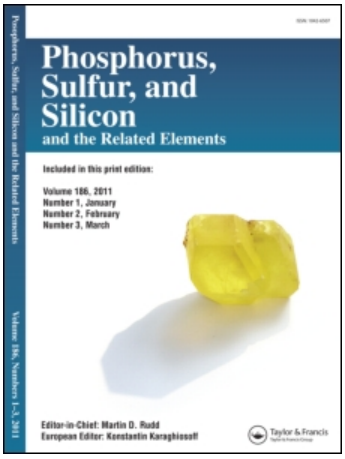

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A Thermolysis Study of Poly(Trimethylene Phenylphosphinate) and Poly(2,2-Dimethyltrimethylene Phenylphosphinate). NMR and X-Ray Structure of 2-Oxo-2-Phenyl-4,4-Dimethyl-1,2-Oxaphospholan

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A THERMOLYSIS STUDY OF POLY(TRIMETHYLENE PHENYLPHOSPHINATE) AND POLY(2,2-DIMETHYLTRIMETHYLENE PHENYLPHOSPHINATE). NMR AND X-RAY STRUCTURE OF 2-OXO-2-PHENYL-4,4-DIMETHYL-1,2-OXAPHOSPHOLAN

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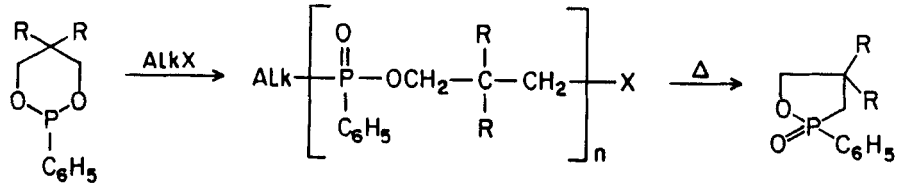
The syntheses of polyphosphinates 2 and 2a by the ring-opening polymerization of cyclic phosphonites 1 and 1a with CH_3I as an initiator have been reported in literature[1-3]. These polymers thermally decompose to give oxaphospholan 3 and 3a. In this paper, we present evidence on the mechanism of their formation.



1: R = H
1a: R = CH_3

2: R = H, X = I, Br
2a: R = CH_3, X = I

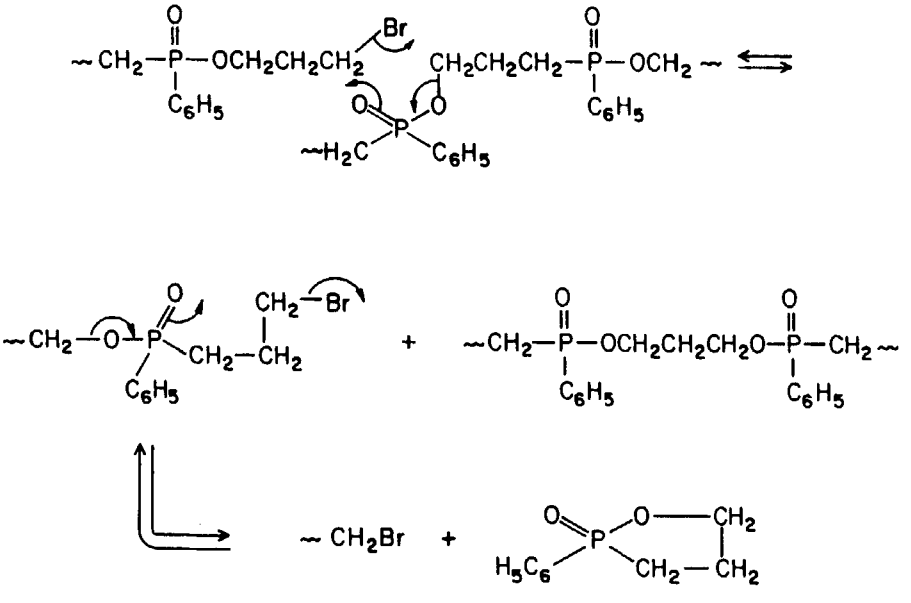
3: R = H
3a: R = CH_3

Further, the X-ray crystal structure of 2-oxo-2-phenyl-4,4-dimethyl-1,2-oxaphospholan (3a) has been determined and compared vs. its preferred conformation in solution derived from ^1H and ^{13}C NMR.

RESULTS AND DISCUSSION

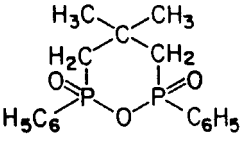
Polymer 2, made from 0.2 mol of 1 and 0.002 mol of n-PrBr as

initiator at 200°C, had 24% of oxaphospholan 3 as the decomposition product. Its concentration was determined by ^{31}P NMR, in which it appeared as a singlet of 58.5 ppm vs. a multiplet (48.0-38.8 ppm) for the linear polymer. Its elimination most likely occurs via an unzipping process following first the rearrangement of the phosphinate end group, presumably involving Sn2 displacement of the halide by the phosphinate group:



The halide group appears to play an important role in the above reaction scheme. For example, when the polymer was heated at 200°C in vacuo, the elimination of 3 essentially stopped because the halide had distilled as 1,3-dibromopropane.

Poly(2,2-dimethyltrimethylene phenylphosphinate) (2a) was made at 180-185°C with CH_3I as initiator. A small amount of 3a was present as decomposition product (δ_{31P} = 59.5 ppm). At temperatures ∿200°C the polymer formation and decomposition occurred simultaneously giving 86-89% of 3a. However, a small amount (∿3%) of the following cyclic anhydride was also isolated. Its



formation points to the rearrangement of at least some of the phosphinate groups, presumably by the same mechanism as in the case of the trimethylene polymer.

X-RAY STRUCTURE AND NMR DATA OF 3α

The X-ray analysis of oxaphospholan 3α (monoclinic crystals) shows that the five-member ring is puckered at C(8) making a dihedral angle of 36.8° between the planes defined by C(7), C(8), C(9) and P(1), O(2), C(7), C(9) as shown in Figure 1.

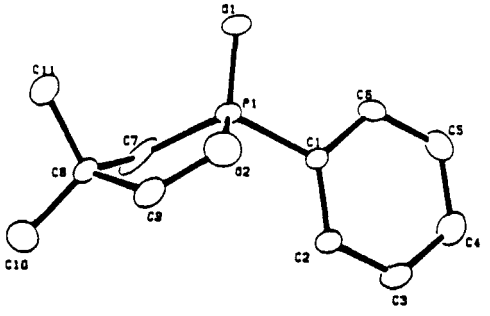
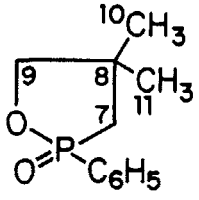


FIGURE 1 X-Ray Structure of 3α

However, the NMR data indicate that 3α exists in a different conformation in solution ($CDCl_3$). Table I lists the PCCC dihedral angles measured from X-ray and those estimated from the vicinal ^{31}P-^{13}C coupling constants using Quin's plot for P(IV) derivatives[4]. The NMR angles would require moving C(8) into the plane of the ring. Further, the P-C bond has to be rotated to position one CH_2 protons trans and the other gauche to the P=O bond to satisfy their $^2J_{PH}$ values of 13.0 Hz and 6.0 Hz, respectively[3]. This rotation would result in puckering the ring at the oxygen atom.

TABLE I NMR and X-Ray Data



Coupling Constants Hz		Dihedral Angles X-Ray	NMR
PC_{11} = 4.3	$PC_7C_8C_{11}$	98.2°	115-120°
PC_{10} = 9.0	$PC_7C_8C_{10}$	153°	138-143°
PC_9 = 4.3	$PC_7C_8C_9$	35.7°	10-20°[a]

[a] Estimated from models and from single pathway $^3J_{PCCC_9}$ of ~10.3 Hz calculated from $^3J_{PCCC_9}$-$^2J_{POC_9}$ = 4.3 Hz and using $^2J_{POC_9}$ of 6.0 Hz from monomeric 2a (n = 1).

ACKNOWLEDGMENT

Dr. J. C. Calabrese determined the X-ray structure of 3a.

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