, a glassy transparent product slowly crystallized. It was ground and crystallized from hexane. The melting points and elemental analyses of the resulting phosphoranes are given in the table. The yields of the products were quantitative.

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