

V.N.Fomin¹, Yu.Yu.Smolenkov², E.P.Vassilets¹, I.E.Rozhkovoy¹¹Academician Y.A.Buketov Karaganda State University;²Institute of problems of complex development of bowels of the Earth of RK, Karaganda
E-mail: vitfomin@mail.ru**Reactions of some 2-*tert*-butoxy-1,3,2-dithiophosphanes with benzaldehyde**

The article describes the interaction of 5-methylthio-, 5-N,N-dimethylamino-2-*tert*-butoxy-1,3,2-dithiophosphanes and 2-*tert*-butoxy-1,3,2-dithiophosphinane with benzaldehyde. It has been given the comparative evaluation of reactivity of the phosphinanes studied. The conclusions about the effect of substituents at the 5th position on the phosphinanes reactivity were made on the basis of quantum-chemical calculations and experiment data.

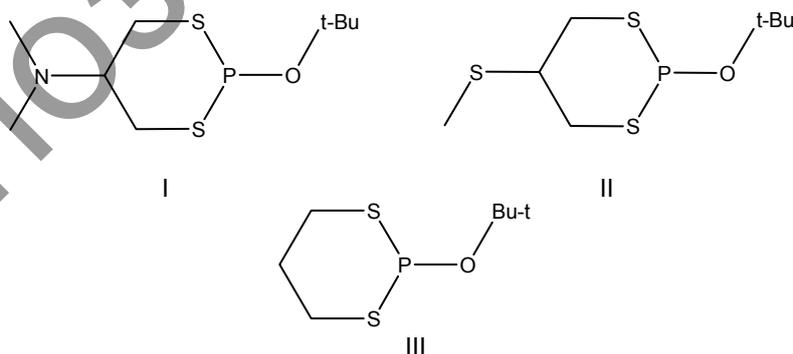
Key words: 2-*tert*-butoxy-1,3,2-dithiophosphinane, 1,2-dithiolanes, 5-N,N-dimethylamino-1,3,2-dithiophosphinane, 5-methylthio-1,3,2-dithiophosphinane.

At the present time 2-*tert*-butoxy-1,3,2-dithiophosphanes remain quite unexplored. The monograph [1] summarizing data about thioderivatives of phosphorus (III) acids does not contain any mentions about the compounds of this type. Analysis of the recent literature revealed a low activity of research in this area. However, it was revealed the attention of researchers to 5-methylthio- and 5-N,N-dimethylamino-1,2-dithiolanes, corresponding to the latter dithianes and their functional derivatives [2,3]. This interest is caused by high insecticide activity of many compounds of this series. The insecticides obtained on their basis, are highly effective and safe for non-target animals. Compounds with phosphonatic structure are also known for insecticidal properties. The combination of the anticholinesterase properties of phosphonates with the sodium-blocking activity of 5-methylthio- and 5-N,N-dimethylamino-1,2-dithialane is possible to give selective insecticides with low application rates.

The elegant method of obtaining a large number of compounds of this class may be the interaction of the corresponding 2-*tert*-butoxy-1,3,2-dithiophosphanes with electrophilic reagents.

We obtained 5-methylthio- and 5-N,N-dimethylamino-2-*tert*-butoxy-1,3,2-dithiophosphanes in order to estimate the reactivity of 2-*tert*-butoxy-1,3,2-dithiophosphanes in reactions with electrophilic reagents. Previously studied methods [2–4] were used for the synthesis of these compounds.

Some differences in the reactivity of phosphites were found in the reaction of these compounds with ethylbromide [4] (the classical Arbuzov reaction). It is logical to assume that the heteroatom in the position 5 of initial dithiophosphanes or related methyl groups affect the reactivity of phosphites in any way.



During the experiments, it was found that 5-N,N-dimethylamino-1,3,2-dithiophosphinane interacts with benzaldehyde less actively than its sulfur-containing analog. The reason of this might be the reduction of the electron density on the phosphorus atom under the influence of nitrogen, as well as competitive reversible binding of electrophilic nitrogen or the screening effect of the methyl groups. Quantum chemical calculations were carried to determine the effect of the substituent in the 5-position on the reactivity of phosphinanes. The results of quantum chemical calculations are presented in Table 1.

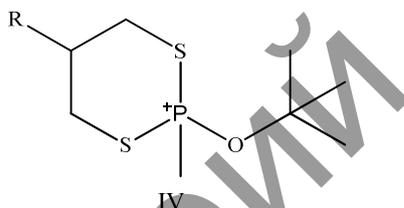
Table 1

The comparative characteristic of electric charges on atoms of various phosphites

Substance	Charge on atom of phosphorus	Charges of other atoms
2- <i>tert</i> -butoxy-5-N,N-dimethylamino-(1,3,2)-dithiaphosphinane (I)	0.6309	S (1,3: -0.2636), -0.2640, N (5: -0,3000), O: -0,6185
2- <i>tert</i> -butoxy-5-S-methylthio-(1,3,2)-dithiophosphinane (II)	0.6360	S (1,3: -0.2646), -0.2744, S (5: -0,1133), O: -0.6170
2- <i>tert</i> -butoxy-1,3,2-dithiaphosphinane (III)	0.6414	S (1,3: -0.2758), -0.2755, O: -0.6217

As seen from the table, positive charge on the phosphorus atom is slightly higher in the sulfur compounds (II) than in the nitrogen analogues (I). Consequently, observed behavior can not be explained by the electronic influence of nitrogen on phosphorus. Negative charges on the hetero atoms in the 5-position is quite close in value, but on the nitrogen electron density is slightly higher than on the sulfur atom. Thus, the nitrogen atom has to compete with the phosphorus atom for the electrophile is somewhat stronger than the sulfur atom. These data can explain higher time of the nereistoxine derivant reactions in comparison with the sulphur-containing analogue.

The stability of the quasi-phosphonic ions was estimated by the computational method on the example of model P-methylated compounds (IV).

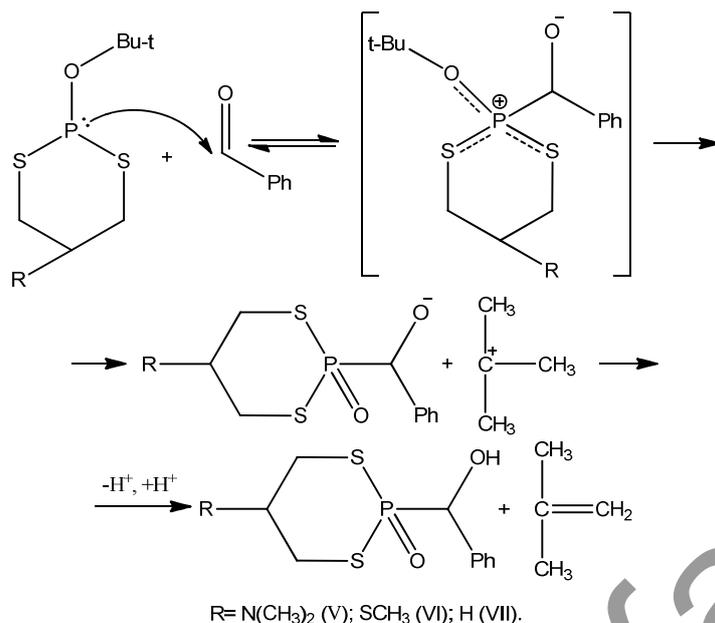


The calculation showed that the quasi-phosphonic ion formed from the charotoxine derivative (R=SCH₃, Heat of formation = 2.04284 kcal/mole) was more stable than nitrogen analogues (R=N(CH₃)₂, Heat of formation = 7.71074 kcal/mole). The calculation does not allow us to say which factor causes the difference in reactivity of the considered phosphites. Perhaps it could be a more or less consistent effect of shielding of the reaction center by methyl groups and the reversible binding of the electrophile to the heteroatom at the position 5. Confirmation of this conclusion can be data obtained from the reaction of benzaldehyde with unsubstituted 2-*tert*-butoxy-1,3,2-dithiophosphinane (III). The rate of reaction of this pair of reagents in the chosen conditions is 20–25 % higher than in the case of 5-substituted phosphinanes (I, II). Obviously, there is no possibility of competition for electrophile in the unsubstituted phosphinane (III). Compared to the compounds (I, II) an increased positive charge on the phosphorus atom does not lead to an increase in reaction time. The latter fact leads to the conclusion that the speed of the process is not determined by the speed of the initial attack of benzaldehyde, but stability of the quasi-phosphonic intermediate formed.

It is known [1] that the stability of the quasi-phosphonic cation depends on the nature of atoms surrounding the phosphorus atom. Oxygen phosphites form the least stable ions. Most stable cations are derived from trithiophosphites. Most authors explain the high stability of the sulphur-containing ions of quasi-phosphonium by relatively low electronegativity of sulfur (a slight negative inductive effect does not destabilize the cation). We can agree with this. It should be noted that sulfur and phosphorus are the elements of one period. This substantially facilitates the redistribution of the electron density in the intermediate (IV).

Given the above, the mechanism of phosphorylation of benzaldehyde by 2-*tert*-butoxy-1,3,2-dithiophosphinanes can be represented by the scheme given below.

Zwitterion is formed as a result of the quaternization of the phosphorus atom, the positive charge is delocalized with sulfur atoms and oxygen. The intermediate eliminates *tert*-butyl cation as a result of intramolecular redistribution of bonds. The resulting ion pair are stabilized by the proton migration.



Summing up the results of the investigation carried out, the following conclusions can be made:

- 1) The reaction of 2-*tert*-butoxy-1,3,2-dithiophosphinane, 5-methylthio- and 5-*N,N*-dimethylamino-2-*tert*-butoxy-1,3,2-dithiophosphinanes with benzaldehyde was investigated.
- 2) On the basis of the experimental data and the quantum-chemical calculations assumptions of the reaction mechanism and the substituent influence in position 5 of phosphinanic cycle on a process course can be done.
- 3) Three new compounds were obtained, two of which contain a fragment which is responsible for the insecticide activity in the structure.

The experimental part

Quantum chemical calculations were performed by using the PM6 method with the help of MOPAC2009 software package.

IR spectra were recorded on a UR-20 instrument in tablets of potassium bromide.

Cryoscopic molecular weight was determined by the Rastan method in camphor. Error of the method is less than 5 %.

Phosphorus content in the products was determined by mineralization, fusion with nitrate and sodium hydroxide followed by precipitation from the acidified solution of the mineralized substance of the ammonium salt of the molybdenum-phosphoric acid and its gravimetric analysis.

Reaction of 2-*tert*-butoxy-5-*N,N*-dimethylamino-1,3,2-dithiophosphinane with benzaldehyde. The mixture of 2.53 g of the phosphinane (0.01 mol) and 1.06 g of benzaldehyde (0.01 mol) was heated without solvent at temperature 60–70 °C in the device for isobutylene collecting. After heating the reaction mixture to the desired temperature, the reaction is completed in 35–45 minutes (there is discontinuation of isobutylene). The resulting viscous mass was treated twice with hexane (10 ml portions) under ice-cooling and air-dried. After recrystallization from the mixture of benzene and hexane, the product V (5-(dimethylamino)-2-(hydroxy(phenyl)methyl)-1,3,2-dithiophosphinane-2-oxide) yield is 88 %.

Molecular formula: C₁₂H₁₈NO₂PS₂. m.p.=123.1–124.2 °C.

M_{exp.}=291.24; M_{theor.}=303.38.

It is found, %: C 47.42; H 5.76; O 10.21; P 10.04; S 20.89; N 4.41.

It is calculated, %: C 47.51; H 5.98; O 10.54; P 10.21; S 21.14; N 4.62.

IR-spectrum, cm⁻¹: N(*tert*) 1096; C-S 642; P=O 1285; P-C 712; C-O-H 1126, 2885–2868.

Reaction of 2-*tert*-butoxy-5-methylthio-1,3,2-dithiophosphinane with benzaldehyde. The mixture of 3.84 g of 2-*tert*-butoxy-5-methylthio-1,3,2-dithiophosphinane (0.015 mol) and 1.59 g of benzaldehyde (0.015 mol) was heated without solvent at temperature 60–70 °C in the device for isobutylene collecting. After heating the reaction mixture to the desired temperature, the reaction is completed in 30–40 minutes (the termination of allocation of isobutylene is observed). The received slush is processed with hexane (portions

on 10 ml) when cooling by ice twice and dry up on air. The resulting viscous mass was treated twice with hexane (10 ml portions) under ice-cooling and air-dried. After recrystallization from the mixture of benzene and hexane, the product VI (2-(hydroxy(phenyl)methyl)-5-(methylthio)-1,3,2-dithiophosphinane-2-oxide) yield is 91 %.

Molecular formula: $C_{11}H_{15}O_2PS_3$. m.p.=122.3–123.8 °C.

$M_{exp} = 294.14$; $M_{theor.} = 306.4$.

It is found, %: C 43.01; H 4.74; O 10.21; P 9.99; S 31.24.

It is calculated, %: C 43.12; H 4.93; O 10.44; P 10.11; S 31.39.

IR-spectrum, cm^{-1} : C–S 654; P=O 1281; P–C 689; C–O–H 1114, 2885–2870.

Reaction of 2-*tert*-butoxy-1,3,2-dithiophosphinane with benzaldehyde. The mixture of 3.15 g of 2-*tert*-butoxy-1,3,2-dithiophosphinane (0.015 mol) and 1.59 g of benzaldehyde (0.015 mol) was heated without solvent at temperature 60–70 °C in the device for isobutylene collecting. After heating the reaction mixture to the desired temperature, the reaction is completed in 25–30 minutes (the termination of allocation of isobutylene is observed). The resulting viscous mass was treated twice with hexane (10 ml portions) under ice-cooling and air-dried. After recrystallization from the mixture of benzene and hexane, the product VII (2-(hydroxy(phenyl)methyl)-1,3,2-dithiophosphinane-2-oxide) yield is 96 %.

Molecular formula: $C_7H_{15}OPS_2$. m.p.=123.5–124.1 °C.

$M_{exp} = 204.35$; $M_{theor.} = 210.3$.

It is found, %: C 43.01; H 4.74; O 10.21; P 9.99; S 31.24.

It is calculated, %: C 39.98; H 7.19; O 7.61; P 14.73; S 30.49.

IR-spectrum, cm^{-1} : P=O 1278; P–C 690; C–O–H 1115, 2880–2870.

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В.Н.Фомин, Ю.Ю.Смоленков, Е.П.Василец, И.Е.Рожковой

Кейбір 2-*трет*-бутокси-1,3,2-дитиофосфинандардың бензальдегидпен әрекеттесуі

Мақалада 2-*трет*-бутокси-1,3,2-дитиофосфин, 5-метилтио- және 5-N,N-диметиламино-2-*трет*-бутокси-1,3,2-дитиофосфинаның бензальдегидпен әрекеттесуі келтірілген. Фосфинаның реакцияны қабілеттілік салыстырмалы бағасы берілген. Эксперименттің нәтижесі және квантты-химиялық есептер негізінде фосфинаның реакция қабілеттілігінің 5 орынға орынбасу әсеріне қорытынды жасалды.

В.Н.Фомин, Ю.Ю.Смоленков, Е.П.Василец, И.Е.Рожковой

Взаимодействие некоторых 2-*трет*-бутокси-1,3,2-дитиофосфинов с бензальдегидом

В статье описано взаимодействие 2-*трет*-бутокси-1,3,2-дитиофосфина, 5-метилтио- и 5-N,N-диметиламино-2-*трет*-бутокси-1,3,2-дитиофосфинов с бензальдегидом. Приведена сравнительная оценка реакционной способности этих фосфинов. На основании данных эксперимента и квантово-химических расчетов делаются выводы о влиянии заместителя в положении 5 на реакционную способность фосфинов.