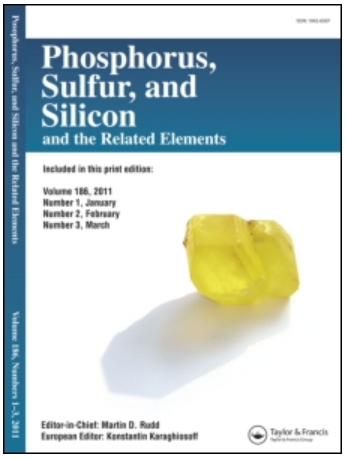

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Fragmentation and Insertion Reactions With 2,3-Oxaphosphabicyclo[2.2.2]oct-5-ene Derivatives; Synthesis of a 1,3,2,6-Oxathiadiphosphorinane

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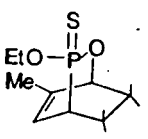
FRAGMENTATION AND INSERTION REACTIONS WITH 2,3-OXAPHOSPHABICYCLO[2.2.2]OCT-5-ENE DERIVATIVES; SYNTHESIS OF A 1,3,2,6-OXATHIADIPHOSPHORINANE

LOUIS D. QUIN, F. H. OSMAN, N. D. SADANANI, A. N. HUGHES, AND R. O. DAY
Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

Abstract Derivatives of the 2,3-oxaphosphabicyclo[2.2.2]oct-5-ene ring system with P in the thiophosphonate state, as in A, have been synthesized. The bridging P-O fragment can be eliminated on either thermal (110°) or photochemical (254 nm) treatment, and appears as the P=O group of the previously unknown and highly reactive species RO-P(=S)=O. In an attempt to replace O by S in B with the thionating reagent $(4\text{-}MeOC_6H_4PS_2)_2$, a product C was obtained which was proved by X-ray analysis to have resulted from cleavage of the O-C bond and insertion of the fragment $4\text{-}MeOC_6H_4PS_2$ into the molecule. This is the first known example of the 1,3,2,6-oxathiadiphosphorinane ring system.



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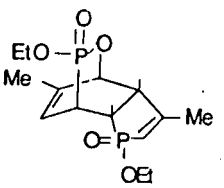

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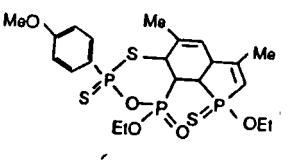
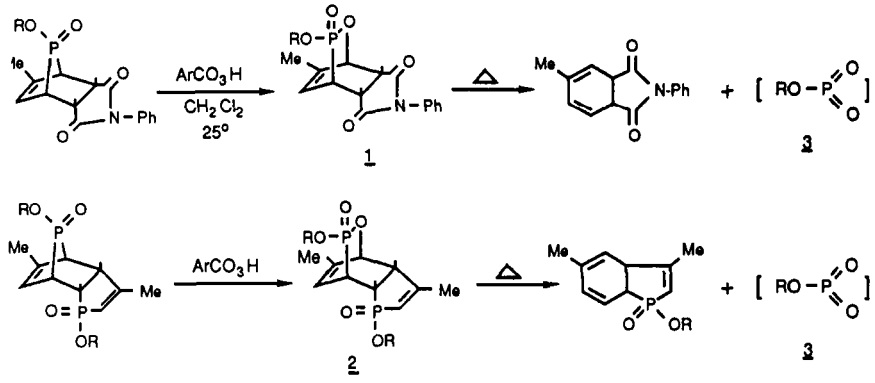


C

INTRODUCTION

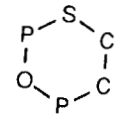
In 1985, we reported[1] that peroxy acids could insert oxygen into the strained C-P bond of phosphinates in the 7-phosphanorbornene ring system. The resulting products are bridged derivatives of the 1,2-oxaphosphorinane ring system; some typical structures are shown as 1 and 2. These compounds are stable crystalline solids at room temperature, but it was found that they underwent fragmentation with the release of the bridging P-O unit on heating

at 110°C. This unit becomes a P=O group in the presumed product 3, a low-coordination form of an alkyl phosphate known as a metaphosphate.



Species 3 are of such high reactivity that they cannot be isolated or even directly observed in solution; their presence must be inferred from trapping reactions with nucleophiles, especially alcohols. Nevertheless, there is much current interest in such low-coordination species as metaphosphates, and the observation of a new way to generate them has prompted continued development of the general method of synthesis of the bridged 1,2-oxaphosphorinane ring system which serves as the precursor. New compounds with this ring system are being sought that would provide an entry to the creation of other types of metaphosphoric acid derivatives, some not yet made by any other synthetic method. In the present study, the first thiono derivatives of the bridged 1,2-oxaphosphorinane system have been prepared, and employed as precursors of the previously unknown alkyl metathiophosphate series. An unexpected discovery of a method for the formation of the 1-oxa-3-thia-2,6-diphosphorinane ring system (4) also resulted from this study. No previous report seems to exist on the

formation of this ring system.



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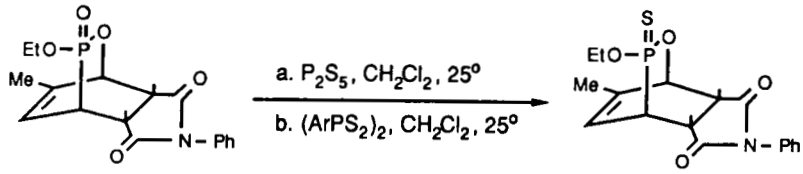
RESULTS AND DISCUSSION

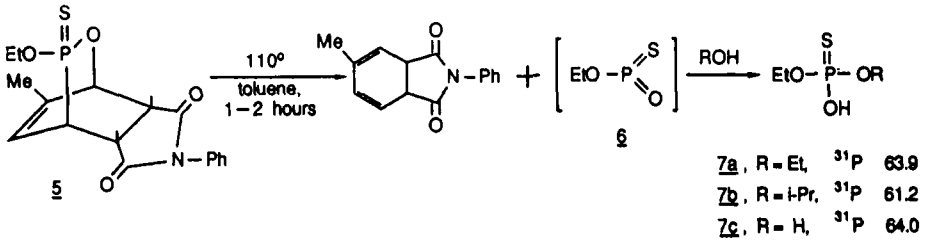
The replacement of the phosphoryl oxygen of compound 1a with sulfur occurred smoothly on reaction with P_2S_5 at room temperature in CH_2Cl_2 solution. Analysis of the reaction mixture by ^{31}P NMR revealed the complete consumption of the starting material (δ27.6) after 5-6 days; the only significant signal in the reaction mixture was that for the product 5 (δ86.1). This compound was isolated as a crystalline solid, m.p.138-139^0, in 40% yield. It was fully characterized by elemental analysis, and by ^1H and ^{13}C NMR spectroscopy, details of which are being published elsewhere[2]. The thionation was also accomplished in similar yield with the commonly used reagent $(4\text{-}MeOC_6H_4PS_2)_2$ (sold commercially as Lawesson's reagent) used under the same conditions.



1a 5

Compound 5 underwent complete release of the bridging P-O unit on being heated in toluene at 110^0 for 2 hr. When no trapping agent was present, the released metathiophosphate 6 gave various products as indicated by the complexity of the ^{31}P NMR spectrum. However, when as little as one equivalent

of an alcohol was present, the metathiophosphate was nearly completely trapped as the O,O-dialkyl ester of phosphorothionic acid. Some typical reaction products are shown as 7. These products were isolated by chromatography on silica gel, and generally characterized by ^{1}H or ^{13}C NMR spectroscopy. Details are reported separately[2]. Water was also used as a trapping agent and provided the monoalkyl ester 7c.

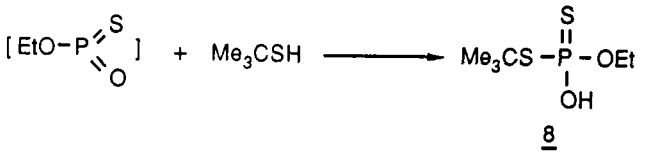


5 6

7a, R = Et, ^{31}P 63.9
7b, R = i-Pr, ^{31}P 61.2
7c, R = H, ^{31}P 64.0

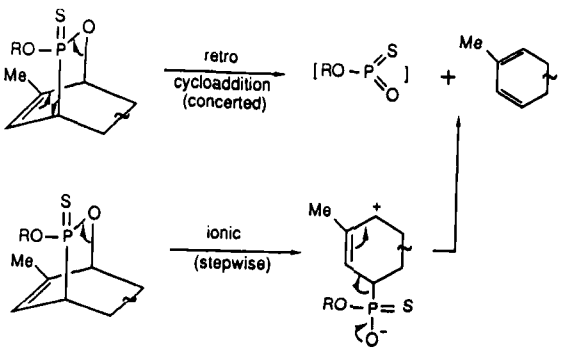
The fragmentation was then performed photochemically, since we had previously found[3] that this was an excellent technique for the formation of $EtO-PO_2$ from the ester 1a. The reaction indeed proceeded quite smoothly when UV light of wavelength 254 nm was used in a quartz reactor. Suitable solvents include dioxane and acetonitrile. The reaction was conducted with air-cooling only, which generally led to temperatures of 35°. The fragmentation was complete in 4-5 hr when a 450 watt lamp was used for a solution of 50 mg of 1a in 50 ml of solvent. As in the thermal fragmentation, a complex product mixture was formed from the released metathiophosphate, but this species could be intercepted with ethanol or 2-propanol. Tert-butyl alcohol was a less effective trapping agent, and a number of other ^{31}P NMR signals than that for the expected ester were found for the reaction product. However, the presence of an equivalent of triethylamine[3] prevented the formation of these products and led to a relatively clean product. We also found that a thiol

(tert-butyl) was an effective trapping agent, forming 8.



8

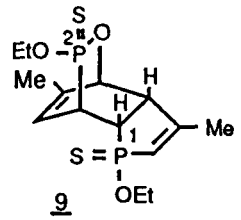
We have therefore demonstrated two fragmentation techniques for the thionophosphonates in the 2,3-oxaphosphabicyclo [2.2.2] octene system. In each, we assume that a metathiophosphate is released, although there is no evidence to support this assumption other than that derived from the trapping reactions. Two mechanisms can be visualized for these fragmentations, as shown below.



For the thermal fragmentation, some observations speak in favor of the ionic mechanism. Thus, the rate of the fragmentation is noticeably faster when conducted in solvents more polar than toluene (e.g., dioxane). Also, in related fragmentations (the N,N-dimethylamide analogue of ester 1) transient intermediates have been detected by ^{31}P NMR[4]. For the photochemical reaction, no evidence is yet available to support either mechanism. However, it is known[5] that benzylic phosphates can be fragmented to benzylic ions photochemically

and this may also be true of allylic esters. The bridged phosphonates (1) and phosphonothionates (5) have the allylic feature, and may therefore fragment by the ionic path.

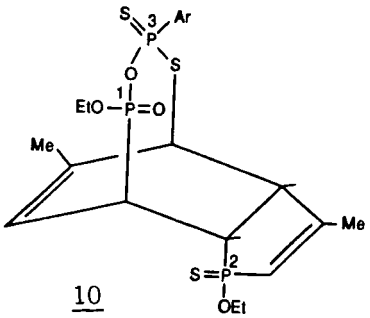
In contrast to the very successful thionation performed on bridged phosphonate 1a, the reaction of the more complicated bridged derivative 2(R=Et) towards the thionation agents gave quite complex mixtures. That from P_2S_5 was judged to be intractable. The mixture from Lawesson's reagent, while still quite complex, nevertheless had ^{31}P NMR signals in the expected region for the dithionation product 9 (δ89.3 and 114.5, J = 77.0 Hz) when the reaction was conducted in methylene chloride at room temperature with one molar equivalent of reagent.



9

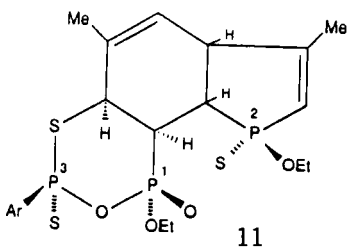
Using the height of the ^{31}P signals as a measure, the content of this substance could be enriched to about 70% by chromatography on Florisil, but it could not be purified further. Of more interest was the observation of a second compound of prominence in the complex reaction mixture; when the reaction was conducted at 55° in toluene solution, this compound was the major product. It was isolated in analytically pure form by chromatography on Florisil; it was a crystalline solid m.p. 159-161°, which by analysis and mass spectrometry was indicated to have the formula $C_{21}H_{29}O_5P_3S_3$, and could be visualized as a combination product of a monomeric unit of the thionating agent and a mono-thionated product from the starting material 2(R=Et). The product gave three ^{31}P NMR signals, a doublet (J 5.5 Hz) at

δ118.2, a doublet at δ86.1 (J 37.9 Hz), and a doublet of doublets at δ18.8 (J 5.5 and 37.9 Hz). A possible structure that was at first indicated by these chemical shifts is shown as 10; the shift of δ18.8 is appropriate for a phosphonate group (P_1), that of δ86.1 for a dithiophosphonate (P_3), and that at δ118.2 for the 2-phospholene unit (P_2).



10

However, structure 10 does not adequately account for the observed coupling constants. The 3-bond value for coupling between P_1 and P_2, where a quite large dihedral angle is present, should be much larger than the 5.5 Hz observed[6]. The true structure of the compound was then determined by single-crystal X-ray diffraction analysis and found to be that shown as 11.



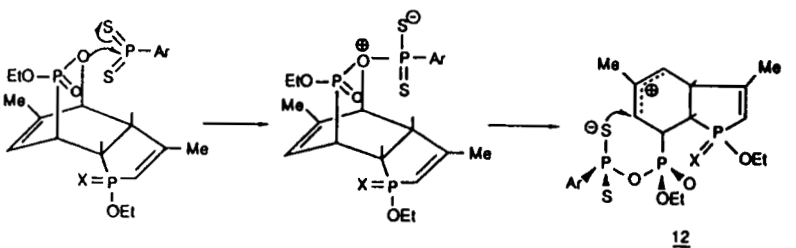
11

This structure is different in one major way from the originally proposed 10; the P-S unit has indeed been inserted in the ring system, but not at the expected site. Instead, an allylic rearrangement has occurred at the time of opening of the original O-C bond in 2(R=Et), and ring closure occurs at a different

(allylic) carbon. This structure adequately accounts for the small size of the 3-bond coupling; the dihedral angle determined for the unit P_1-C-C-P_2 is 81.7°, a value close to that (90°) where coupling is minimal. The location of the atoms as revealed by the X-ray analysis is shown as Fig. 1. Of particular note is the chair shape seen in Fig. 1 and 2 for the oxathiadiphosphorinane moiety of the molecule. The complete analysis will be published elsewhere[7]; some data pertinent to the new ring system are summarized in Fig. 3.

Since the formation of 11 occurs under mild conditions where there is no tendency for the O-C bond of the starting ester 2(R=Et) to open, it must be assumed that the reaction of the ester with the monomeric species from the thionating agent actually causes the ring opening. Furthermore, the stereochemistry of the product 11 suggests that the attack has occurred at the oxygen bonded to carbon, and not at the more likely site of the phosphoryl oxygen. This follows from the fact that the product has the retained stereochemical configuration at the phosphonate phosphorus; attack at the phosphoryl oxygen would have given inversion of the phosphorus configuration when the ring is re-closed. The proposed course of the reaction is shown as Scheme 1.

Scheme 1



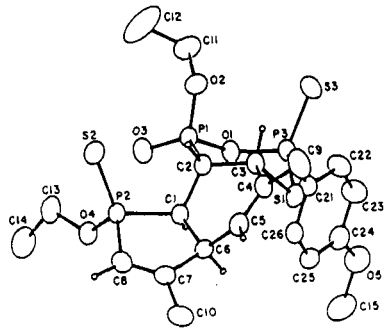


FIGURE 1 ORTEP plot of 11 with thermal ellipsoids at the 30% probability level. Hydrogen atoms, except those of the fused ring system which are represented by spheres of arbitrary radii, are omitted for purposes of clarity. The enantiomer shown is the mirror image of that used in the schematics.

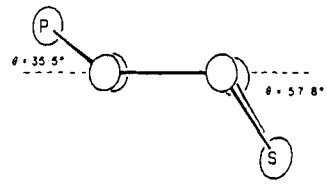


FIGURE 2 ORTEP plot of the oxathiadiphosphorinane ring system in 11 viewed parallel to the four-atom plane of the chair. The θ values are the dihedral angles between this plane and the three atom planes defined by the out-of-plane atoms and their two nearest neighbors.

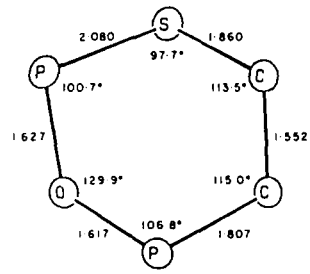
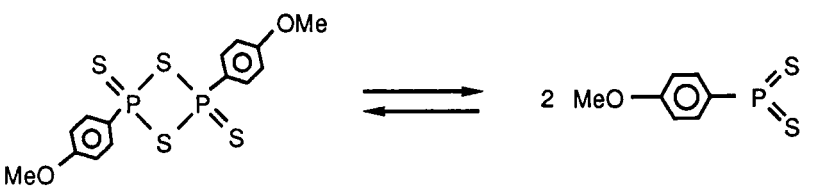


FIGURE 3 ORTEP plot including bond lengths (Å) and bond angles (deg) for the oxathiadiphosphorinane ring system in 11. The view is normal to the four-atom plane of the chair.

The X-ray analysis also shows the configuration at all other chiral centers, but of interest is that at the dithiophosphonate group, where two configurations could result when the cis-fused ring is formed. This possibility arises from the presence in intermediate 12 of two identical S-atoms, either of which could attack carbon to close the ring. In fact, the reaction mixture does exhibit ^{31}P NMR signals that could well belong to the other isomer. However, the substance giving rise to these signals [δ18.8 (J = 5.5 and 37.9 Hz), δ86.1 (37.9 Hz), and δ118.2 (5.5Hz)] has not been isolated or further considered.

The literature contains other reports of the monomeric form of the thionating reagent acting to insert a P-S unit in a substrate. Apparently an equilibrium is present between the monomer and the (dominant) dimer.



It therefore seemed that the P-S insertion reaction could take place also with other derivatives of the 2,3-oxaphosphabicyclo [2.2.2]octene ring system so as to form additional representatives of the 1-oxa-3-thia-2,6-diphosphorinane ring system. We performed the reaction of 1a with Lawesson's reagent under the same conditions that were effective for reaction with 2(R=Et). The resulting reaction mixture was quite complex, as judged by its ^{31}P NMR spectrum. There were no signals that could be assigned to the expected P-S insertion product. No other applications of the insertion reaction have yet been attempted.

ACKNOWLEDGEMENT

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REFERENCES

1. L. D. Quin and B. G. Marsi, J. Am. Chem. Soc., 107, 3389 (1985).
2. L. D. Quin and N. D. Sadanani, in preparation.
3. L. D. Quin, B. Pete, J. Szewczyk, and A. N. Hughes, Tetrahedron Lett., 29, 2627 (1988).
4. L. D. Quin, J. Szewczyk, K. M. Szewczyk, and A. T. McPhail, J. Org. Chem., 51, 3341 (1986).
5. R. S. Givens and B. Matuszewski, J. Am. Chem. Soc., 106, 6860 (1984).
6. R. Couffignal, H. B. Kagan, F. Mathey, O. Samuel, and C. C. Santini, Compt. Rend. Acad. Sci. Paris, Series C, 291, 29 (1980).
7. L. D. Quin, F. H. Osman, R. O. Day, A. N. Hughes, X.-P. Wu, and L.-Q. Wang, Nouv. J. Chim., in press.
8. S.-O. Lawesson, in "Phosphorus Chemistry: Proceedings of the 1981 Conference," Am. Chem. Soc., Symposium Series 171, p. 279.