

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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

Gurdial Singh^a

^a Inc., Textile Fibers Department, Pioneering Research Laboratory, E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

To cite this Article Singh, Gurdial(1983) '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', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 18: 1, 217 — 220

To link to this Article: DOI: 10.1080/03086648308076005

URL: <http://dx.doi.org/10.1080/03086648308076005>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

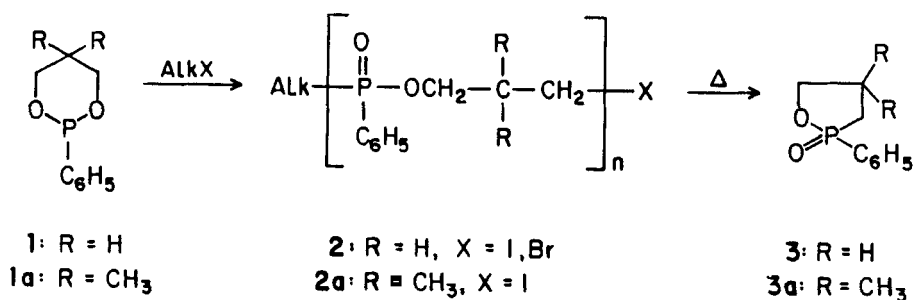
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

GURDIAL SINGH

E. I. du Pont de Nemours and Company, Inc., Textile Fibers Department, Pioneering Research Laboratory, Experimental Station, Wilmington, Delaware, U.S.A.

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 literature¹⁻³. These polymers thermally decompose to give oxaphospholan **3** and **3a**. In this paper, we present evidence on the mechanism of their formation.

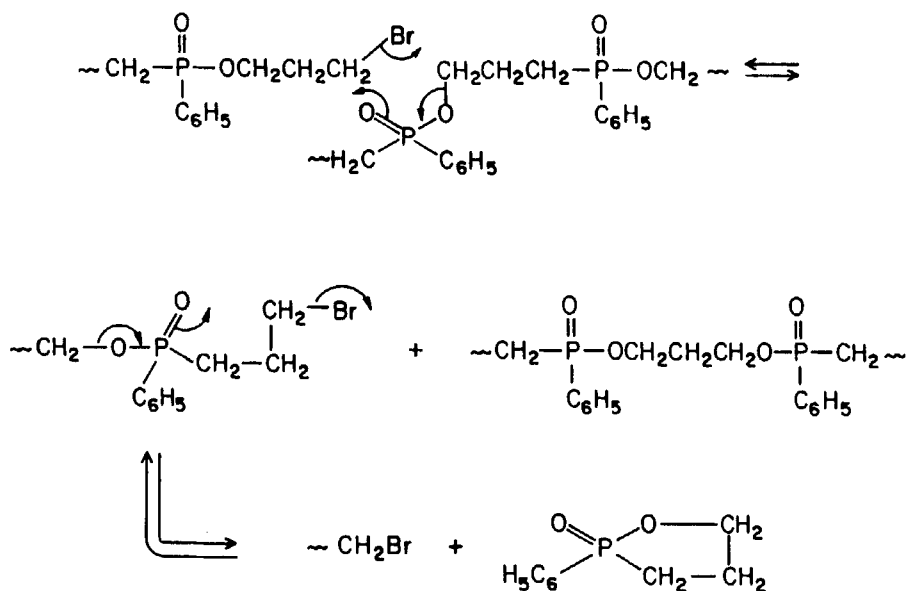


Further, the X-ray crystal structure of 2-oxo-2-phenyl-4,4-dimethyl-1,2-oxaphospholan (**3a**) has been determined and compared vs. its preferred conformation in solution derived from ¹H and ¹³C NMR.

RESULTS AND DISCUSSION

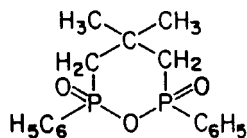
Polymer **2**, made from 0.2 mol of **1** and 0.002 mol of *n*-PrBr as

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 $\text{S}_\text{N}2$ 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) (2Q) was made at 180-185°C with CH_3I as initiator. A small amount of 3Q was present as decomposition product ($\delta_{31\text{P}} = 59.5$ ppm). At temperatures $\sim 200^\circ\text{C}$ the polymer formation and decomposition occurred simultaneously giving 86-89% of 3Q. However, a small amount ($\sim 3\%$) 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 3a

The X-ray analysis of oxaphospholan **3a** (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.

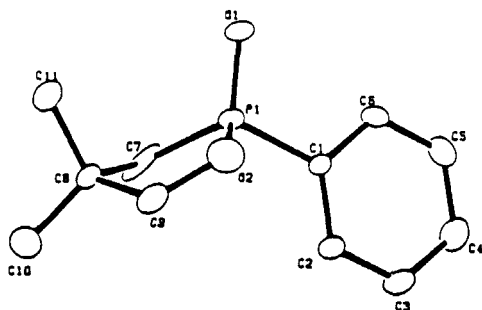
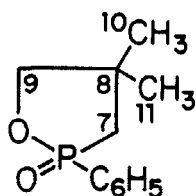


FIGURE 1 X-Ray Structure of **3a**

However, the NMR data indicate that **3a** 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) derivatives⁴. 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 $\text{P}=\text{O}$ bond to satisfy their $^2J_{\text{PH}}$ values of 13.0 Hz and 6.0 Hz, respectively³. 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 $2d$ ($n = 1$).

ACKNOWLEDGMENT

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

REFERENCES

1. K. A. Petrov, E. A. Nefantev, and I. I. Sopikova, *Vysokomol. Soedin.*, **2**, No. 5, 685 (1960); *Chem. Abstr.*, **55**, 9935 (1961).
2. T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).
3. G. Singh, *J. Org. Chem.*, **44**, 1060 (1979).
4. L. D. Quin, *The Heterocyclic Chemistry of Phosphorus* (John Wiley & Sons, New York, 1981), p. 281.