AD-A103 532

TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY
STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS INCLUDING A NE--ETC(U)
AUG 81 R H NEILSON, P WISIAN-NEILSON DAA029-80-C-0044

F/S 7/3

UNCLASSIFIED

ARO-16266.7-C

NL

For
A 04582

END
DATE
FILMED
10-81
DTIC

AD 103532 7-C

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 6	2. GOVT ACCESSION NO. AD A103532	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Studies of Silicon-Nitrogen-Phosphorus Compounds Including a New Synthesis of Phosphazenes.		5. TYPE OF REPORT & PERIOD COVERED Final Report (1/1/79 - 5/31/81)
7. AUTHOR(s) 10 Robert H. Neilson & Patty Wisian-Neilson Department of Chemistry-Texas Christian University, Fort Worth, TX 76129		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Texas Christian University Fort Worth, Texas 76129		8. CONTRACT OR GRANT NUMBER(s) DAAG29-79-G-00044 DAAG29-80-C-0044 15 DAAG-1-1-G-0044
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
12. REPORT DATE 11 August 11, 1981		13. NUMBER OF PAGES 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 9 Final rept. 1 Jan 79-31 May 81		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. (18) ARO (12) 6		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) poly(dialkylphosphazenes) N-silylphosphinimines silylaminophosphines silicon-nitrogen-phosphorus phosphazenes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This program of research has been directed toward the development of new synthesis of polyphosphazenes, particularly those with alkyl and/or aryl substituents, via the elimination of substituted silanes from N-silylphosphinimines. The synthesis and characterization of both the new polymers and their precursors has been investigated.		

LEVEL

DTIC
ELECTED
SEP 1 1981
H

DTIC FILE COPY

STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS
INCLUDING A NEW SYNTHESIS OF PHOSPHAZENES

Final Report

by

Robert H. Neilson and
Patty Wisian-Neilson

August 11, 1981

U.S. ARMY RESEARCH OFFICE

Grant No. DAAG29-79-G-0004

Contract No. DAAG29-80-C-0044

Texas Christain University

Fort Worth, Texas 76129

APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

An important, common feature of each of these oxidation reactions is subsequent cleavage of a Si-N bond as seen in the migration of Me₃Si from nitrogen to oxygen in eq 2 and 4 and in the elimination of Me₃SiBr in eq 3. Of particular importance is a similar Si-N bond cleavage upon thermolysis of the P-bromo, N-silylphosphinimine products in eq 3 to form exclusively cyclic phosphazenes (R₂PN)_n (n=3,4,5) (eq 5).

Since no evidence for polymer formation via Me₃SiBr elimination was observed, the effect of changing the leaving group from Br to NMe₂, OMe, and OCH₂CF₃ was studied. The N-silylphosphinimine precursors were prepared from the P-bromophosphinimines (eq 6). Although

the NMe₂ and OMe derivatives were remarkably thermally stable, the OCH₂CF₃ substituted phosphinimine readily eliminated Me₃SiOCH₂CF₃ to give quantitative yields of poly(dimethylphosphazene) (eq 7). Polymerization occurs on heating at 175 to 190°C in a sealed glass

Accession for	☒ ☐ ☐
PLS CHAI	
PLC T.B	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist Special	
A

$$\bar{M}_w = 50,000$$

$$T_g = 42^\circ\text{C}, T_m = 158^\circ\text{C}$$

ampoule or in a stainless bomb, or in refluxing benzene, or under neat reflux. The phosphinimine also decomposes slowly on standing at room temperature for extended periods of time.

The process was extended to prepare a number of new alkyl and/or aryl substituted polymers (eq 8). In general, higher temperatures

were required to facilitate polymer formation. Some of the physical properties that have been determined by AMMRC for $[\text{Ph}(\text{Me})\text{PN}]_n$ are $T_g = 37^\circ\text{C}$, $[\eta] = 0.396 \text{ dl/g}$, $M_n = 53,900 \pm 1700 \text{ g/mole}$. Data for $[\text{Ph}(\text{Et})\text{PN}]_n$ have not been received and no data is available for $(\text{Et}_2\text{PN})_n$ due to its insolubility. Thermolysis of $\text{Ph}_2\text{P}(\text{OCH}_2\text{CF}_3)_2=\text{NSiMe}_3$ at 225° for 10 days resulted in only trace amounts of polymer as well as cyclic trimer and tetramer and undecomposed starting material.

Copolymerization of mixtures of differently substituted phosphinimines was also investigated. Heating of equimolar amounts of $\text{Ph}(\text{Et})\text{P}(\text{OCH}_2\text{CF}_3)_2=\text{NSiMe}_3$ and $\text{Et}_2\text{P}(\text{OCH}_2\text{CF}_3)_2=\text{NSiMe}_3$ or $\text{Ph}(\text{Me})\text{P}(\text{OCH}_2\text{CF}_3)_2=\text{NSiMe}_3$ and $\text{Me}_2\text{P}(\text{OCH}_2\text{CF}_3)_2=\text{NSiMe}_3$ proceeded smoothly to give two new polymeric materials. Complete characterization of these compounds is in progress.

Publications

- 1) J.C. Wilburn and R.H. Neilson, "Synthesis of (Silylmethyl)-phosphinimines via Silyl Migration from Nitrogen to Carbon" Inorg. Chem., 18, 347 (1979).
- 2) R.H. Neilson and W.A. Kusterbeck, "Synthesis of Silicon-Nitrogen-Phosphorus Halides Stabilized by the tert-Butyl-dimethylsilyl Group," J. Organometal. Chem., 166, 309 (1979).
- 3) J.C. Wilburn, P. Wisian-Neilson, and R.H. Neilson, "Synthesis and Structural Isomerism of Some Silylaminophosphinimines," Inorg. Chem., 18, 1429 (1979)
- 4) R.H. Neilson and D.W. Goebel, "Novel Reactions of Silylamino-phosphines with Ketones," J. Chem. Soc. Chem. Commun., 769 (1979).
- 5) R.H. Neilson, P. Wisian-Neilson, and J.C. Wilburn, "Synthesis and Structural Isomerism of Some (Silylamino)phosphine Oxides," Inorg. Chem., 19, 413 (1980).
- 6) P. Wisian-Neilson and R.H. Neilson, "Poly(dimethylphosphazene), $(\text{Me}_2\text{PN})_n$," J. Am. Chem. Soc., 102, 2848 (1980).
- 7) P. Wisian-Neilson and R.H. Neilson, "Synthesis of New N-Silylphosphinimines: Phosphazene Precursors," Inorg. Chem., 19, 1975 (1980).
- 8) R.H. Neilson and P. Wisian-Neilson, "Synthesis of Poly(dialkylphosphazenes) from N-Silylphosphinimines," J. Macromol. Sci., Chem., A16, 425 (1981).
- 9) R.H. Neilson and P. Wisian-Neilson, "Polyphosphazene Compounds and Method of Preparation," U.S. Patent Application, Ser. No. 232,518, February 9, 1981.