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Polyhalogenalkoxy(aryloxy)chloro- and Bromophosphoranes

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ABSTRACT

The data on the synthesis, stereochemistry, and molecular dynamics of alkoxy(aryloxy)halogenphosphoranes of acyclic structure, as well as of halogenphosphoranes containing the pentacoordinate phosphorus atom in the 1,4,2-dioxophospholane cycle and the node of bicyclo[2.2.2]octane system, are systematized. The influence of spatial properties of polyhalogenalkyl substituents on thermal stability and structure of adducts from tris(polyhalogenalkyl) phosphites with chlorine and bromine is ascertained. The effect of the phosphorus atom inclusion into the cycle and node of the bicyclooctane system on its pentacoordinate state stability is investigated.

INTRODUCTION

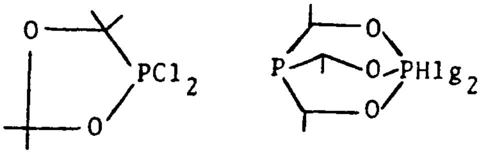
Interest in alkoxy(aryloxy)halogenphosphoranes results from a number of reasons. These compounds are postulated as intermediates or final products formed either by reaction of alcohols and phenols with P-Hlg-phosphoranes of other types or by reaction of esters of trivalent phosphorus acids with chlorine. Alkoxy(aryloxy)halogenphosphoranes are the starting compounds for synthesizing oxyphosphoranes of other types notable for diverse reactivity [1]. At the same time, in contrast to alkoxy(aryloxy)fluorophosphoranes [2–6], the corresponding chloro- and bromophosphoranes have not yet been studied in much detail. This state of affairs seems to be connected first of all with their low thermal stability. Unlike aryloxyphosphoranes based on the pyrocatechol in which the stabilizing role is played by a dioxophospholane fragment, as shown by Prof. J. Michalski and co-workers [7, 8], not all the factors responsible for thermal stability and chemical properties of other oxychlorophosphoranes have so far been elucidated. In a number of cases it has not been determined whether there is any difference in the structure between halogenphosphoranes in the solid state and those in solution. The data on stereochemistry and molecular dynamics are rarely available. In this report we have attempted to illustrate the experimental data on the above-mentioned problems with examples of the phosphoranes of the types **1–6** (Scheme 1)

$ArO\text{-}PCl_4$ $\quad$ $(ArO)_2PCl_3$

1 $\quad$ 2

$(ArO)_3PCl_2$ $\quad$ $(AlkO)_3PHlg_2$

3 $\quad$ 4



5 $\quad$ 6

SCHEME 1

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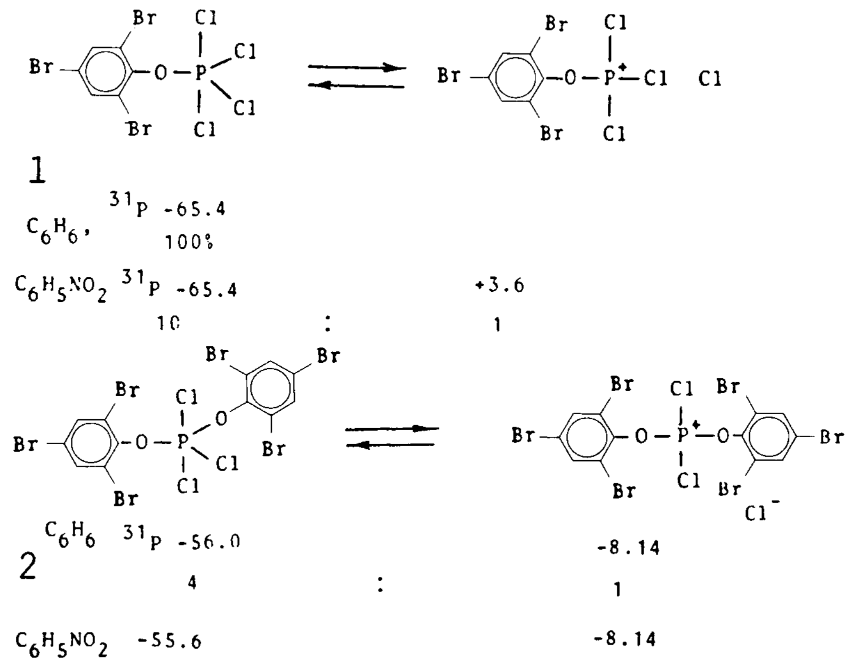
RESULTS AND DISCUSSION

In most cases the data on the structure and molecular dynamics of phosphoranes are generally obtained by the ^{31}P NMR spectroscopy of their solutions. The majority of well-known acyclic alkoxy-, aryloxychloro-, and bromophosphoranes exist in solutions as phosphonium salts [4, 8–11]. Therefore, the NMR method cannot yield sufficient information to analyze their structure, stereochemistry, and molecular dynamics. Only aryloxytetrachlorophosphoranes retain their pentacoordination structure in solution. However, with an increase of either the number of aryloxyl substituents or the solvent polarity, the tendency of aryloxychlorophosphoranes to exist in solution as phosphonium salts increases. This was confirmed by studying the phosphoranes **1** and **2** in solution (Scheme 2).

A promising method for studying the stereochemistry of solid chlorophosphoranes is by the use of ^{35}Cl NQR spectroscopy [12–14]. Appreciable differences in the resonance frequencies between the equatorial and axial chlorine atoms in trigonal bipyramidal structures enables one to determine the arrangement of the substituents around the central phosphorus atom [14] (Table 1).

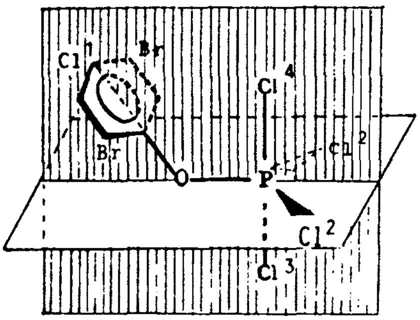
As follows from the spectral data analysis, trichloromethyl groups occupy axial positions in the trigonal bipyramid of chlorophosphorane molecules and haloidphenoxyl groups occupy equatorial positions. Nonequivalence of the axial chlorine atoms in aryloxytetrachlorophosphoranes (**1**) is due to the fact that the POC^{Ar} angle is less than 180°C, the plane of the benzene ring being turned to one of the axial chlorine atoms. Equivalence of both equatorial chlorine atoms, shown by one NMR line of double intensity, indicates the existence of a symmetry plane crossing an oxygen atom and two axial chlorine atoms in the molecules under study. Of two resonance lines of axially positioned ^{35}Cl nuclei, that of lower frequency belongs to the Cl^4 atom, being on the same side of the equatorial plane as the aryl radical. Such a conclusion can be drawn allowing for the stereoelectronic effect of lone electron pairs of the oxygen atom in the $P–O–C^{Ar}$ equatorial fragment. Interaction between lone electron pairs and the antibonding orbital of the antiperiplanar $P–Cl^4$ bond results in the growth of electron density in this orbital and, thus, to a loosening of the corresponding $P–Cl^4$ bond, its subsequent elongation and an increase in ionisity, which, in turn, lowers the ^{35}Cl NMR frequency (Figure 1) [14].

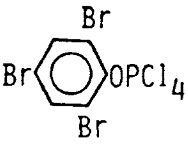
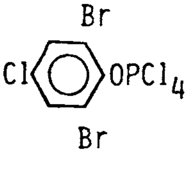
Aryloxytetrachlorophosphoranes (**1**) are considered to be stereochemically nonrigid compounds in which the ligands change positions rather easily (without bond cleavage) resulting from the pseudorotation process. We have found that the ^{35}Cl NQR method makes it possible to study the pseudorotation process in solid chlorophosphoranes. Upon heating the crystalline sample **1a**, spectral lines of the $Cl^{2,3,4}$ atoms steadily disappear, whereas the Cl^1 line is recorded up to melting point (Figure 1). These observations prove that axial and equatorial chlorine atoms are involved in the Arrhenius thermoactivation process of the pseudorotation type. Data on the temperature-dependent spin-lattice relaxation time (Figure 2) show that, in the crystalline



SCHEME 2

TABLE 1 ^{35}Cl NQR Frequencies at 77K, MHz



Compound	*P–Cl$_{ax}$*	*P–Cl$_{eq}$*	*C–Cl*
CCl_3PCl_4	28.850(1)	31.952(3)	39.689(3)
$(CCl_3)_2PCl_3$	—	29.458(3)	39.609(3) 39.749(3)
	27.417(1) 29.483(1)	33.220(2)	—
 1a	27.495(1) 29.381(1)	33.302(2)	36.302(1)

phosphorane (**1a**), there exist two independent exchange motions, these being chlorine atom rearrangements proceeding at different rates [14]. The activation energy of the rapid motion involving both equatorial chlorine atoms and an axial one with higher ^{35}Cl frequency is 41.4 kJ/mol, and that of the retarded motion is 68.2 kJ/mol. The retardation may be due either to intermolecular coordination of the P–Cl^4-bonded chlorine atom with an aromatic ring or to the steric effect of bromine atoms. The first motion belongs to the type of intermolecular atom rearrangements known as a trigonal twist. The second one may also be of the trigonal twist variety based upon another atom triad (2Cl$_{eq}$ and 1Cl$^4_{ax}$) or it may proceed by a rearrangement type involving all four chlorine atoms at phosphorus.

The existence of alkoxychlorophosphoranes in solution as phosphonium salts, as well as the property of the known compounds of this type to decompose by the Arbuzov reaction at temperatures above −70°C, make for difficulties in the study of their stereochemistry [8]. Moreover, such low thermal stability is an obstacle to their synthetic applications. The presence of strongly electron-accepting substituents on phosphorus should be a factor increasing the thermal stability of such compounds. Thus, the dihalogenphosphoranes **4** containing three 1-trifluoromethyl-2,2,2-trifluoroethoxy groups are notable for their high thermal stability [4]. The comparatively high electron-withdrawing properties of the α,α,ω-trihydropolyfluoroalkyloxy groups on the phosphites **8** gave us reason to believe in the possibility for obtaining rather stable dihalogenophosphoranes **7** in their reactions with halogens

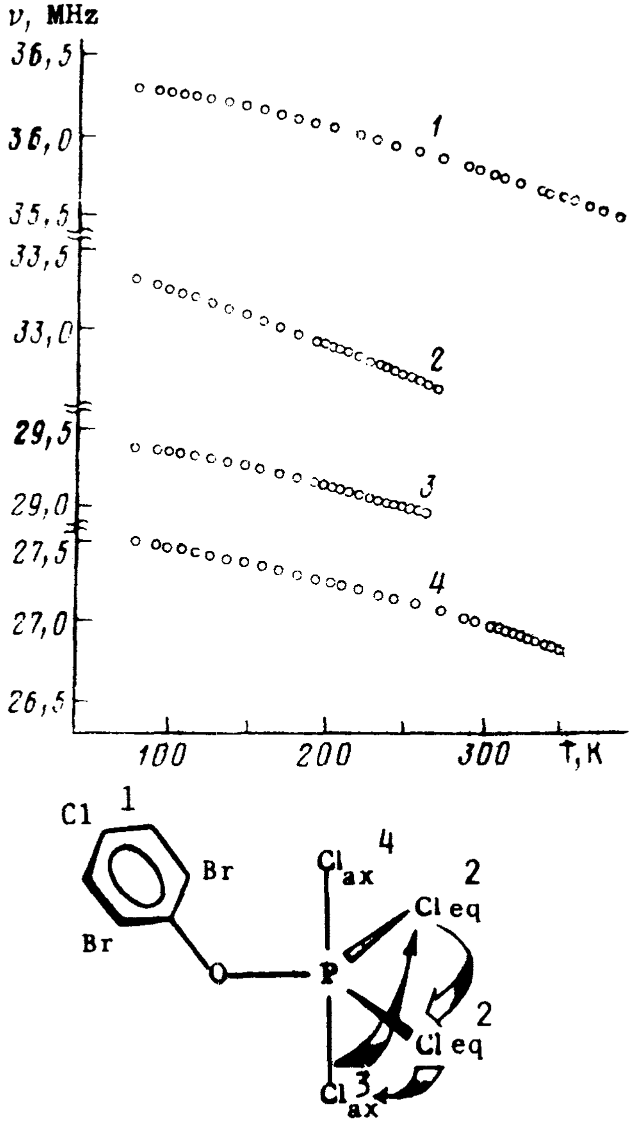


FIGURE 1 ^{35}Cl NQR frequency temperature dependence in bonds of crystalline phosphorane **1a**
1: C–Cl, 2: P–Cl$_{eq}$, 3: P–Cl$^3_{ax}$, 4: P–Cl$^4_{ax}$.

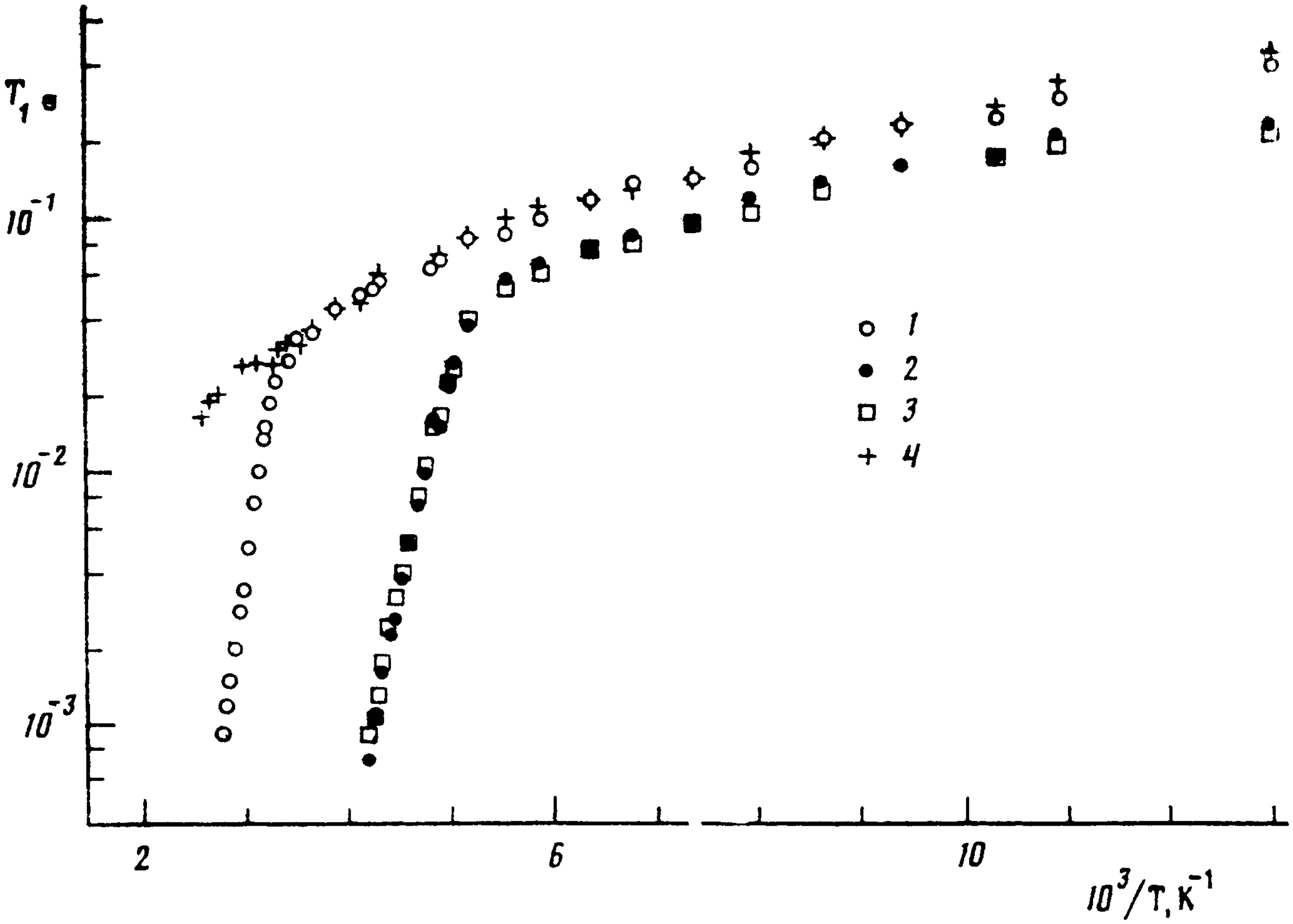
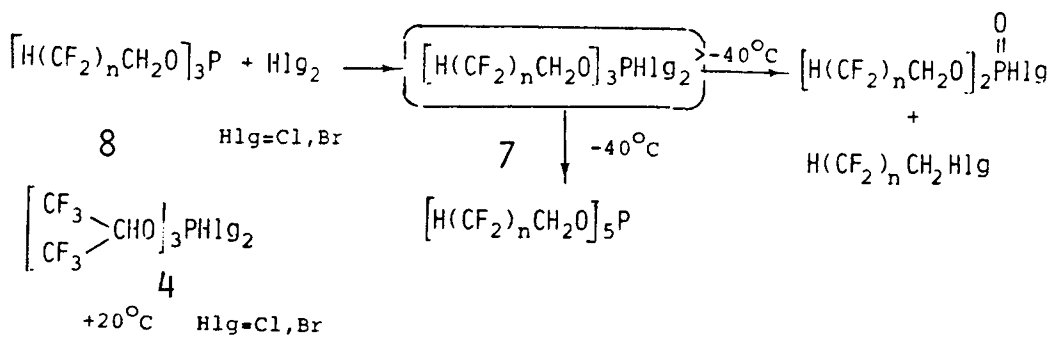


FIGURE 2 Temperature dependence of ^{35}Cl quadrupole spin-lattice relaxation time T_1 in chemical bonds of crystalline phosphorane **1a** 1: P–Cl$^4_{ax}$, 2: P–Cl$^3_{ax}$, 3: P–Cl$^2_{eq}$, 4: C–Cl^1.

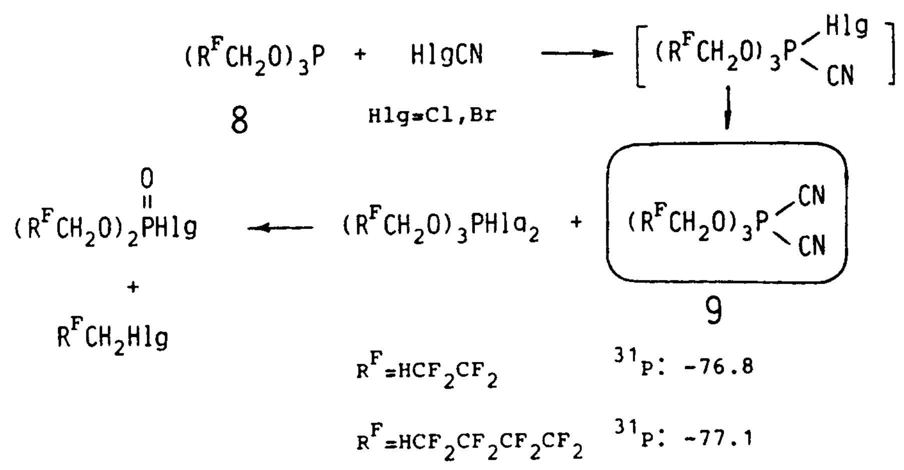
and pseudohalogens. The phosphites **8** react with chlorine or bromine at low temperature to form the corresponding adducts **7**, which, unlike the phosphoranes **4** [4], decompose at room temperature. At the same time, the adducts **7** are rather stable in solutions at −40°C, and that enables them to be applied successfully in various synthetic procedures (Scheme 3).

The reaction of phosphites **8** with cyanogen chloride or cyanogen bromide results in the formation of tris(polyfluoroalkoxy)dicyanophosphoranes **9**, the first examples of previously unknown types of pseudohalogenalkoxyphosphoranes of acyclic structure [16] (Scheme 4). In contrast to the known alkoxyhalogen- [15] and alkoxypseudohalogenphosphoranes [17], which readily decompose by the Arbuzov reaction, the compounds **9** are distillable in vacuum.

Comparison of the properties of dihalogenphosphoranes **4** and **7** shows the compounds **4** to



SCHEME 3

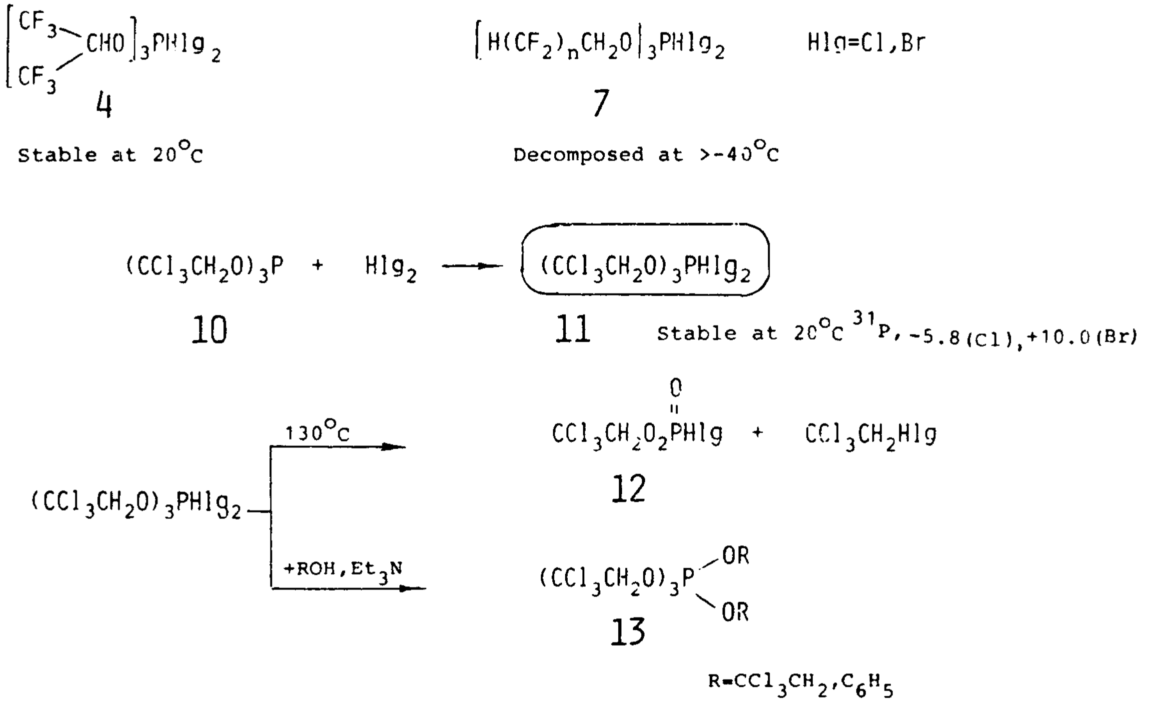


SCHEME 4

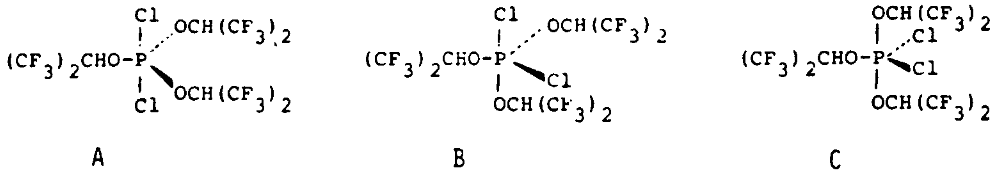
be of higher thermal stability. This may be due to the greater electron-withdrawing properties of the 1-trifluoromethyl-2,2,2-trifluoroethyl substituents. However, the enhanced stability of the phosphoranes **4** is also likely to be conditioned by the screening effect of 1-trifluoromethyl-2,2,2-trifluoroethyl groups. To evaluate the relative influences of these two effects we have synthesized from tris(2,2,2-trichloroethyl)phosphite **10** the compound **11** containing substituents of similiar electron-accepting properties but more bulky than trihydropolyfluoroalkyl ones [11] (Scheme 5). The adducts **11** formed by the reaction of the phosphite **10** with halogens turned out to be rather stable at 20°C, in contrast to the compounds **7**. Values of phosphorus nuclei chemical shifts of the compounds **11** show that they exist in various solutions as phosphonium salts. Unlike the adducts **7**, the compounds **11** are transformed into the corresponding phosphorus acid halides **12** only at 130°C. In this case, the bulky trichloromethyl groups seem to prevent attack of halide ions at the carbon atom of the methylene group, which generally occurs as an S$_N$2 process [7].

The compounds **11**, like the adducts **4** and **7**, react with alcohols and phenols to form the crystalline pentaalkoxyphosphoranes **13**, the first examples of thermally stable pentaalkoxyphosphoranes containing no fluorinated substituents [11].

Thermal stability comparisons for compounds



SCHEME 5



4

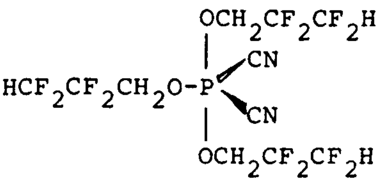
SCHEME 6

4, **7**, and **11** lead to the conclusion that the bulk of a polyhalogenalkyl substituent contributes considerably to the increase in thermal stability of adducts from halogens with acyclic polyhalogenalkylphosphites. At the same time, the adducts' structures are determined by the relative electron-accepting abilities of the substituents. The phosphorane structure is typical only of compound **4** containing the most electron-accepting 1-trifluoromethyl-2,2,2-trifluoroethyl substituents [4].

Spatial structures of the acyclic phosphoranes **4** in solution have not been ascertained. According to the literature [4], signals for the fluorine nuclei of a polyfluoroalkyl group in the ^{19}F NMR spectrum of the compound **4** (Hlg = Cl) remain equivalent even at −90°C. Taking into account chlorine electronegativity, the trigonal bipyramidal structure A is the most probable. However, structures B and C are not excluded completely by Schmutzler et al. [4] since even traces of HCl or 1-trifluoromethyl-2,2,2-trifluoroethanol are able to cause rapid exchange of ligands resulting in the equivalence of the polyfluoroalkyl groups (Scheme 6).

As for compounds **7** and **9**, we managed to record experimentally the trigonal–bipyramidal structure only in the case of the tris(polyfluoroalkoxy)dicyanophosphorane **9** [18]. The ^{19}F NMR spectrum of compound **9a** at −50°C shows two sets of signals for polyfluoroalkyl groups with a ratio of integral intensities of 1:2 (coalescence temperature is about 0°C). The ^{13}C NMR spectrum at −50°C contains a double set of multiplet signals for carbon nuclei of tetrafluoropropyl groups and only one signal for carbon nuclei of nitrile groups. Such a spectral picture enables us to assume that, at temperatures below −40°C, molecule **9a** has a trigonal–bipyramidal structure, two polyfluoroalkoxyl groups of which are apically positioned, with the nitrile groups being equatorial (Scheme 7).

The results given above show that acyclic compounds of pentacoordinated phosphorus containing polyhalogenalkoxyl substituents possess enhanced thermal stability. Another known way to improve alkoxyphosphoranes stability is to incorporate the phosphorus atom into a five-membered ring [19, 20]. The best studied compounds among five-membered cyclic alkoxyhalogenphosphoranes are those containing the 1,3,2-dioxaphospholane fragment [21]. Polyfluoroalkoxyphosphoranes of this type, generally obtained from hexafluoroacetone, are of high thermal stability [21–23]. Until recently, scant evidence for the influence of polyfluoroalkoxyl groups on the stability of alkoxyphosphoranes with five-membered cyclic moieties of other types was available. We have investigated this question by evaluating an example of alkoxyphosphoranes containing the phosphorus atom in the 1,4,2-dioxaphospholane cycle.



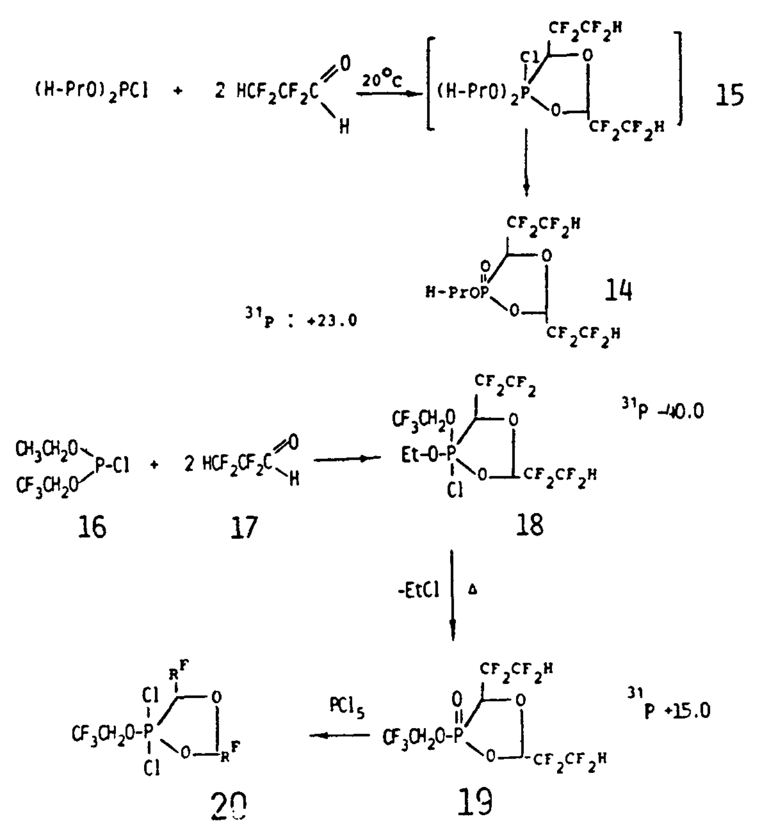
9a

SCHEME 7

The first relatively stable compound of this type was obtained by the reaction between fluoral and trimethyl phosphite [24]. We found that polyfluoroaldehydes readily react, not only with high-nucleophilic trialkyl phosphites, but also with low-nucleophilic polyfluoroalkyl phosphites [25] and dialkyl chlorophosphites [26]. The reaction with dipropyl chlorophosphite gave the 1,4,2-dioxaphospholane **14**, which apparently results from the rapid transformation of the phosphorane **15**, formed at the first stage (Scheme 8).

We managed to improve the thermal stability of chlorophosphoranes of the type **15** by increasing the electron-accepting properties of the exocyclic alkoxyl substituents. Thus, the phosphorane **18**, obtained by the reaction of the chlorophosphite **16** with the aldehyde **17**, is stable at 0°C and slowly decomposes only at room temperature. By the reaction of the dioxaphospholane **19** with phosphorus pentachloride, the first thermally stable alkoxydichlorophosphorane **20** containing the 1,4,2-dioxaphospholane ring was obtained [26].

To understand the reasons for the relatively high stability of cyclic alkoxyhalogenphosphoranes both synthesized by us and containing the 1,3,2-dioxaphospholane ring, the conclusion arrived at by F. Ramirez and co-workers [27] when studying five-membered cyclic phosphoranes seems to be of great importance. They reasoned that the oxygen atoms positioned in a five-membered ring and bonded with pentacoordinated phosphorus are less capable of π-



SCHEME 8

electron donation at phosphorus than exocyclic ones. In other words, such steric inhibition of π-bonding is equivalent to an increase in electron-accepting properties of substituents at phosphorus, leading in turn to the stabilization of the phosphorane structure.

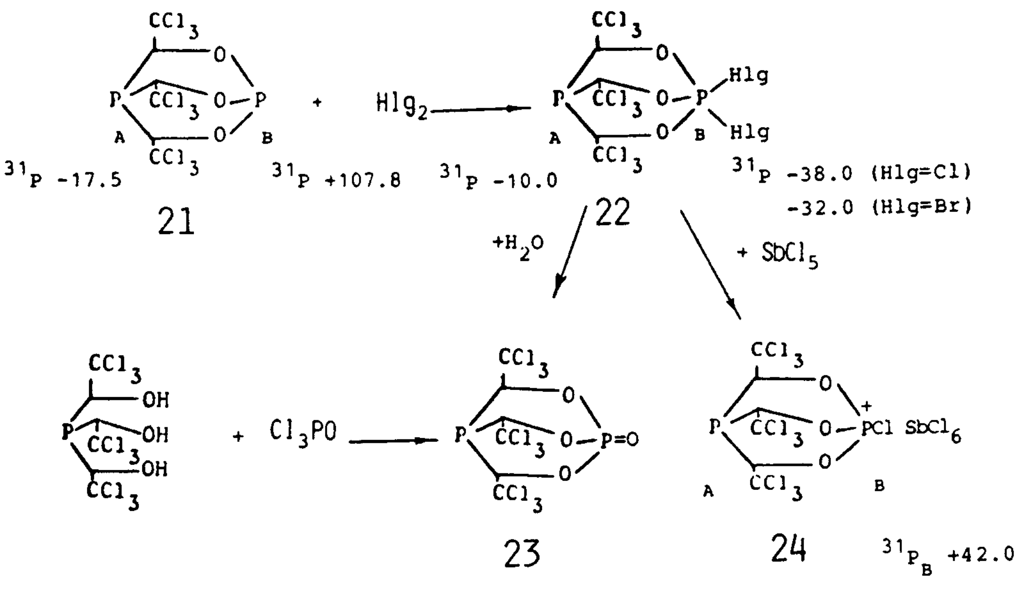
The question arises as to how essential the steric inhibition of endocyclic oxygens' π-bonding with the phosphorus atom is for the stabilization of other cyclic oxyphosphoranes. It should be noted that the effect of the heteroatom inclusion into the node of cage systems upon their properties has been attracting keen attention for a long time. Of particular interest are the bicyclo[2.2.2]octane systems [28, 29]. In contrast to the compounds containing three- and four-coordinate phosphorus atoms, the derivatives of phosphabicyclooctanes with pentacoordinated phosphorus have been studied insufficiently [30] due to the fact that the adducts from the bicyclic phosphites with chlorine decompose by the Arbuzov reaction, starting with very low temperatures [31, 32].

As shown above, the stability of the adducts from phosphites with halogens is enhanced when polyhalogenphosphites are used. In this connection, we have used the 1,4-diphosphabicyclooctane **21** as the starting compound. We have found that the reaction of the bicyclic phosphite **21** with chlorine or bromine gives dihalogenphosphoranes **22** stable at 20°C. The data on the ^{31}P NMR spectra and hydrolysis to the phosphate **23** confirm the supposition that the halogens add to the phosphite phosphorus atom [33] (Scheme 9).

Solubility in nonpolar solvents as well as the high field shift of the ^{31}P NMR signal give evidence for the covalent phosphorane structure of compound **22**. The phosphorane structure is also supported by the low field shift of the signal for the phosphorus nucleus in the chlorophosphonium salt **24**, which results from the action of antimony pentachloride on the phosphorane **22a**.

Comparison of compound **22** with the acyclic adducts **11** leads to the conclusion that the cellular structure of the bicyclooctane type in combination with the presence of bulky trichloromethyl substituents favors the pentacovalent halogenphosphorane formation.

Another approach has also confirmed that the bicyclooctane moiety stabilizes the pentacoordinated state of the phosphorus atom. The existence of phosphazo compounds in dimeric form is known to be a specific test to ascertain the effect of structural factors upon the stability of pentacoordinated phosphorus compounds. It has been reported that the reaction of halogenphosphoranes **22** with aniline results only in the dimers **25** whose structure is proved by ^{31}P NMR spectroscopy and a molecular weight determination. It should be noted that the



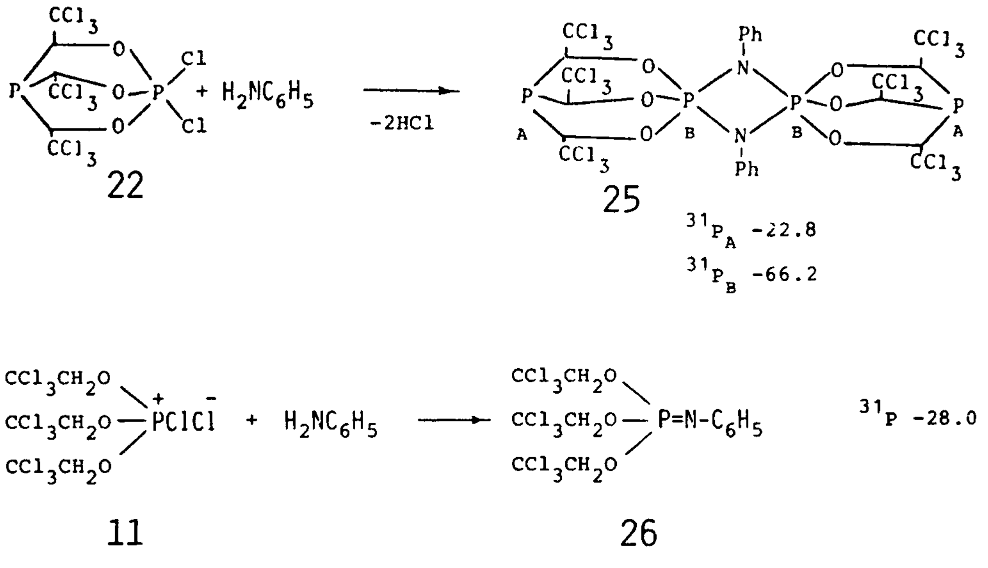
SCHEME 9

acyclic phosphazo compound **26** synthesized for comparison exists in the isomeric state (Scheme 10) [34].

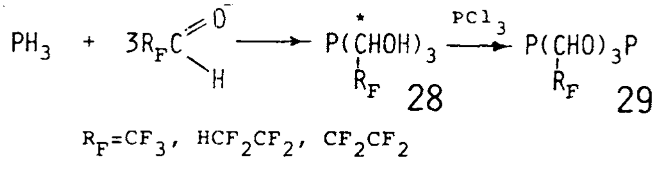
The revealed effect that the presence of the bicyclooctane moiety stabilizes the phosphorane structure seems to be conditioned by the overall influence of both the bicyclic fragment and the bulky electron-withdrawing trichloromethyl groups. It is evident that evidence of the influence of spatial factors upon phosphorane stabilization can be obtained by comparing the properties of the compounds **22** with their analogues **27** containing electron-withdrawing but not bulky substituents.

For this purpose, we have carried out the synthesis of tris(1-hydroxypolyfluoroalkyl)phosphines **28** and bicyclic phosphites **29** on the basis of a previous report [35]. The phosphines **28** resulting from the reaction of phosphine with polyfluorinated aliphatic aldehydes exist as a mixture of two stereoisomeric forms (Scheme 11; Table 2) [35]. For further study we have used individual stereoisomers [35, 36].

The most pronounced chemical effect of the phosphorus atom inclusion into the node of the bicyclooctane system is the passivation of the phosphine phosphorus atom with respect to electrophilic reagents. Thus, the reaction of the phosphites **29** with excess tert-butylhydroperoxide leads to oxidation of the phosphite phosphorus atom only, whereas the acyclic phosphines **28** are readily converted into the oxides **31** under these conditions (Scheme 12) [36].



SCHEME 10



SCHEME 11

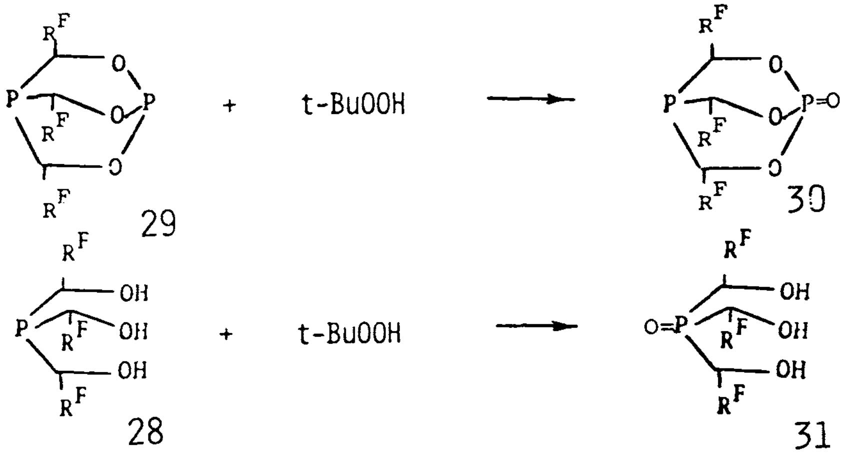
TABLE 2

	Compound	^{31}P, p.p.m.	Stereoisomers (rate, %)
28a	$P(\underset{CF_3}{CHOH})_3$	−6.13, 13.56	50:50
28b	$P(\underset{CF_2CF_2H}{CHOH})_3$	−8.30, −18.60	90:10
28c	$P(\underset{CF_2CF_2CF_2CF_2H}{CHOH})_3$	−4.10, −11.07	50:50

The compounds **29** react with chlorine and bromine at low temperature to form adducts at the phosphite phosphorus atom. The adducts **27** have the dihalogenphosphorane structure [36], which is confirmed by ^{31}P NMR low-temperature spectroscopy. This assignment of signals has been justified by studying hydrolysis of the phosphoranes **27** to the phosphates **30**. The compounds **27** turned out to be less stable than their trichloromethyl analogues **22** (Scheme 13). They decompose at temperatures above −60°C, whereas their analogues are rather stable at 20°C.

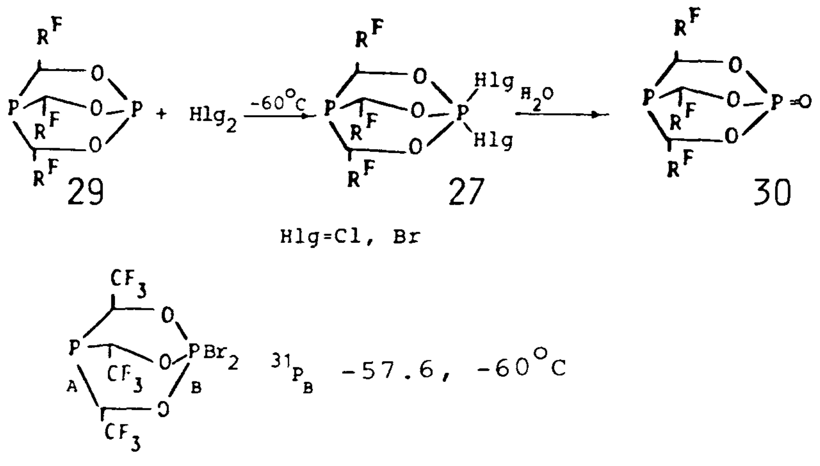
The data obtained indicate that, as in the case of the phosphoranes **22**, the bicyclooctane moiety with polyfluoroalkyl substituents stabilizes the pentacoordinated state of the phosphorus atom. However, the bulk of the electron-withdrawing substituents is of essential importance for thermal stability of these compounds.

To elucidate possible reasons for the low reactivity of the phosphine phosphorus atom toward electrophiles and for the tendency of the bicyclic compounds **29** to form phosphoranes, we have stud-

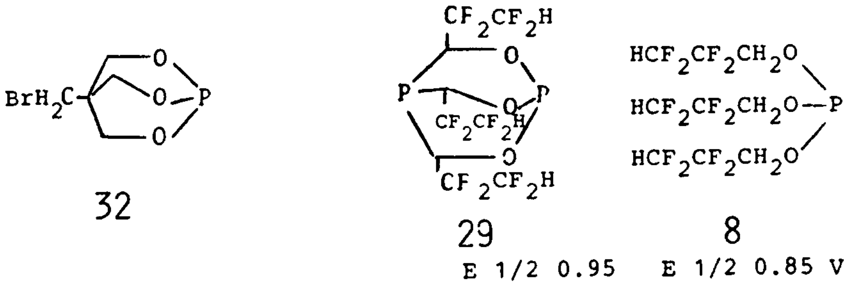


$R^F = CF_3,\ HCF_2CF_3,\ HCF_2CF_2CF_2CF_2$

SCHEME 12



SCHEME 13



SCHEME 14

ied these compounds by using X-ray analysis and polarography.

While studying the compounds **32**, J. Verkade and co-workers [29] have found a certain decrease in the POC angle as compared with the acyclic phosphites. Resulting from this, the oxygen atoms' hybridization changes from sp^2 to sp^3, thus decreasing π-bonding with phosphorus, i.e. increasing its positive charge.

While determining the oxidation half wave potentials of the compounds **8** and **29** by the polarographic method, we have proved that the phosphite phosphorus atom in the bicyclooctane **29** possesses a higher positive charge than that of the phosphite **8** (Scheme 14).

In other words, the overall electron-accepting ability of the bicyclic substituent is higher than that of three acyclic polyfluoroalkoxyl ones. It may be just the increase in electron-accepting properties of the structural fragment that contributes to the pentacoordinated phosphorus state stabilization in the compounds **22** and **27** by transformation of the acyclic structure into the bicyclic one.

As to one possible reason for the POC angles decrease, it may be associated with the spatial interaction available between the nodal phosphorus atoms resulting in the transfer of electron density from the phosphine phosphorus atom to the phosphite one. This interaction reduces the phosphine phosphorus atom reactivity toward electrophiles and results in a shortening of the distance between the phosphorus atoms and a decrease in the POC angle. This phenomenon is evidenced by abnormally high constants of the spin–spin interaction between the nodal phosphorus atoms [36]. For instance, J_{PP} for the compound (**29a**) is 35.0 Hz and that for the compound (**29c**) is 41.4 Hz. It is also proved by X-ray analysis [37] of the phosphite (**30**) showing the distance between the phosphorus atoms to be 3.03 Å, which is less than the sum of the phosphorus atoms Van der Waals radii (3.8 Å).

Thus, in the series of trivalent phosphorus compounds containing halogen that were investigated, the structure and thermal stability of the adducts from these compounds with chlorine and bromine depend considerably upon the bulk and electron-accepting properties of substituents and can be changed by the nature of the polyhalogenalkoxyl substituents or by peculiarities of cyclic structures.

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