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Thermal stability of 2,2-Diaryl/dialkyl-4,4,5,5-tetraaryl-1,3-dioxa-2-siloles

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Abstract Fully substituted 1,3-dioxa-2-siloles contain a strained carbon–carbon bond that will undergo thermolysis at modest temperatures to generate a diradical capable of initiating vinyl polymerization. If the substituents contain flame-retarding moieties, e.g., halogen or phophorus-containing groups, the use of such compounds as initiators serves to incorporate a flame-retarding unit into the polymer mainchain. Both 2,2-dialkyl- and 2,2-diaryl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-siloles may be prepared from the appropriate tetra(bromoaryl)-1,2-ethanediol and are obtained as white solids. Thermal decomposition (thermogravimetry) of these materials occurs in two stages. Initial decomposition is observed at about 250 °C and corresponds to the loss of nearly half of the initial sample mass.

Keywords Thermally-labile carbon–carbon bonds · Dioxaheterocycles · Polymerization initiators · Radical pair decomposition

Introduction

Halogenated compounds, particularly brominated aromatics, have long been used as cost effective, very effective gas-phase flame retardants for polymeric materials [1, 2]. Multiply brominated diphenyl ethers have been among the most widely used of the compounds in this class. Although these compounds are highly effective as flame retardants, they tend to bioaccumulate when released into the environment [3]. Because of concern about potential health risks that might be associated with these compounds their use has come under increasing regulatory pressure worldwide [4–21]. Two of these, pentabromo- and octabromodiphenyl ether, have been voluntarily withdrawn from the market. A third, decabromodiphenyl ether, was thought to offer lower health risks and its position in the market was maintained. However, this compound is persistent in the environment-oxidative degradation is difficult. Now the manufacturers of this compound have reached an agreement with the US Environmental Protection Agency to phase out its use [22, 23]. Because of the projected lack of availability of the brominated diphenyl ethers, there is intense interest in finding suitable replacements for them. A simple substitution is the use of 1,2-di(pentabromophenyl)ethane. However, more elaborate compounds based on bio-based renewable resources are being developed [24]. In another approach, the development of organohalogen flame retardants that are less mobile (lower likelihood for leakage into the environment), more effective, and with greater potential for biodegradation may be based on five-membered dioxaheterocyclic compounds containing a strained carbon–carbon bond which will undergo thermolysis at modest temperature to generate a diradical capable of initiating vinyl polymerization [25]. Properly substituted the heterocycle may contain either halogen or phosphorus or both or other flame-retarding moieties. Using the substituted heterocycle to initiate polymerization generates polymer chains containing, at least, one flame-retarding unit per chain. If the heterocylce also acts as a monomer, i.e., if it is reactive toward propagating radicals, several

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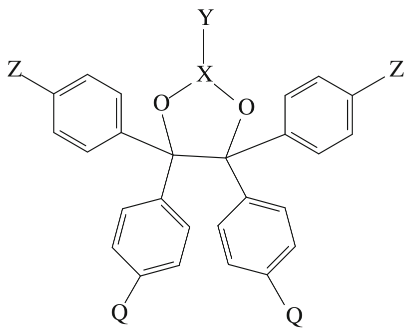


X = P, PO, S, Si, other

Y = oxygen, halogen, alkoxy, aryl, alkyl, other

Z = a phosphorus containing moiety

Q = Br, $-OCH_3$, $-\!(O-CH_2-CH_2)\!-$, other

Fig. 1 Strained dioxaheterocycle containing flame-retarding moieties

flame-retarding units may be incorporated per chain. A typical heterocycle is shown in Fig. 1 below.

Initiation of vinyl polymerization using compounds of this kind is illustrated in Scheme 1. The strained carbon–carbon bond undergoes thermolysis to form a diradical which initiates polymerization.

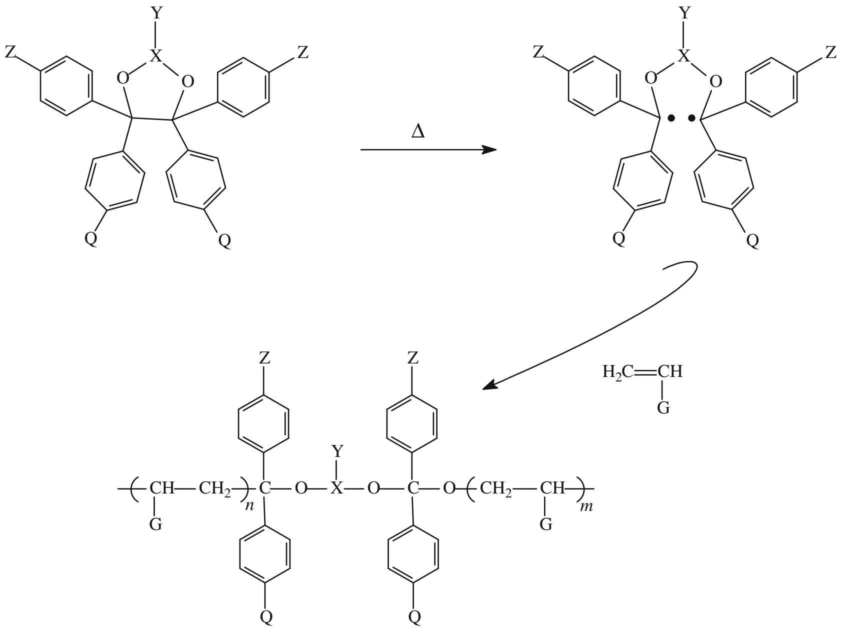
In general, these heterocycles may be prepared from the corresponding diols which are available from reductive coupling of the appropriate ketones (Scheme 2).

Experimental

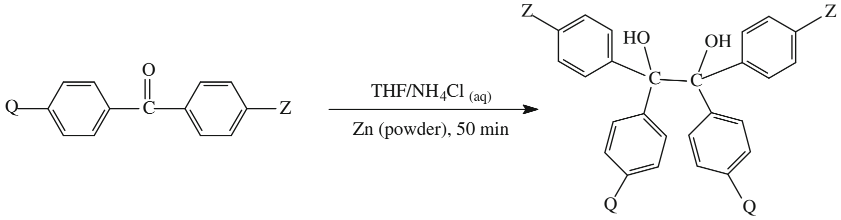
General

In general, reactions were carried out in a dry (all glassware was dried in an oven overnight at 120 °C and allowed to cool under a stream of dry nitrogen prior to use) three-necked, round-bottomed flask fitted with 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^{-1} in a constant nitrogen purge of 50 mL min^{-1}. Thermal-decomposition temperatures were obtained using a TA Instruments 2950 Hi-Res TG instrument interfaced with the Thermal Analyst 2100 control unit. Most generally, a heating rate of 5 °C min^{-1} 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^{-1} during analysis. Nuclear magnetic resonance (NMR) spectra were obtained using a 10–25% 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-

Scheme 1 Dioxaheterocycle initiation of vinyl polymerization



Scheme 2 Reductive coupling of a substituted phenone to generate a 1,2-diol



million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.00$). Phosphorus chemical shifts are in δ with respect to triphenyl phosphate as internal reference ($\delta = -18.0$). Infrared (IR) spectra were obtained using thin films between sodium chloride plates or solid solutions (1%) in anhydrous potassium bromide (as disks) 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 trietylamine were obtained from the Aldrich Chemical Company and used as received. Diphenylchlorosilane and dimethylchlorosilane were obtained from Celest, 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 7 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 2 h. 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 1 h [28]. 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, m.p. 180 °C (DSC), decomposition onset 274 °C (TG); ^{1}H NMR (δ, CDCl$_3$) 2.41 (broad, s, 1H, hydroxyl proton), 5.65 (s, 1H, benzylic proton), 7.43 (s, 4H), aromatic protons *ortho* to bromine, 7.62 (s, 2H), aromatic protons *ortho* to two bromine atoms; ^{13}C NMR (δ, CDCl$_3$) 73.8 (benzylic carbon atom), 123.4, 128.2, 133.8, 146.1; FTIR (cm^{-1}, NaCl) 3320 (m, broad), hydroxyl group, 3080 (w), C$_{sp2}$–H, 2930 (s), 2886 (m), 1595 (m) aromatic nucleus; mass spectrum, *m/z* (% of base), 502 (7.3), 500 (30.1), 498 (42.9), 496 (29.4), 494 (7.8), 265 (48.6), 263 (100), 261 (52.8), 237 (18.7), 235 (35.2), 233 (18.1), 156 (9.6), 155 (7.7), 154 (9.7), 153 (4.4), 151 (3.5), 75 (22.8), 74 (14.6).

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 [29]. The resulting mixture was stirred 1.5 h 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. Recrystallization from hexane afforded a white crystalline solid, m.p. 181 °C (DSC), degradation onset 248 °C (TG); ^{1}H NMR (δ, CDCl$_3$) 7.80 (s, 4H), aromatic protons *ortho* to bromine, 7.93 (s, 2H), aromatic protons *ortho* to two bromine atoms; ^{13}C NMR (δ, $CDCl_3$) 123.5, 131.3, 138.4, 139.3 190.9 (C=O); FTIR (cm^{-1}, NaCl) 3070 (w), C_{sp2}–H, 1662 (s), carbonyl group; mass spectrum, *m/z* (% of base), 504 (3.5), 502 (15.3), 500 (25.3), 498 (19.9), 496 (6.8), 265 (5.8), 263 (54.9), 261 (100), 237 (19.3), 236 (10.7), 235 (20.5), 233 (7.0), 185 (10.6), 183 (10.6), 158 (19.9), 157 (15.2), 156 (25.1), 155 (7.2), 77 (6.9), 76 (7.7), 75 (21.4), 74 (11.5).

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 [30]. Within a few minutes an exothermic reaction ensued. The mixture was stirred for 1 h 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, m.p. 167 °C (DSC), decomposition onset 248 °C (TG); ^{1}H NMR (δ, $CDCl_3$) 2.48 (broad s, 1H), hydroxyl proton 7.42, 7.61, aromatic protons; ^{13}C NMR (δ, $CDCl_3$) 82.0 (benzylic carbon atom), 123.3, 128.3, 133.8, 145.8.

2,2,4,4,5,5-Hexaphenyl-1,3-dioxa-2-silole

A mixture of 18.21 g (0.10 mol) of benzophenone, 1.22 g (0.05 mol) of magnesium turnings, 5.0 mL (0.03 mol) of hexamethylphosphoramide (HMPA), 4.2 mL (5.2 g, 0.02 mol) of diphenyldichlorosilane and 250 mL of anhydrous THF was stirred at room temperature [26]. After 5 min, an exothermic reaction ensued with the generation of a brown color. Within 1 h most of magnesium had been consumed and the color of the mixture had lightened to yellow. The mixture was allowed to stir overnight at room temperature. The mixture was filtered through a sintered glass filter to remove magnesium salts and the solvent was removed by rotary evaporation at reduced pressure to afford 15.5 g of crude product as a semisolid. This material was subjected to chromatography on silica gel with hexane/dichloromethane (95/5–75/25) followed by dichloromethane/ethyl acetate (90/10) as eluent. Fractions containing product (TLC) were combined and the solvent was removed by rotary evaporation at reduced pressure to provide 3.51 g (15.4% yield) of 2,2,4,4,5,5-hexaphenyl-1,3-dioxa-2-silole as a white solid: m.p. 61 °C (DSC) [lit. [25] 59.5–61 °C], decomposition 156 °C (TG); ^{1}H NMR (δ, $CDCl_3$) 6.89–7.95 (m, aromatic protons); ^{13}C NMR (δ, $CDCl_3$) 91.55 (benzylic carbon adjacent to oxygen), 126.66, 126.86, 129.01, 144.56 (carbon atoms of phenyl groups attached to silicon), 127.34/127.74, 130.38/130.47, 132.27/133.93, 134.32/135.36 (carbon atoms of remaining phenyl groups); FTIR (cm^{-1}, KBr) aromatic carbon-hydrogen stretching at 3070, 3054, and 2917 cm^{-1}, aromatic nucleus at 1591 cm^{-1} and silicon-oxygen stretching at 1125 and 699 cm^{-1}.

2,2-Dimethyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole

To a cold (near 0 °C) solution of 22.36 g (0.071 mol) of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol and 24.6 mL (0.178 mol) of triethylamine in 150 mL of methylene chloride was added, dropwise, over a period of 0.5 h a solution of 8.6 mL (0.071 mol) of dimethylchlorosilane in 10 mL of methylene chloride [26]. The resulting mixture was allowed to warm at room temperature and stirred for 5 h. Water (100 mL) was added dropwise. The large volume of triethylammonium chloride which had formed dissolved. The layers were separated. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford a white residual solid. Recrystallization of this material from ethanol provided the silole (39.6 g, 53.3% yield) as white needles, m.p. 149 °C (DSC); ^{1}H NMR (δ, $CDCl_3$) 0.21 (s, 6H, methyl protons), 7.42 (s, 4H, aromatic protons); ^{13}C NMR (δ, $CDCl_3$) 0.20 (carbon atoms attached to silicon), 87.5 (benzylic carbon atom), 123.3 (carbon atoms adjacent to bromine), 129.8 (*ortho* carbon atoms), 139.2 (*para* carbon atoms), 146.8 (substituted carbon atoms).

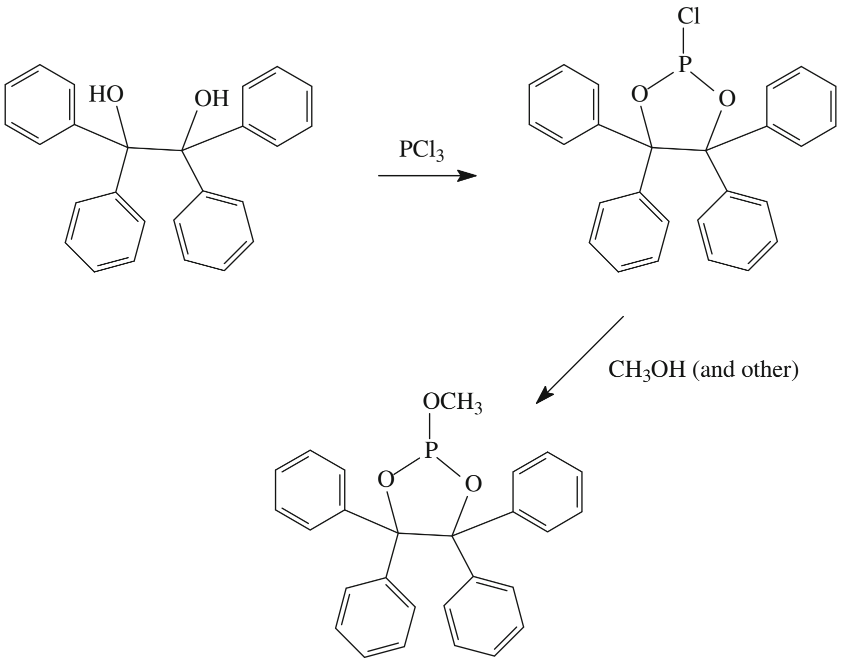
2,2-Diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole

To a stirred, cold (near 0 °C) solution of 2.69 g (2.71 mmol) of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol and 0.93 mL (6.80 mmol) of triethylamine was added, dropwise, over a period of 0.5 h 0.53 mL (2.71 mmol) of diphenylchlorosilane in 10 mL of methylene chloride [26]. The solution was allowed to warm and stirred 5 h at room temperature. Water (50 mL) was added dropwise. Triethylammonium chloride dissolved. The layers were separated. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford a residual solid. Recrystallization of this material provided the silole (2.91 g, 65.8% yield) as white needles; ^{13}C NMR (δ, $CDCl_3$) 95.9 (benzylic carbon atoms), 123.2 (carbon atoms adjacent to bromine), 127.3, 127.7, 129.9, 130.2, 130.4, 132.3, 133.8, 133.9, 134.2, 141.9 (carbon atoms adjacent to silicon), 146.2.

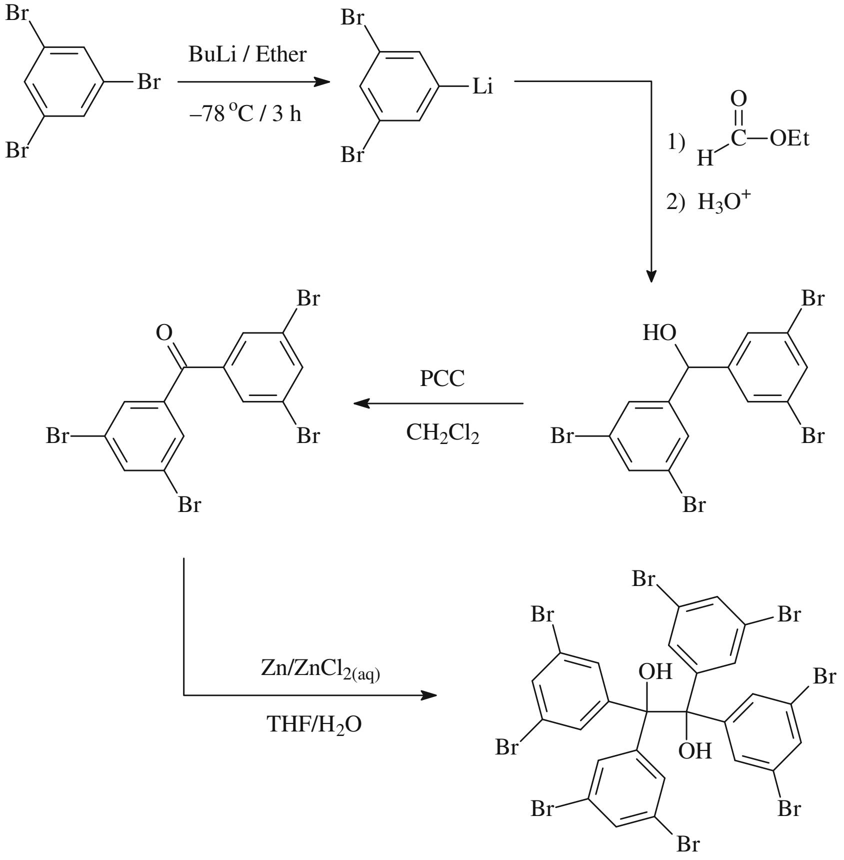
Results and discussion

Dioxaheterocyclic compounds may be utilized to introduce flame-retarding structures into oligomeric materials. These

Scheme 3 Generation of dioxaphosphorus heterocycles from a 1,2-diol



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



compounds contain a strained carbon–carbon bond which will undergo thermolysis to generate a diradical capable of initiating vinyl polymerization [25]. If the heterocycle contains substituents bearing flame-retarding moieties, the resulting oligomer/polymer contains, at least, one flame-retarding unit per chain. If the heterocycle also acts as a monomer, i.e., if it is reactive toward propagating radicals, the level of flame retardance introduced may be much greater. Several such heterocycles have been investigated as potential initiators/flame retardants for vinyl polymers. An initial focus has been phosphorus heterocycles. These may conveniently be prepared from a fully substituted 1,2-diol and a suitable phosphorus reagent. This is illustrated in Scheme 3.

The phosphorus heterocycle examined most thoroughly has been 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane. This compound has limited thermal stability and undergoes smooth rearrangement to another material, presumed to be the linear polymer [27]. Because of the limited stability of this phosphorus compound, the corresponding silicon heterocycles have been considered as compounds suitable for incorporating a flame-retarding unit into vinyl polymers. This, of course, requires that the phenyl groups of the heterocycle be suitably substituted with halogen functionality.

The preparation of the necessary halogenated benzopinacol 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 [28]. Mild oxidation of the alcohol generated the ketone, di(3,5-dibromophenyl)methanone [29]. Zinc promoted reductive coupling of the ketone provided the diol [30]. This

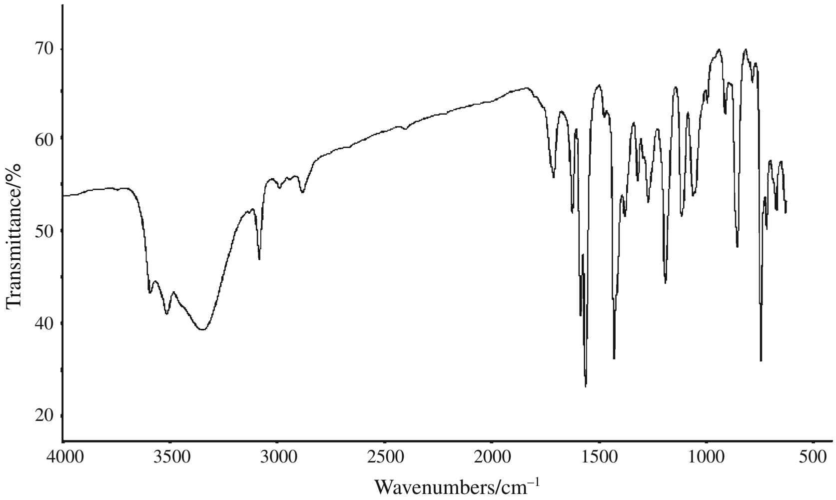


Fig. 2 Infrared spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol

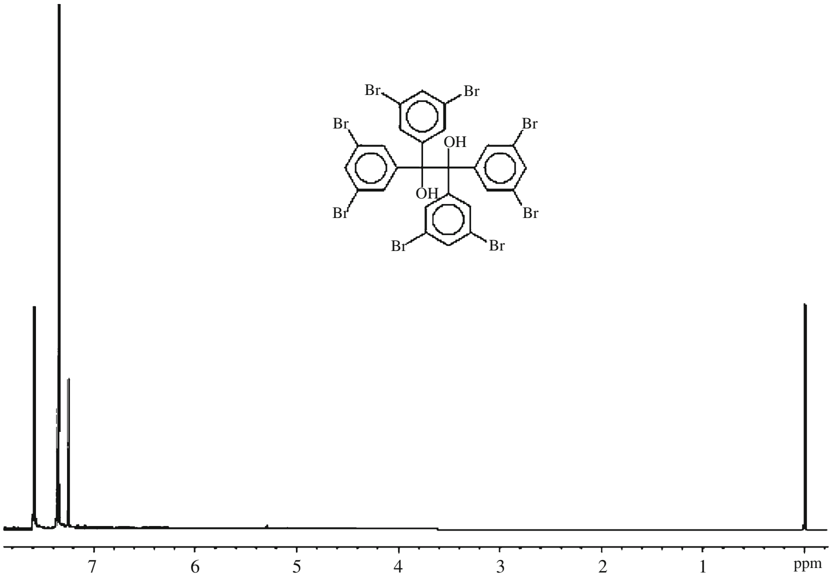


Fig. 3 Proton NMR spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol

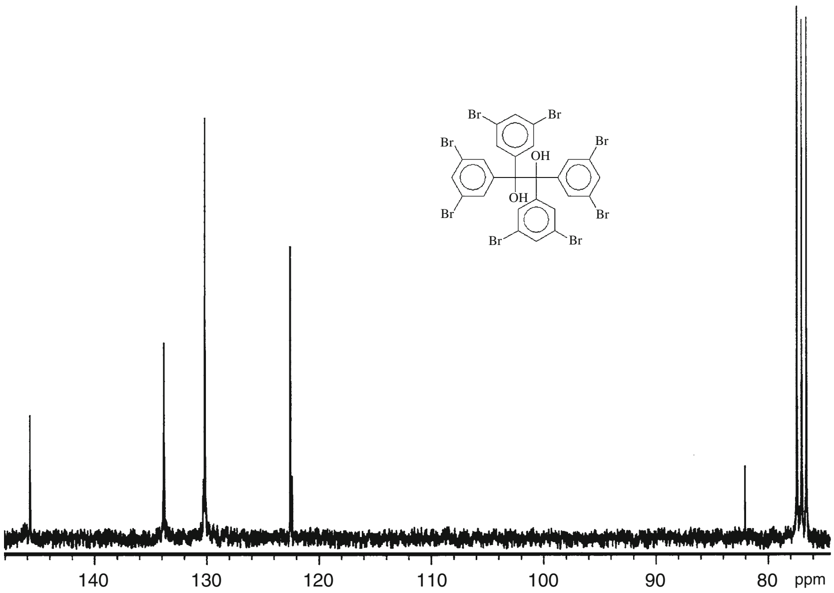
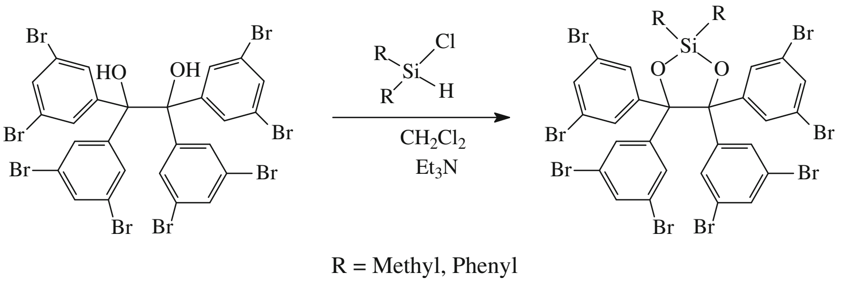


Fig. 4 Carbon-13 NMR spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol



Scheme 5 Conversion of a tetraaryl-1,2-ethandiol to the corresponding silole

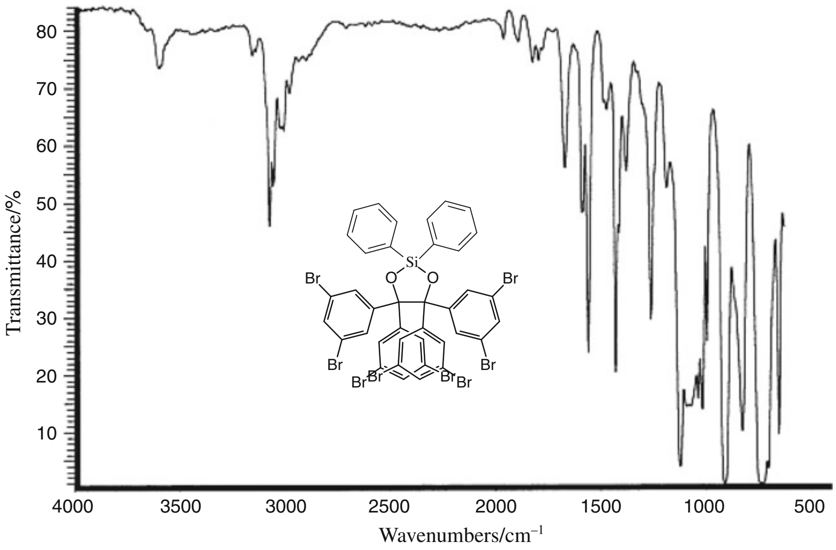


Fig. 5 Infrared spectrum of 2,2-diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole

compound was obtained as a white solid, m.p. 167 °C (DSC) which could be fully characterized spectroscopically (Scheme 4).

The infrared spectrum (Fig. 2) contains strong hydroxyl absorption at 3556, 3379 cm^{-1} and aromatic absorption at 1579 cm^{-1}.

The proton NMR spectrum (Fig. 3) of this material contains the expected absorption due to aromatic protons at δ 7.4–7.8.

The carbon-13 NMR spectrum (Figs. 4) 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 conversion 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 the appropriate chlorosilane (Scheme 5).

Both 2,2-dimethyl- and 2,2-diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole were obtained as white crystalline solids.

The infrared spectrum of the diphenyl compound shown in Fig. 5 contains absorbtion for an aromatic nucleus at 1555 cm^{-1} and strong silicon-oxygen absorbtions at 1118, 910, and 740 cm^{-1}.

The carbon-13 NMR spectrum of this compound (Fig. 6) contains, in addition to the absorptions arising from the dibromophenyl groups, eight new absorptions corresponding to the nonequivalent phenyl groups at silicon. This is completely consistent with the structure of the corresponding model compound containing no bromine [25].

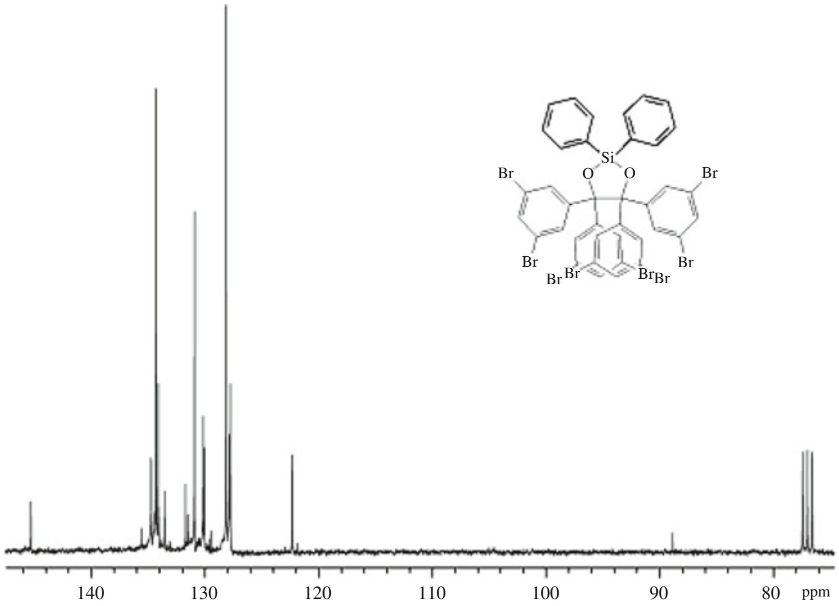


Fig. 6 Carbon-13 NMR spectrum of 2,2-Diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole

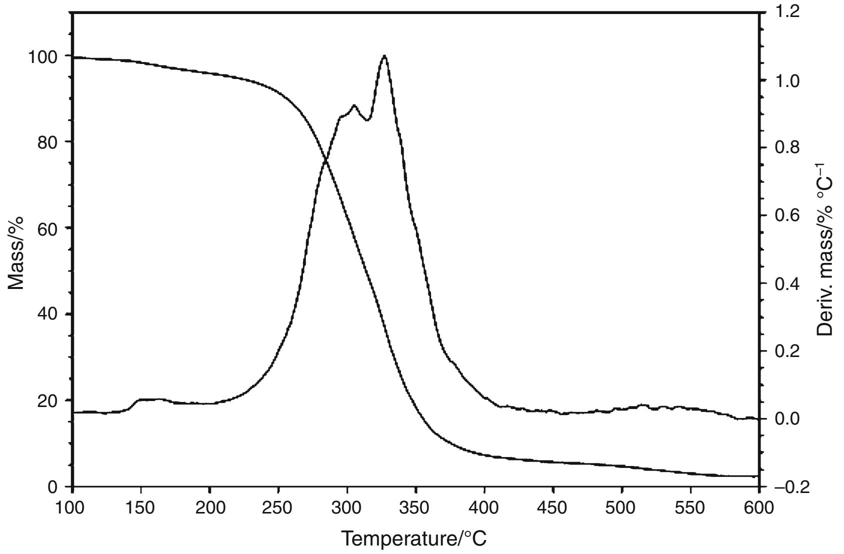


Fig. 7 Thermal decomposition of 2,2-dimethyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-silole

The dimethyl compound gives rise to similar spectra: ^{1}H NMR (δ) 0.21 (s, 6H, methyl protons), 7.42, 7.57 (aromatic protons); ^{13}C NMR (δ) 0.20 (carbon atoms attached to silicon), 87.5 (benzylic carbon atoms), 123.3 (carbon atoms adjacent to bromine), 129.8, 139.2, 146.8.

This compound undergoes a two-stage decomposition at 251 °C (Fig. 7). The initial loss corresponds to approximately half the initial sample mass. Thermolysis of the strained carbon–carbon bond followed by extrusion of the stable ketone, di(3,5-dibromophenyl)methanone, would correspond to a loss of 47.2% of the initial mass.

Conclusions

Both 2,2-dialkyl- or 2,2-diaryl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxa-2-siloles offer great potential for radical initiation of vinyl polymerization to introduce a flame-retarding unit into the polymer main chain. These compounds may be prepared from the appropriate tetra (bromoaryl)-1,2-ethanediol and the proper chlorosilane and are obtained as white crystalline solids. These compounds have been characterized by spectroscopic and thermal methods. Thermal decomposition (thermogravimetry) of these materials occurs in two stages. The initial decomposition (250 °C) corresponds to nearly half the initial mass and probably reflects the expulsion of di(3,5-dibromophenyl)methanone.

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