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Dioxaheteroatom Cyclics as Initiators for Radical Polymerization

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Summary: An attractive way to incorporate flame-retarding moieties into oligomers or polymers is to use strained heterocyclic compounds which contain a thermally-labile carbon-carbon bond which will undergo thermolysis at modest temperature to generate a diradical capable of initiating vinyl polymerization. Suitably substituted, they may contain either bromine or phosphorus-containing moieties, or both. The diol precursors to these heterocycles are generally available from reductive coupling of the corresponding ketones. Conversion of the diols to the heterocycles can be accomplished using standard reagents. Phospholanes generated in this way tend to be quite thermally unstable and often degrade within hours to generate a variety of products. On the other hand, siloles derived from appropriate diols display much greater thermal stability. They can be isolated as crystalline solids and may be used to initiate polymerization at 100-200 °C. Incorporation of heterocycle-derived units into the mainchain can impart polymer flame retardancy directly. Alternately, oligomers may be generated for use as flame retardant additives for polymeric materials.

Keywords: dual functional flame retardants; halogenated siloles; heterocyclic flame retardants; reductive ketone coupling; thermal rearrangement

Introduction

For most applications, polymeric materials must be flame retarded. This may be accomplished in a number of ways depending on the intended end use of the polymer.[1] In the US, organohalogen compounds, principally brominated aromatics, are widely used.[2] These compounds, particularly, decabromodiphenyl ether, are readily available at modest cost and highly effective as flame retardants. However, increasing concern about bioaccumulation of these materials in the environment and potential negative health impacts has spurred increasing effort directed toward finding suitable alternatives. Organophosphorus compounds may act as effective flame retardants and offer the greatest potential to serve as replacements for organohalogen compounds in many applications.[3–5] In particular, new organophosphorus compounds have been developed to replace tetrabromobisphenol A for flame reatarding epoxy resins.[6,7] In this instance, strained five-membered dioxaheterocyclic compounds have been utilized as vehicles by which flame-retarding moieties may be incorporated into vinyl polymers. One of these, 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane, undergoes smooth thermal rearrangement to a new compound presumed to be the corresponding linear polymer.

Experimental Part

General

In general, reactions were carried out in a dry (all glassware was dried in a oven

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overnight at 120° C and allowed to cool under a stream of dry nitrogen prior to use) three-necked, round-bottomed flask fitted with a Liebig condenser bearing a gas-inlet tube, a magnetic stirring bar (or Trubore stirrer), and a pressure-equalizing dropping funnel (or syringe port). Chromatography was accomplished using SilaFlash P60 (230-400 mesh silica; Silicycle) in a column of appropriate size and hexane/ethyl acetate as eluant. Silica-coated Mylar plates (ThermoFisher Scientific) were used for thin layer chromatography (TLC). Melting points were determined by differential scanning calorimetry (DSC) using TA Instruments 2910 MDSC. All samples were analyzed at a heating rate of 5 °C/min in a constant nitrogen purge of 50 ml/min. Thermal decomposition temperatures were obtained using a TA Instruments 2950 Hi-Res TGA instrument interfaced with the Thermal Analyst 2100 control unit. Most generally, a heating rate of 5 °C/min was used. TA Thermal Advantage software was used for data analysis. Samples (5-10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 ml/min during analysis. Nuclear magnetic resonance (NMR) spectra were obtained using a 10% to 25% solution in deuterochloroform or dimethyl sulfoxide-d_6 and a Varian Mercury 300 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.00$). Phosphorus chemical shifts are in δ with respect to 85% aqueous phosphoric acid solution as external reference ($\delta = 0.00$). Infrared (IR) spectra were obtained using thin films between sodium chloride plates or solid solutions (1%) in anhydrous potassium bromide (as discs) and a Nicolet MAGNA-IR 560 spectrometer. Absorptions were recorded in wave numbers (cm^{-1}), and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), and medium (m), strong (s), and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Hewlett-Packard 5890A gas chromatograph/mass spectrometer (MSD) with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90-200 °C).

Materials

Common solvents and reagents were obtained from ThermoFisher Scientific or the Aldrich Chemical Company. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use; methylene chloride from calcium hydride. Chlorodiphenylphosphine (diphenylphosphinous chloride), 1,3,5-tribromobenzene, butyllithium in hexane, ethyl formate, pyridinium chlorochromate, zinc powder and triethylamine were obtained from the Aldrich Chemical Company and used as received. Diphenylchlorosilane was obtained from Gelest, Inc.

Synthesis

1,1,2,2-Tetraphenyl-1,2-ethanediol

A solution of 120 g (0.66 mol) of benzophenone in 1000 ml of isopropanol containing a few drops of glacial acetic acid was placed in a closed round-bottomed flask and allowed to stand in direct sunlight for seven days. During this period, long white needles crystallized from the solution. The mixture was cooled to 0 °C and the solid was collected by filtration at reduced pressure to afford nearly pure diol.

Di(3,5-dibromophenyl)methanol

To a cold (–78 °C), stirred solution of 28.0 g (0.09 mol) of 1,3,5-tribromobenzene in 400 mL of anhydrous ether was added, dropwise over a period of 0.5 h, 36 mL (0.09 mol) of a 2.5 M solution of butyllithium in hexane. The resulting solution was allowed to stir at –78 °C for two hours. A solution of 3.60 mL (0.045 mol) of ethyl formate in 50 mL of anhydrous ether was then added dropwise over a period of one hour [16]. The stirred mixture was allowed to warm slowly to room temperature (overnight). Water (100 mL) was added dropwise over a period of 0.5 h. The layers were separated and the aqueous layer was extracted with three 50-mL portions of ether. The ether layers were combined and washed with two 50-mL portions of saturated aqueous sodium chloride solution. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford 18.7 g (83.1% yield) of crude alcohol as brown crystals. Recrystallization from hexane provided the alcohol as white needles.

Di(3,5-dibromophenyl)methanone

To a stirred suspension of 30.3 g (0.14 mol) of pyridinium chlorochromate in 200 mL of dichloromethane was added a solution of 26.2 g (0.05 mol) of di(3,5-dibromophenyl)-methanol in 100 mL of dichloromethane [12]. The resulting mixture was stirred 1.5 hours at room temperature. Ether, 200 mL, was added and the mixture was filtered through a short column of alumina. Solvent was removed from the filtrate by rotary evaporation at reduced pressure to provide 23.6 g (94.8% yield) of the crude ketone as pale yellow crystals.

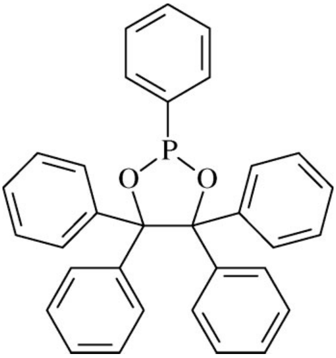
1,1,2,2-Tetra(3,5-dibromophenyl)ethane-1,2-diol

To a solution of 20.0 g (0.04 mol) of di(3,5-dibromophenyl)methanone in 200 mL of THF was added 120 mL of saturated aqueous ammonium chloride solution. Zinc powder 5.23 g (0.08 mol) was added portionwise to the stirred mixture [18]. Within a few minutes an exothermic reaction ensued. The mixture was stirred for one hour at room temperature. The mixture was diluted with 100 mL of ether and filtered through Celite. The layers were separated and the aqueous layer was extracted with three 30 mL-portions of diethyl ether. The ether layers were combined and washed successively with two 50-mL portions of saturated aqueous sodium chloride solution. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford a yellow solid. Recrystallization of the solid from ethanol provided 12.31 g (61.6% yield) of the diol as white needles.

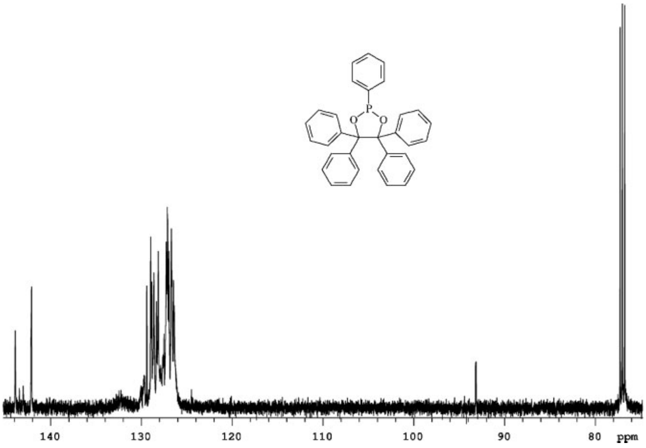
Results and Discussion

The preparation of a five-membered heterocycle containing flame retarding properties was based on a suitable 1,2-diol as a precursor. In initial work phosphorus reagents were utilized in an attempt to form phospholanes. This was done for several reasons. First, the necessary diol is generally available from reductive coupling of ketones. Further there was precedent for the generation of cyclic phosphorus compounds from fully functionalized 1,2-diols.[8,9] This is illustrated in Scheme 1 below. Similar compounds had been prepared from less highly functionalized 1,2-diols.[10,11]

It is possible to prepare such a compound (structure below) from benzopinacol and dichloro(phenyl)phosphine. Although this compound has limited stability, it (or the linear polymer analog) could be utilized to initiate styrene polymerization to produce a polymer containing phosphorus in the mainchain.[12,13]



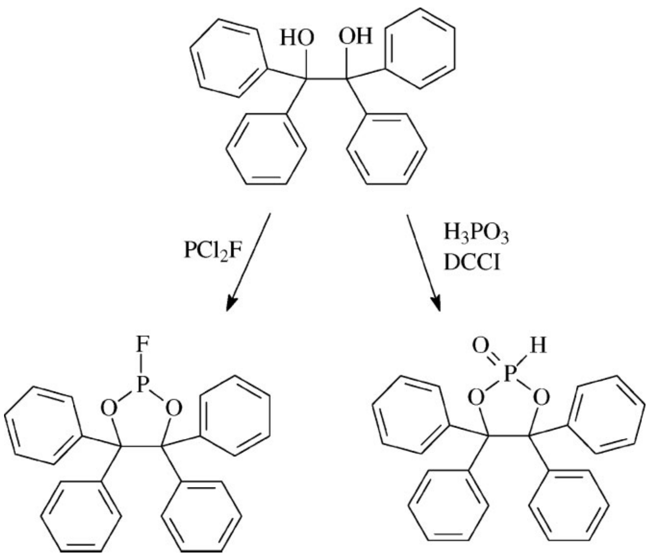
The apparent thermal transformation of this compound to the corresponding linear polymer may be conventially monitored by using carbon-13 NMR spectroscopy. The absorption corresponding to the benzylic carbon atom of the phosphate appears at δ 93˙1; that for the corresponding absorption for the rearanged structure at δ 97.8.



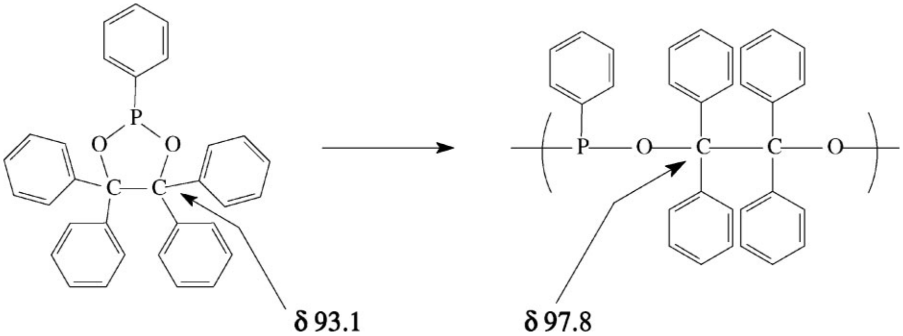
The intensity of the peak at δ 93.1 decreases as a function of time while that attributed to the linear polymer, δ 97.8, increases. The conversion is depicted below. The corresponding compound fully oxidized at phosphorus, i.e., 2-oxo-2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane, is even less stable.

Because of the fragility of the cyclic phosphorus compounds the corresponding silicon heterocycles have been considered as compounds suitable for incorporating a flame-retarding moiety into vinyl polymers. This, of course, requires that the phenyl groups of the heterocycle be suitably substituted with either halogen or phosphorus-containing functionality. In this case, the substituents are bromine atoms. As a model for the desired transformation, the conversion of the unsubstituted benzopinacol to the corresponding diphenylsilole was examined.[14,15] This may be conveniently accomplished by treating the diol with diphenylchlorosilane.

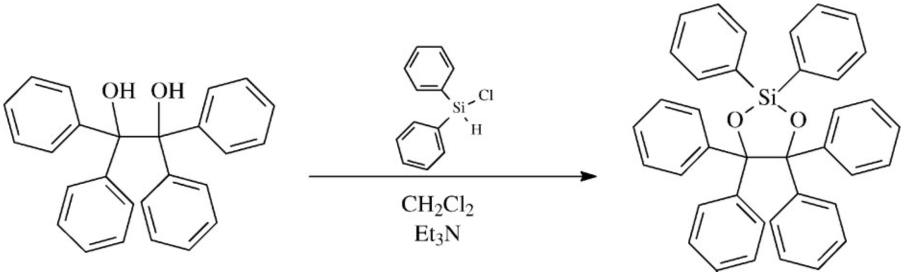
This material is a white solid, mp 61 °C (DSC). Interestingly, the carbon-13 NMR



Scheme 1.
Formation of phosphorus heterocycles from fully-functionalized 1,2-ethanediols.



Scheme 2.
Thermal conversion of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane to the corresponding polymer.



Scheme 3.
Preparation of 2,2,4,4,5,5-hexaphenyl-1,3-dioxa-2-silole.

spectrum of this compound suggests that the two phenyl groups at silicon are not equivalent.

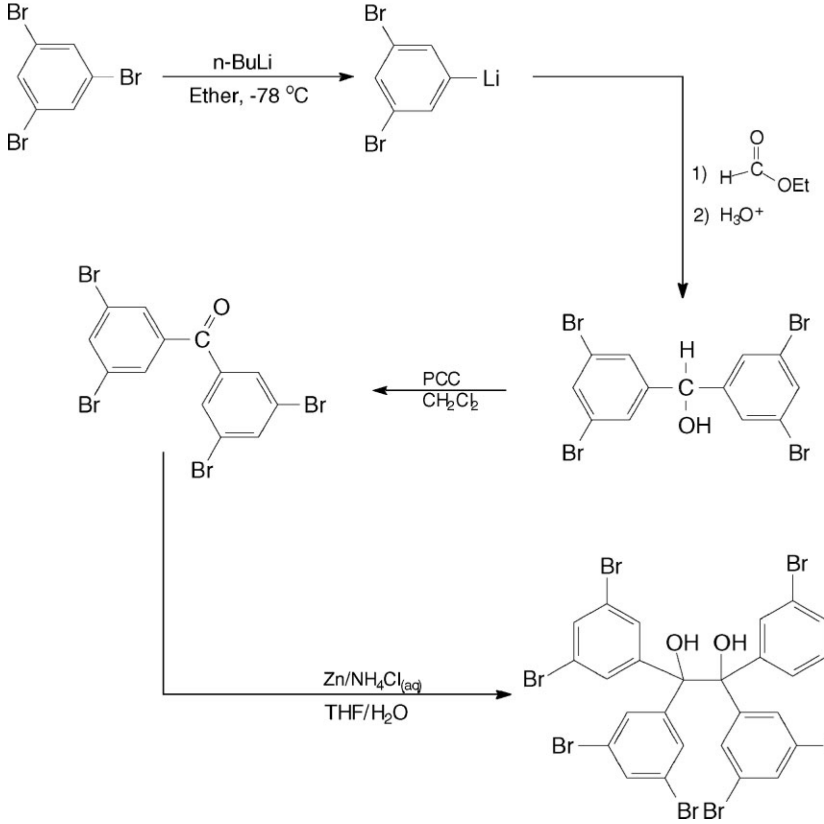
The non-equivalency of the two phenyl groups attached to silicon in this compound is an interesting observation and suggests that the silole exists in a fixed conformation in which one phenyl group is directed toward the interior of the molecule and the other away. The generality of this conformational rigidity for heterocycles of this type has yet to be established.

The methodology developed for the synthesis of this compound should be applicable to the generation of a highly brominated analog. This requires the preparation of the appropriately substituted benzopinacol. This was accomplished from 1,3,5-tribromobenzene as starting material. Lithium-halogen exchange generated 3,5-dibromophenyllithium which could be condensed with ethyl formate to form di(3,5-dibromophenyl)methanol.[16] Mild oxidation of the alcohol generated the ketone, di(3,5-dibromophenyl)methanone.[17] Zinc promoted reductive coupling of the ketone provided the diol.[18] This compound was obtained as a white solid, mp 167 °C (DSC) which could be fully characterized spectroscopically.

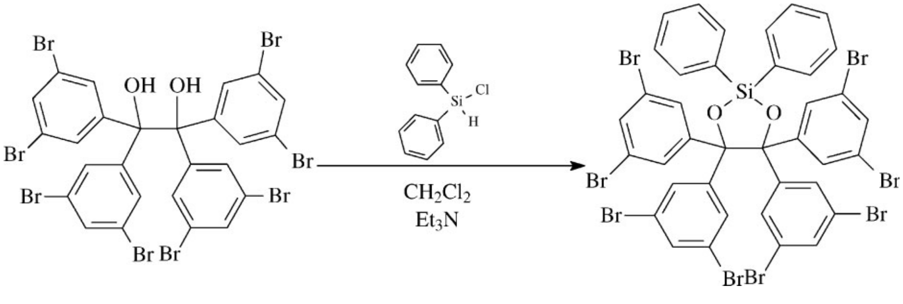
The infrared spectrum (Figure 3) contains strong hydroxyl absorption at 3556, 3379 cm^{-1} and aromatic absorption at 1579 cm^{-1}.

The proton NMR spectrum (Figure 4) of this material contains the expected absorption due to aromatic protons at δ 7.4 – 7.8.

The carbon-13 NMR spectrum (Figure 5) of this compound contains aromatic absorptions at δ 130.1 (*ortho* carbon atoms), 122.5 (*meta* carbon atoms attached to bromine), 133.8 (*para* carbon atom), and 145.8 (carbon atom attached to the benzylic carbon atom). The most diagnostic peak in the spectrum (and the one most useful for monitoring the con-



Scheme 4.
Synthesis of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol.



Scheme 5.
Preparation of 2,2-diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole.

version of diol to silole) is that at δ 82.0 corresponding to the benzylic carbon atoms in the diol structure. Conversion to the silole was accomplished by treating the diol with diphenylchlorosilane.

The silole was obtained as a white solid. The infrared spectrum shown in Figure 6 contains absorption for an aromatic nucleus at 1555 cm^{-1} and strong silicon-oxygen absorption at 1118, 910 and 740 cm^{-1}.

The carbon-13 NMR spectrum of this compound (Figure 7) contains, in addition to the absorptions arising from the dibromophenyl groups, eight new absorptions

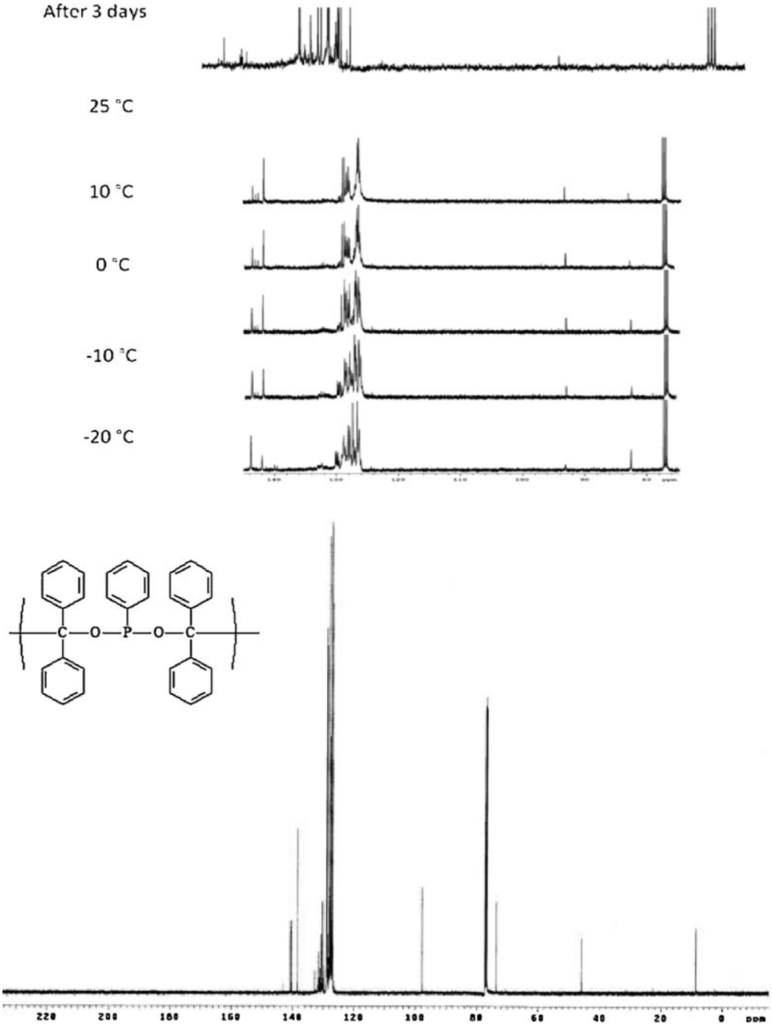


Figure 1.
Carbon-13 NMR spectral changes as 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane undergoes conversion to the corresponding rearranged structure.

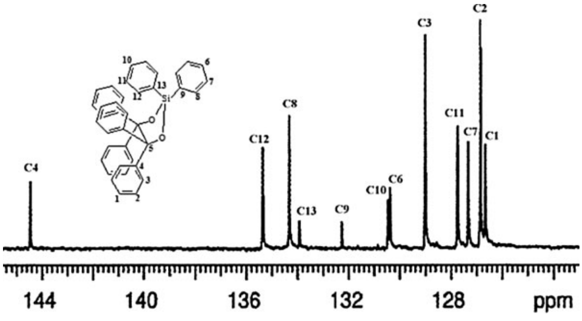


Figure 2.
Aromatic region of the carbon-13 NMR spectrum of 2,2,4,4,5,5-hexaphenyl-1,3-dioxa-2-silole.

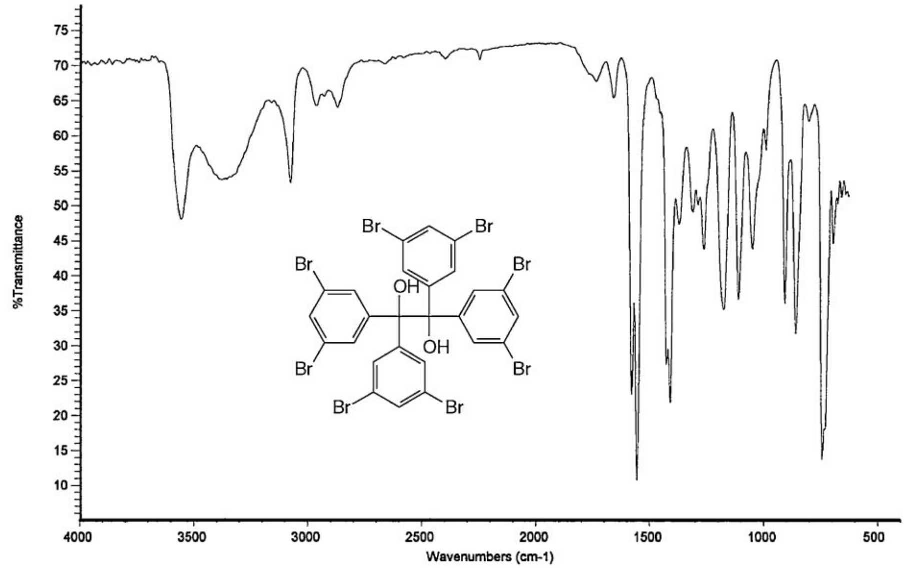


Figure 3.
Infrared spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol.

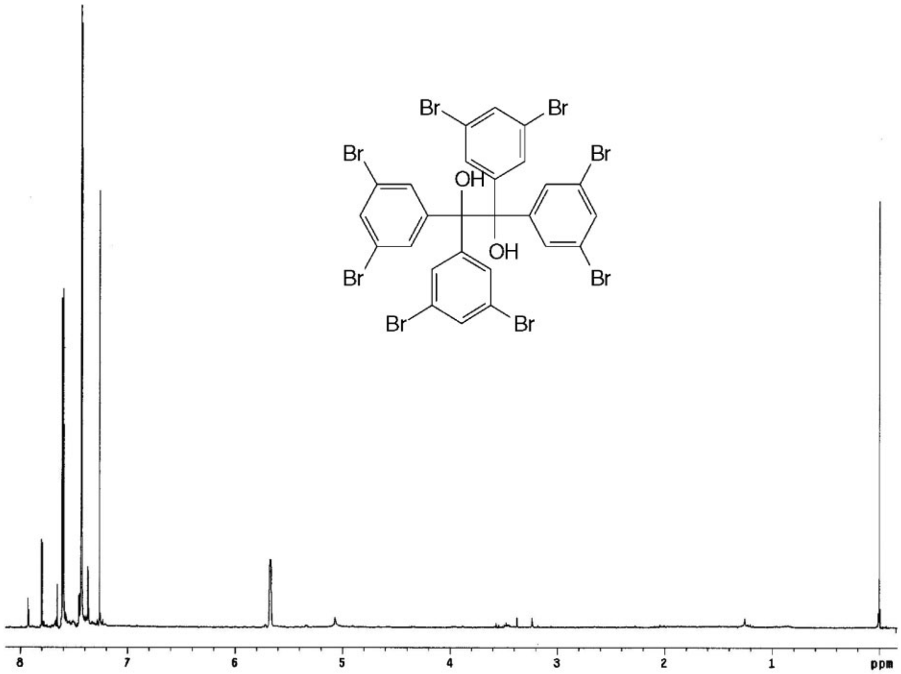


Figure 4.
Proton NMR spectrum of 1,1,2,2-Tetra(3,5-dibromophenyl)-1,2-ethanediol.

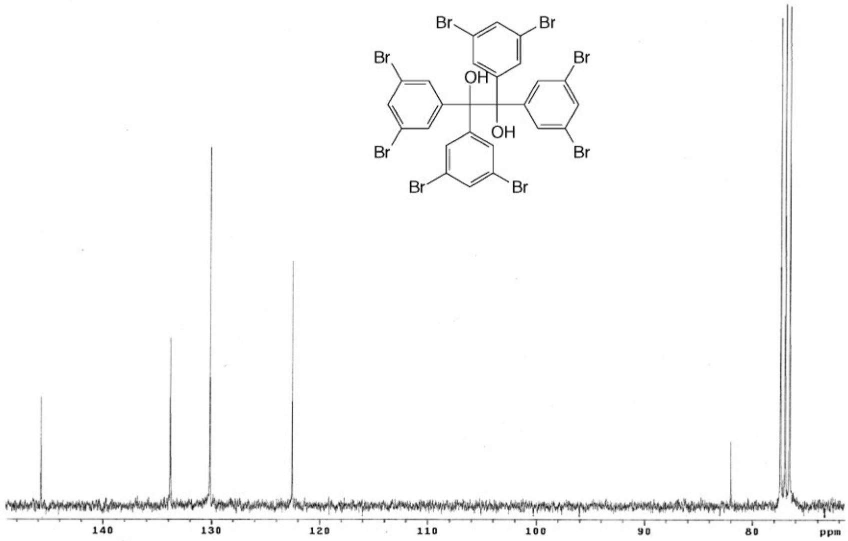


Figure 5.
Carbon-13 NMR spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol.

corresponding to nonequivalent phenyl groups at silicon. This is completely consistent with the structure of the corresponding model compound containing no bromine.

Conclusion

A number of five-membered dioxaheterocyclic (heteroatoms: P, Si, S) compounds have been prepared and characterized by

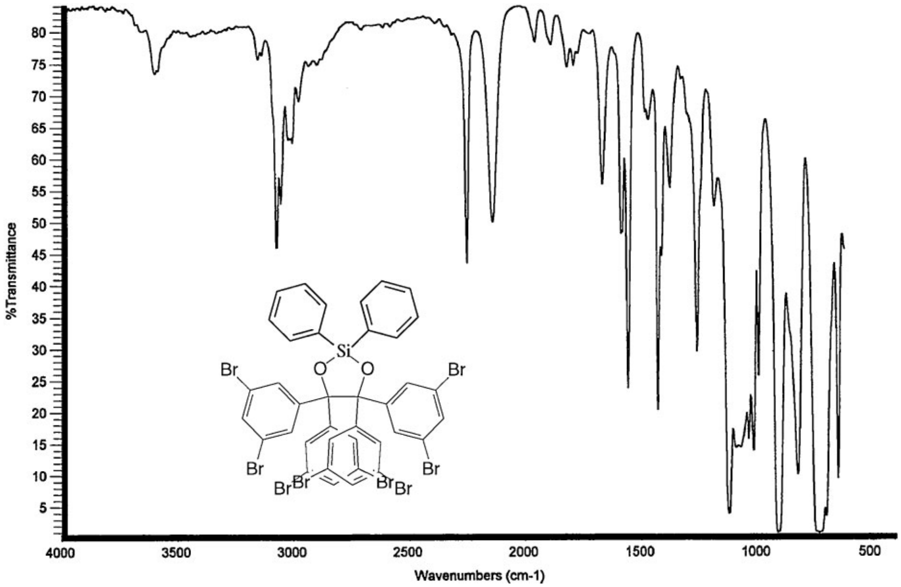


Figure 6.
Infrared spectrum of 2,2-diphenyl-4,4,5,5-tetra(3,5-dibroniophenyl)-1,3-dioxa-2-silole.

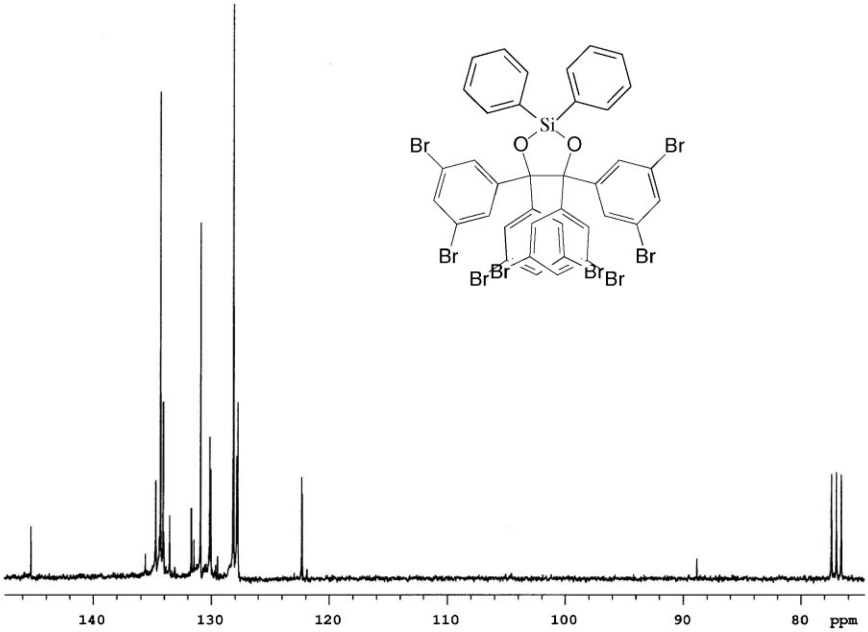


Figure 7.
Carbon-13 NMR spectrum of 2,2-diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole.

thermal and spectroscopic methods. The thermal decomposition of one of these, 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane, has been detailed using carbon-13 NMR spectroscopy. Five-membered siloles are considerably more thermally stable than the corresponding phospholanes. Those containing either halogen or phosphorus functionality offer potential for the development of oligomers for use as flame retardant additives.

[1] M. Lewin, "Physical and Chemical Mechanisms of the Flame Retarding of Polymers", in: M. LeBras, G. Camino, S. Bourbigot, R. Delobel, eds., *Fire Retardancy of Polymers- the Use of Intumescence*, The Royal Society of Chemistry, Cambridge, UK **1998**, p. 1–32.

[2] R. G. Gann, "Flame Retardants: Our View", vol. 10, *Kirk- Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., New York, NY **1993**, p. 930.

[3] E. D. Weil, "Phosphorus-based Flame Retardants" in: R. E. Engel, ed., *Handbook of Organophosphorus Chemistry*, Marcel Dekker, New York, NY **1992**.

[4] E. D. Weil, S. V. Levchik, M. Ravey, W. M. Zhu, *Phosphorus Sulfur Silicon Relat. Elem.*, **1999**, *146*, 17.

[5] S. Y. Lu, I. Hamerton, *Prog. Polym. Sci.*, **2002**, *27*, 1661.

[6] M. Ciesielski, A. Schafer, M. Doering, *Polym. Adv. Technol.*, **2008**, *19*, 507.

[7] R. M. Perez, J. K. W. Sandler, V. Altstadt, T. Hoffman, D. Pospiech, J. Artner, M. Ciecielski, M. Doering, A. J. Balabanovich, U. Knoll, U. Braun, B. Schartel, *J. Appl. Polym. Sci.*, **2007**, *105*, 2744.

[8] T. G. Meyer, A. Fischer, P. G. Jones, R. Schmutzler, *Nautrforsch.*, **2003**, *486*, 659.

[9] A. Munoz, C. Hubert, J. L. Luche, *J. Org. Chem.*, **1996**, *61*, 6015.

[10] R. Chauvin, *Tetrahedron Asymmetry*, **1990**, *1*, 737.

[11] B. Brodesser, M. Braun, *Phosphorus, Sulfur and Silicon*, **1998**, *44*, 217.

[12] B. A. Howell, J. Uzibor, *J. Therm. Anal. Cal.*, **2006**, *85*, 45.

[13] B. A. Howell, J. Uzibor, *J. Vinyl Addit. Technol.*, **2006**, *12*, 192.

[14] J. V. Crivello, J. L. Lee, D. A. Conlon, *Polym. Bull.*, **1986**, *16*, 95.

[15] Z. Feng, M. S. Thesis, Central Michigan University, Mt. Pleasant, MI 2008.

[16] A. Rajca, R. Padmakumar, D. J. Smithhisler, S. R. Desai, C. R. Ross, II J. J. Stezowski, *J. Org. Chem.*, **1994**, *59*, 7701.

[17] G. Piancatell, A. Scettri, M. D'Auria, *Synthesis*, **1982**, 245–258.

[18] R. Hekmatshoar, I. Yavari, Y. S. Beheshtiha, M. M. Heravi, *Monat. Chem.*, **2001**, *132*, 689.