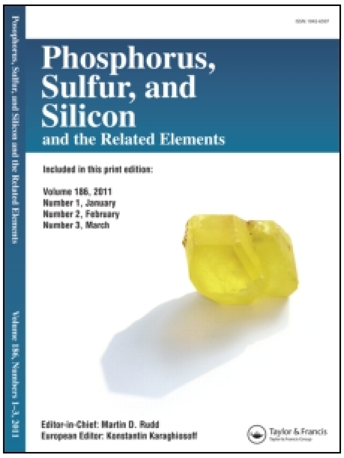

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ELECTRON SPIN RESONANCE STUDY OF PHOSPHORANYL RADICALS I. INFLUENCE OF STERIC AND ELECTRONIC EFFECTS ON RADICAL FORMATION IN SOLUTION

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ELECTRON SPIN RESONANCE STUDY OF PHOSPHORANYL RADICALS I. INFLUENCE OF STERIC AND ELECTRONIC EFFECTS ON RADICAL FORMATION IN SOLUTION

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An electron spin resonance study of phosphoranyl radicals, generated by u.v. irradiation of solutions containing a trialkylphosphite and a dialkylperoxide, enabled us to examine the influence of steric and electronic factors on radical formation. It was demonstrated that the influence of steric factors, such as α- or β-branching of the alkyl groups, on the magnitude of radical formation was present in both trialkyl- and methyldialkylphosphites, but not in dimethylalkylphosphites. Furthermore, the study of additional hetero atoms in the alkyl ligand of the dimethylalkylphosphites clearly revealed the influence of the gauche-effect. It was demonstrated that the presence of the gauche-effect, which causes a conformational preference in which a larger steric hindrance is produced, resulted in a decrease of radical formation.

INTRODUCTION

The use of spin resonance techniques such as Electron Spin Resonance (ESR) and Electron Nuclear Double Resonance (ENDOR) to study and identify radiation-induced radical species in nucleic acids and their constituents has received considerable attention.[1] Unfortunately these studies revealed much more about damage in the bases than in the sugar-phosphate backbone. The purpose of the present work is to attain more knowledge about radiation damage in the sugar-phosphate backbone. Phosphate esters are, of course, of fundamental importance in biological systems and considerable attention has been paid to the effects of high energy radiation on biological phosphates and model compounds.[2] However, the possible involvement of phosphoranyl radicals has received little attention. Our aim in this paper is to come to a better understanding of the basic factors that govern the formation and stability of the phosphoranyl radicals that might be involved.

Phosphoranyl radicals can be generated by high intensity u.v. irradiation of solutions containing the corresponding phosphite and a dialkylperoxide.[3] The study of radical species generated in this fashion, will enable us to understand and predict the basic properties of phosphoranyl radicals in solution.

Future work will focus on the formation of phosphoranyl radicals from the corresponding phosphates, by means of X-irradiation, in order to attain a complete insight in the behaviour of phosphoranyl radicals both in solid state and in solution.

RESULTS AND DISCUSSIONS

1. Steric Effects in Trialkylphosphites

Using di-t-butyl peroxide as a photolytic source of t-butoxyl radicals, we have examined a series of trialkoxy-t-butoxy phosphoranyl radicals (see Figure 1).

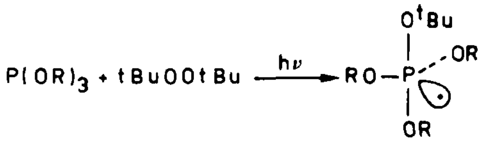
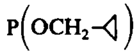
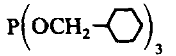
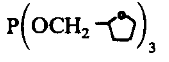
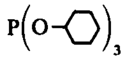


FIGURE 1 Phosphoranyl radicals generated from t-butoxyl radicals and trialkylphosphites.

When a solution, usually in n-pentane, of a trialkylphosphite and di-t-butyl peroxide was irradiated at −95°C, the ESR-spectrum of the corresponding tetra-alkoxy phosphoranyl radical was observed. The radicals and their spectro-

TABLE I

Trialkoxy-t-butoxy phosphoranyl radicals, t-BuO$\dot{P}$(OR)$_3$, obtained from the interaction of t-butoxyl radicals with trialkylphosphites

Phosphite[a]	t/°C	a(P)/G[b]
1. $P(OCH_3)_3$	−95	883
2. $P(OC_2H_5)_3$	−95	887
3. $P(OC_4H_9)_3$	−95	886
4. $P(OC_8H_{17})_3$	−95	896
5. $P(OCH_2CH(CH_3)_2)_3$	−95	882
6. $P(OCH_2CH(C_2H_5)_2)_3$	−100	862
7. $P(OCH_2CH(C_2H_5)(C_4H_9))_3$	−100	—
8. $P(OCH_2C(CH_3)_3)_3$	−95	877
9. $P(OCH_2CH_2CH(CH_3)_2)_3$	−95	882
10. $P(OCH_2(CH_2)_4CH(CH_3)_2)_3$	−80	891
11. $P(OCH(CH_3)_2)_3$	−95	905
12. $P(OCH(CH_3)(C_2H_5))_3$	−95	—
13. $P(OCH(CH_3)(C_3H_7))_3$	−95	—
14. $P(OCH(CH_3)(CH(CH_3)_2))_3$	−95	—
15. $P(OCH(C_2H_5)_2)_3$	−95	—
16. $P(OC(CH_3)_3)_3$	−95	910
17. $P(OC(CH_3)_2(C_2H_5))_3$	−95	—
18. 	−95	881
19. 	−95	891
20. 	−80	893
21. 	−95	897

[a] Solvent n-pentane except no. 20 toluene.

[b] Calculated using the Breit–Rabi equation; a(P) ± 1G. All g-factors were 2.003 ± 0.001.

scopic parameters are listed in Table I. The radicals described were observed only in the presence of both phosphite and dialkylperoxide. No phosphoranyl radicals were detected when di-t-butyl peroxide was irradiated in the presence of the corresponding phosphate. The phosphoranyl radicals exhibit a large doublet splitting from phosphorus with no further fine structure. In general the ESR-lines of the phosphoranyl doublet were of unequal width, especially at low temperatures, when tumbling of the radicals in solution was inhibited. Normally, the high-field line was broader than that at low-field. As the temperature was increased, the concentration of the phosphoranyl radicals decreased and an additional spectrum of the t-butyl radical, formed by β-scission of the phosphoranyl radical, was detected. On interruption of the irradiation the lines decayed within the response time of the instrument. All these observations are in agreement with those reported in previous studies.[4]

The phosphites listed are divided into six groups:

Group (1) *Primary Unbranched Alkylphosphites.*

$P(OR)_3$; $R = CH_3$; C_2H_5; C_4H_9; C_8H_{17}.

All phosphites examined showed a strong phosphoranyl doublet. The intensity of the lines decreased with increasing bulk of the alkyl groups.

Group (2) *Primary Branched Alkylphosphites.*

$P(OR)_3$; $R = CH_2CH(CH_3)_2$; $CH_2CH(C_2H_5)_2$;
$CH_2CH(C_2H_5)(C_4H_9)$; $CH_2C(CH_3)_3$; $CH_2CH_2CH(CH_3)_2$;
$CH_2(CH_2)_4CH(CH_3)_2$.

With exception of the tris(2-ethylhexyl)phosphite ($R = CH_2CH(C_2H_5)(C_4H_9)$), all compounds examined in this group revealed the features of a phosphoranyl radical. Both the triisopentyl ($R = CH_2CH_2CH(CH_3)_2$) and triisooctyl ($R = CH_2(CH_2)_4CH(CH_3)_2$) phosphites showed almost the same stability and a(P)-value as the unbranched analogs of group (1). In the β-branched alkylphosphites a decrease in signal strength with increasing bulk of the β-branching alkyl groups was observed. The strongest signals were observed with the triisobutylphosphite ($R = CH_2CH(CH_3)_2$), while in case of the tris(2-ethylhexyl)phosphite no phosphoranyl radicals were formed. This was confirmed by product analysis which indicated that, even after prolonged irradiation, the only species present was the parent phosphite.

Group (3) *Secondary Alkylphosphites.*

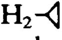
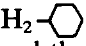
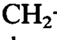
$P(OR)_3$; $R = CH(CH_3)_2$; $CH(CH_3)(C_2H_5)$; $CH(CH_3)(C_3H_7)$;
$CH(CH_3)(CH(CH_3)_2)$; $CH(C_2H_5)_2$.

Only in case of the triisopropylphosphite ($R = CH(CH_3)_2$) we were able to detect t-butyl and phosphoranyl radicals. The signal intensity of the phosphoranyl doublet was comparable to that of the β-branched phosphites of group (2). In all other cases no radicals were observed. Product analysis after prolonged irradiation demonstrated that in case no phosphoranyl radicals were observed, only the parent phosphite was present.

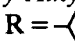
Group (4) *Tertiary Alkylphosphites.*

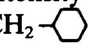
$P(OR)_3$; $R = C(CH_3)_3$; $C(CH_3)_2(C_2H_5)$.

Only the tri-t-butylphosphite ($R = C(CH_3)_3$) gave rise to the formation of phosphoranyl radicals. The signal strength and a(P)-value of the radicals were comparable to those of the triisopropylphosphite in group (3).

Group (5) *Primary Alkylphosphites Containing an Alkylring.*
$P(OR)_3$; R = CH$_2$; CH$_2$; CH$_2$.

All the phosphites examined showed the phosphoranyl doublet. In case of the tris(cyclopropylmethyl)phosphite (R = CH$_2$) the intensity of the signals was comparable to that of the primary phosphite containing the $CH_2CH(CH_3)_2$-fragment. In the phosphite containing the cyclohexylring, the signal strength was larger than that of the acyclic analogon ($R = CH_2CH(C_2H_5)_2$). The tris(tetrahydrofurfuryl)phosphite (R = CH$_2$) behaved in a similar way as the cyclohexyl compound, except for the signal strength which was smaller than that of the cyclohexyl compound.

Group (6) *Secondary Alkylphosphites Containing an Alkylring.*
$P(OR)_3$; R = .

Examining this phosphite, only very weak signals were observed. The signal intensity was smaller than that of the tris(cyclohexylmethyl)phosphite (R = CH$_2$) in group (5), but larger than the acyclic analogon ($R = CH(C_2H_5)_2$) which did not show any phosphoranyl radicals.

In order to complete the set of experiments, two additional groups were selected. Two series of phosphites, derived from the compounds of group (3), who failed to produce phosphoranyl radicals, were synthesized and studied. The radicals were generated according to the method used for the trialkylphosphites. The radicals and their spectroscopic parameters are listed in Table II.

Group (7) *Methyldialkylphosphites.*
$CH_3OP(OR)_2$; $R = CH(CH_3)_2$; $CH(CH_3)(C_2H_5)$; $CH(CH_3)(C_3H_7)$; $CH(C_2H_5)_2$.

All phosphites examined revealed the features of a phosphoranyl radical. The signal strength decreased with increasing bulk of the α-branching alkylgroup.

Group (8) *Dimethylalkylphosphites.*
$(CH_3O)_2POR$; $R = CH(CH_3)_2$; $CH(CH_3)(C_2H_5)$; $CH(CH_3)(C_3H_7)$; $CH(C_2H_5)_2$; $CH(CH_3)(CH(CH_3)_2)$.

TABLE II

Trialkoxy-t-butoxy phosphoranyl radicals $tBuO\dot{P}(OCH_3)(OR)_2$ and $tBuO\dot{P}(OCH_3)_2(OR)$, obtained from the reaction of t-butoxyl radicals with methyldialkylphosphites and dimethylalkylphosphites respectively

Phosphite[a]	t/°C	a(P)/G[b]
1. $CH_3OP(OCH(CH_3)_2)_2$	−86	898
2. $CH_3OP(OCH(CH_3)(C_2H_5))_2$	−86	891
3. $CH_3OP(OCH(CH_3)(C_3H_7))_2$	−86	891
4. $CH_3OP(OCH(C_2H_5)_2)_2$	−86	897
5. $(CH_3O)_2POCH(CH_3)_2$	−95	886
6. $(CH_3O)_2POCH(CH_3)(C_2H_5)$	−95	886
7. $(CH_3O)_2POCH(CH_3)(C_3H_7)$	−95	887
8. $(CH_3O)_2POCH(C_2H_5)_2$	−95	887
9. $(CH_3O)_2POCH(CH_3)(CH(CH_3)_2)$	−95	886

[a] Solvent n-pentane.

[b] Calculated using the Breit–Rabi equation; a(P) ± 1G. All g-factors were 2.003 ± 0.001.

The signal intensity of the phosphoranyl doublet varied only little within this group. The magnitude of the signals was comparable to that of the phosphoranyl radicals produced upon irradiation of trimethyl- or triethylphosphite in group (1).

DISCUSSION

Analysing these data it is obvious that the phosphites of group (1) behave as expected: Increasing the bulk of the alkyl groups results in an increase of viscosity and a decrease of molar concentration, which leads to a gradually decreasing signal strength.

The phosphites of group (2) show similar properties, but in case of the β-branched compounds an additional decrease in signal intensity occurs. This additional decrease is not the result of increasing viscosity or decreasing concentration. This can be concluded from the comparison of the triisooctylphosphite ($R = CH_2(CH_2)_4CH(CH_3)_2$) with the tris(2-ethylhexyl)phosphite ($R = CH_2CH(C_2H_5)(C_4H_9)$). The molar concentration is the same in both cases, while the viscosity of the more compact tris(2-ethylhexyl)phosphite is even smaller than that of the triisooctylphosphite. Yet the latter showed a strong phosphoranyl doublet, while in case of the former no radicals could be detected.

The reason for the remarkable behaviour of the trialkylphosphites can be understood taking a closer look at the phosphites of group (3) and group (4). From the data obtained, we conclude that in case the parent phosphite only contains α-methyl or α-hydrogen groups, phosphoranyl radicals will be formed. If one of the α-methyl or α-hydrogen groups is replaced by a more bulkier substituent (i.e. ethyl group or larger alkyl group), phosphoranyl radicals can no longer be formed. Again it is obvious that this behaviour is not the result of increased viscosity and decreased molar concentration only.

We believe that this behaviour has to be ascribed to extreme steric hindrance, caused by the larger α-branching alkyl fragments, which prevents the t-butoxyl radicals of reaching the phosphorus atom and inhibits the formation of phosphoranyl radicals.

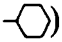
At first it seems strange that the phosphites of group (3) do not show the phosphoranyl doublet, while the tri-t-butylphosphite in which there appears to be a large steric hindrance, produces phosphoranyl radicals to a considerable extent. If, however, we take into account that the rotational barriers in the P—O—C-linkage are small, than it is clear that even at low temperature a considerable degree of rotational freedom is present. Hence, it follows that the shielding of the lone-pair at the phosphorus atom will not be considerably larger in the tri-t-butyl-phosphite ($R = C(CH_3)_3$) as compared to the triisopropylphosphite ($R = CH(CH_3)_2$). The experiments demonstrated that the strength of the tetra-t-butoxy phosphoranyl doublet is only slightly smaller than that of the t-butoxy-triisopropoxy phosphoranyl radical. The steric effects are also present, to some extent, in the phosphites of group (2). Effective shielding, caused by the β-branched alkyl groups, is only accomplished when the $CH_2CH(C_2H_5)(C_4H_9)$-group is present.

The ring containing phosphites of group (5) and group (6) do not attain a complete shielding, in contrast with their acyclic analogs. This behaviour has to be attributed to the more rigid conformations of the ring systems, as compared to the acyclic alkyl groups, which results in a less effective shielding of the lone-pair of the phosphorus atom.

Examining the data in Table II (vide supra), we conclude that steric effects are indeed the main reason for the decrease in radical formation. In the group (7) phosphites, a decrease in signal strength as a result of the larger α-branching alkyl groups occurs. The effect is less distinctive as compared to the trialkylphosphites, which can be expected considering the absence of one of the shielding alkyl groups. In the phosphites of group (8), the two methoxy groups provide sufficient room for the t-butoxyl radicals to reach the phosphorus atom unhampered, and produce phosphoranyl radicals. The size and shape of the third alkyl group have no influence on the radical formation.

The stability of all phosphoranyl radicals studied was of the same magnitude, which indicates that steric effects do not have a significant influence on their stability in solution. Steric effects are, however, very important in the formation of phosphoranyl radicals from the corresponding trialkyl- and methyldialkylphosphites. The use of dimethylalkylphosphites provides an excellent means of studying phosphoranyl radicals in solution, because of the total absence of steric hindrance due to the remaining alkyl group.

2. *Electronic Effects in Dimethylalkylphosphites*

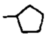
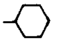
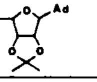
Interpreting the data of Table I, the tris(tetrahydrofurfuryl)phosphite ($P(OR)_3$; $R = CH_2$) in group (6) especially attracted our attention. Although the phosphite produced the corresponding phosphoranyl radical, the signal strength was considerably smaller than that of the tris(cyclohexylmethyl)phosphite ($R = CH_2$) in the same group. There is no reason to assume that the five-membered tetrahydrofurfuryl ring would cause a larger steric hindrance than the six-membered cyclohexyl ring. On the contrary, considering the larger flexibility of the six-membered ring, a more effective shielding of the phosphorus atom resulting in a smaller signal strength would be expected. Therefore, other effects have to be responsible for the difference in radical production.

The only difference between the two compounds, except for the ring-size, is the presence of an oxygen atom in the five-membered ring. If the presence of a hetero atom, at this position in the molecule, has a significant influence upon the radical formation, it could be of fundamental importance for our knowledge about phosphoranyl radicals in solution, especially if we take into consideration that biologically relevant phosphorus compounds also contain a hetero atom at this position in the molecule.

In order to examine the effect of additional hetero atoms in the ligands of the phosphites, a number of model compounds was synthesized and studied in the same way as the alkylphosphites in the preceding part. The radicals and their spectroscopic parameters are listed in Table III.

TABLE III

Trialkoxy-t-butoxy phosphoranyl radicals $tBuO\dot{P}(OCH_3)_2(OR)$ and $tBuO\dot{P}(OCH_3)(OR)_2$ obtained from the interaction of t-butoxyl radicals with dimethylalkylphosphites and methyldialkylphosphites containing additional electronegative hetero atoms

Phosphite	Solvent[a]	t/°C	a(P)/G[b]
1. $(CH_3O)_2POCH_2CH_2CH_2CH_3$	P	−95	886
2. $(CH_3O)_2POCH_2CH_2OCH_3$	P	−95	886
3. $(CH_3O)_2POCH_2CH_2SCH_3$	P	−95	886
4. $CH_3OP(OCH_2CH_2CH_2CH_3)_2$	T	−65	889
5. $CH_3OP(OCH_2CH_2OCH_3)_2$	T	−65	891
6. $CH_3OP(OCH_2CH_2SCH_3)_2$	T	−65	891
7. $(CH_3O)_2POCH_2CH_2CH(CH_3)_2$	P	−95	882
8. $(CH_3O)_2POCH_2CH_2N(CH_3)_2$	P	−95	884
9. $CH_3O(POCH_2CH_2CH(CH_3)_2)_2$	P	−95	882
10. $CH_3O(POCH_2CH_2N(CH_3)_2)_2$	P	−95	886
11. $(CH_3O)_2POCH_2$ 	T	−70	895
12. $(CH_3O)_2POCH_2$ 	T	−70	890
13. $(CH_3O)_2POCH_2$ 	P	−95	877
14. $(CH_3O)_2POCH_2$ 	P	−95	871
15. $(CH_3O)_2POCH_2$ 	A	−80	887
16. $(CH_3O)_2POCH_2$ 	A	−80	887

[a] Solvent P = n-pentane; T = toluene; A = acetone.

[b] Calculated using the Breit–Rabi equation; a(P) ± 1G. All g-factors were 2.003 ± 0.001.

The compounds listed are divided into three main groups, each consisting of a number of closely related phosphites. The only distinction between the compounds is the nature of the additional hetero atom. In all cases the phosphites containing the CH_2-group, resulting in the normal dimethylalkyl- or methyldialkylphosphites, were used as a reference. All phosphites examined showed a strong phosphoranyl doublet. The signal intensity, however, varied considerably with the hetero atom present.

Group (1) *Methyldialkyl- and Dimethylalkylphosphites.*
$CH_3OP(OR)_2$ and $(CH_3O)_2POR$; $R = CH_2CH_2XCH_3$
$(X = CH_2, S, O)$.

The difference in signal strength is more pronounced at low temperatures. The intensities decrease upon going from $X = S$, via $X = CH_2$ to $X = O$. Increasing the temperature results in a diminishing difference in signal intensity between the compounds examined. Methyldialkylphosphites show the same properties as their dimethylalkyl analogs. The signal strength of the former, however, was already less than that of the latter, due to the decreasing molar concentration.

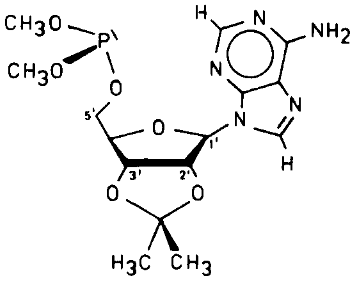
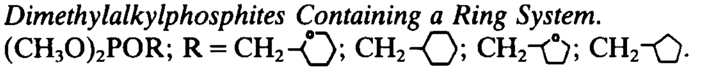


FIGURE 2 The 2′,3′-O-Isopropylidene adenosine-5′-dimethylphosphite.

Group (2) *Methyldialkyl- and Dimethylalkylphosphites Containing a Triply Connected Hetero Atom.*
$CH_3OP(OR)_2$ and $(CH_3O)_2POR$; $R = CH_2CH_2X(CH_3)_2$
$(X = CH, N)$.

The phosphites of this group showed the same features as those in group (1). At low temperatures a large difference in signal intensity between the CH- and N-compounds is present. Upon increasing the temperature, the difference in intensity diminishes and finally disappears.

Group (3) *Dimethylalkylphosphites Containing a Ring System.*

$(CH_3O)_2POR$; $R = CH_2$-; CH_2-; CH_2-; CH_2-.

The phosphoranyl radicals produced by these phosphites all revealed the same properties as already mentioned for the previous groups. In all cases the CH_2-compound produced the strongest signals. The magnitude of the effect seems practically the same in both cases. However, a direct comparison is not possible, due to the difference in molecular weight between the five- and six-membered ring phosphites.

The last pair of phosphites studied consisted of two compounds, both containing the tetrahydrofurfuryl group. In the first compound, the tetrahydrofurfuryl group was the only substituent present, whereas the second also contained an adenine base at the 1′-position of the ring system (see Figure 2).

Only a small difference in signal intensity, probably due to the difference in molecular weight and molar concentration, could be detected. There was no difference in stability between the two compounds.

DISCUSSION

Analysing these data, we conclude that the presence of an additional electronegative hetero atom in the phosphorus ligands has a dramatic effect on the radical formation. If we take a closer look at the data obtained for the three main groups, we see that the introduction of a nitrogen or oxygen atom in the P—O—C—C—X—C fragment results in a decrease in signal strength, especially at low temperatures. The introduction of a sulfur atom has a somewhat different effect, resulting in an increase in signal intensity.

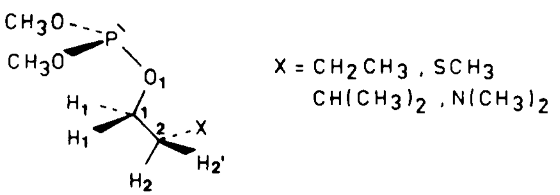


FIGURE 3 Acyclic dimethylalkylphosphites containing a hetero atom in the alkyl ligand.

We believe that this interesting phenomenon can be explained as a result of the well-known gauche-effect.[5] This effect is based on the conformational preference for a gauche orientation of the vicinal oxygen atoms in the common P—O—C—C—O fragment. A recent study,[6] concerning the influence of the gauche-effect on the conformation of phosphates and phosphoranes corresponding to the phosphites of the present study, clearly showed the influence of the nature of the additional hetero atom. In an additional investigation[7] it was demonstrated that the results of the electronic effects present in the phosphate compounds are also valid, to the same extent, in the corresponding phosphite compounds (see Figure 3).

Conformational analysis[8] of the C_1—C_2 bond in the phosphites accurately reflect the properties of the substituting hetero atom. In case $X = CH_2$ or $CH(CH_3)$, the C_1—C_2 bond strongly tends to the sterically favourable trans-conformation, especially at low temperatures. Replacement of $X = CH_2$ by $X = O$, or $X = CH(CH_3)$ by $X = N(CH_3)$ results in a distinct preference for the gauche state, due to the already mentioned gauche-effect. The expected electrostatic repulsion between the hetero atoms is fully expressed in case $X = S$. It is known that between oxygen and sulfur no gauche-effect occurs[5b] and although sulfur nominally possesses the same electronegativity as carbon,[9] there is a charge density on sulfur due to the ability of sulfur to use its d-orbitals as polarization functions.[10] This results in a strong preference for the trans orientation of O_1 and S in the compounds investigated. The relevant data of the investigations are collected in Table IV. The results of this study can be compared with earlier work on the conformation of the cyclic phosphorus analogs (e.g. the tetrahydrofurfuryl phosphates and phosphoranes), which have a highly similar conformation.[11]

TABLE IV

C_1—C_2 conformation[8] of the phosphites $(CH_3O)_2POCH_2CH_2XCH_3$

X	x_g	x_t
S	0.35	0.65
CH_2	0.47	0.53
O	0.76	0.24
$CH(CH_3)$	0.43	0.57
$N(CH_3)$	0.51	0.49

From these data we may conclude that in case a hetero atom is introduced into the P—O_1—C_1—C_2—X—C fragment, the conformation around the C_1—C_2 bond changes considerably. Furthermore, taking into account that the gauche conformation (O_1 and X gauche) produces the largest steric hindrance, we can understand the results on the compounds listed in Table III.

At low temperatures, the sulfur containing phosphites mainly occur in a trans-conformation, in which steric hindrance is reduced to a minimum. As a result, the phosphites produce a very strong phosphoranyl doublet. The phosphites containing the CH_2 or $CH(CH_3)$ group behave as expected. They mainly appear in a trans-conformation, although the population density is somewhat less than in the sulfur analog, resulting in a fairly strong phosphoranyl doublet.

The phosphites possessing the nitrogen or oxygen groups preferably obtain a gauche-conformation at low temperature. This results in a larger steric hindrance and a decrease in signal intensity as compared to the sulfur and carbon analogs. The disappearance of this effect upon raising the temperature has to be ascribed to the diminishing difference in population densities, which results in comparable steric hindrances and therefore a comparable signal strength for all compounds examined.

The data obtained for the adenosine phosphoranyl radicals show that the radicals possess the same stability and ease of formation as the normal tetrahydrofurfuryl compound.

Concluding Remarks

This study clearly demonstrates the steric and electronic effects that govern the formation of phosphoranyl radicals in solution. It also shows that the ESR-technique provides an excellent means of studying the influence of the gauche-effect on radical formation. The results are in excellent agreement with the data obtained from other studies concerning the gauche-effect.

EXPERIMENTAL

The techniques employed for the detection of ESR-spectra during continuous u.v. irradiation have been described previously.[12] A Varian E-4 ESR-spectrometer, equipped with a variable temperature accessory, was used in conjunction with a Philips 500W mercury lamp equipped with a collimating lens system. A condensing lens focused the light into the cavity of the spectrometer. The samples, consisting of the peroxide (15% v/v) and the phosphite (10% v/v)[13] in n-pentane or toluene solvent, were prepared using deoxygenated reagents and solvents. The samples were prepared in 4 mm quartz tubes[14] and sealed under a nitrogen atmosphere just prior to insertion into the spectrometer. Sample temperatures were monitored by a thermocouple inside the spectrometer. The reactions were performed in the ESR-tube, directly in the cavity. The samples were photolysed only for a short period of time, in order to avoid any complications resulting from the build-up of products. The signal intensities were measured using the low-field line of the phosphoranyl doublet. These lines approximately possessed the same shape and line-width, thus permitting a quantitative comparison of the various compounds.

The trialkylphosphites used in this work were either commercially available or were prepared according to standard procedures.[15] The dimethylalkylphosphites were prepared from chlorodimethoxyphosphine and the desired alcohol, whereas the methyldialkylphosphites were prepared analogous to a method described by Michalski *et al.*[16] All phosphites were distilled under reduced pressure prior to usage. Their purity was checked by ^1H and ^{31}P NMR techniques. N-pentane, toluene and acetone were distilled and dried over molecular sieves. Di-t-butyl peroxide was obtained from Merck and was purified before use.

The spectroscopic parameters of the phosphoranyl radicals studied were calculated using the Breit–Rabi equation.[17] Product analyses were performed after prolonged irradiation using ^1H and ^{31}P NMR techniques. ^1H NMR-spectra were run on a Hitachi–Perkin Elmer R-24B spectrometer at 60 Mhz, using TMS as internal standard. ^{31}P NMR-spectra were run in the FT-mode at 36.4 Mhz on a Bruker HX-90 spectrometer with a Digilab FT-NMR-3 pulsing accessory. ^{31}P chemical shifts were related to 85% H_3PO_4 as external standard.

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8. The conformation around the C_1—C_2 bond is an equilibrium between three staggered rotamers, but as two of these rotamers are mirror images and have identical populations, a two-state description with a gauche (g) and a trans (t) state is used (Figure 4). The population densities x_g and x_t of these states have been determined from the vicinal proton–proton coupling constants.[6]

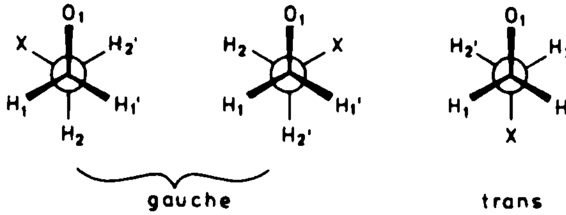

FIGURE 4 Staggered rotamers around the C_1—C_2 bond.

9. The electronegativity of the elements relative to hydrogen has been derived from the Huggins scale: $\Delta\chi_O = 1.3$; $\Delta\chi_N = 0.85$; $\Delta\chi_S = \Delta\chi_C = 0.4$.
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13. In case a direct comparison of the methyldialkyl- or dimethylalkylphosphite pairs was concerned,

we used a more accurate weighing method in order to obtain the same molar concentrations in both samples.

14. An exception was made in case of the adenosine phosphite, which was studied in acetone because of solubility reasons. The measurements were conducted in a 0.5 mm flat cell, in order to avoid signal absorption.
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