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4,4,5,5-Tetra(3,5-dibromophenyl)-2,2-diphenyl-1,3-dioxa-2-silole and related compounds as precursors to flame retardant oligomers

Bob A. Howell*, Young-Jun Cho

Center for Applications in Polymer Science, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859-0001, USA

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ABSTRACT

Certain strained five-membered heterocycles undergo thermally-induced, carbon–carbon bond homolysis to generate diradicals capable of initiating vinyl polymerization. These compounds usually contain two oxygen atoms and a larger heteroatom (silicon, phosphorus, sulfur) in addition to carbon. If the heterocycle is suitably substituted with halogen (particularly bromine) containing moities it may function as a vehicle to permit incorporation of flame-retarding units into a polymer or oligomer. When an appropriate heterocycle is used as an initiator for radical polymerization each polymer chain formed contains at least one flame-retarding unit. One such heterocycle is 4,4,5,5-tetra(3,5-dibromophenyl)-2,2-diphenyl-1,3-dioxa-2-silole. In instances in which the heterocycle also acts as a monomer, i.e., it is reactive toward chain-propagating radicals, additional flame-retarding activity may be incorporated into the polymer.

1. 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 are 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.

2. Experimental

2.1. General

In general, reactions were carried out in a dry (all glassware was dried in a 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 a 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 10–25% 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

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* Corresponding author. Tel.: +1 989 774 3582; fax: +1 989 774 3883.
E-mail addresses: bob.a.howell@cmich.edu (B.A. Howell), cho1y@cmich.edu (Y.-J. Cho).

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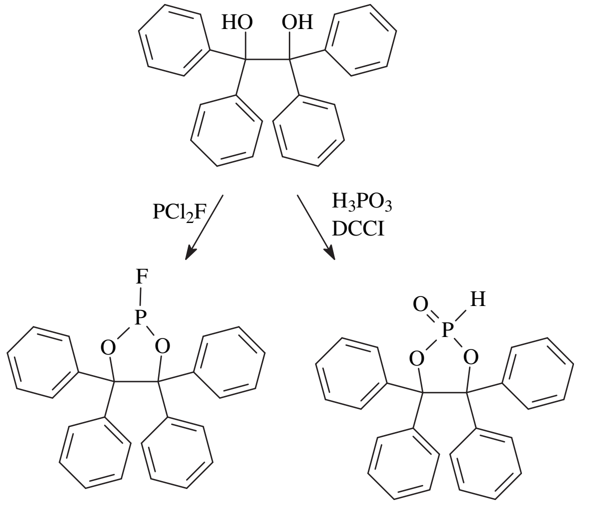


Scheme 1. Formation of Phosphorus Heterocycles from Fully-functionalized 1,2-Ethanediols.

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).

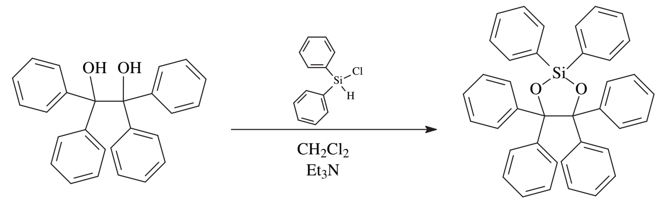
2.2. Materials

Common solvents and reagents were obtained from Thermo-Fisher 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 was obtained from Celest, Inc.

2.3. Synthesis

2.3.1. Synthesis of 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 in a closed round-bottomed flask was 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.



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

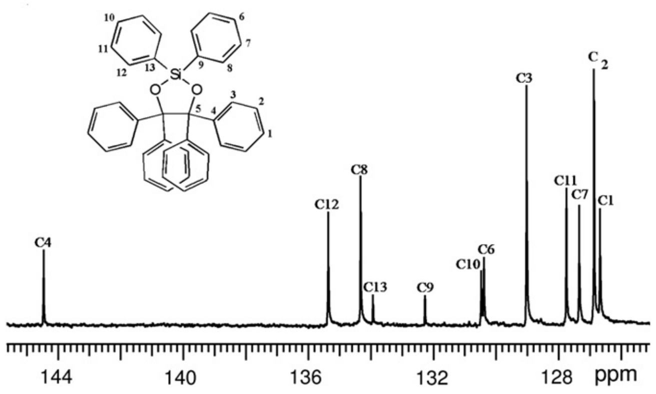
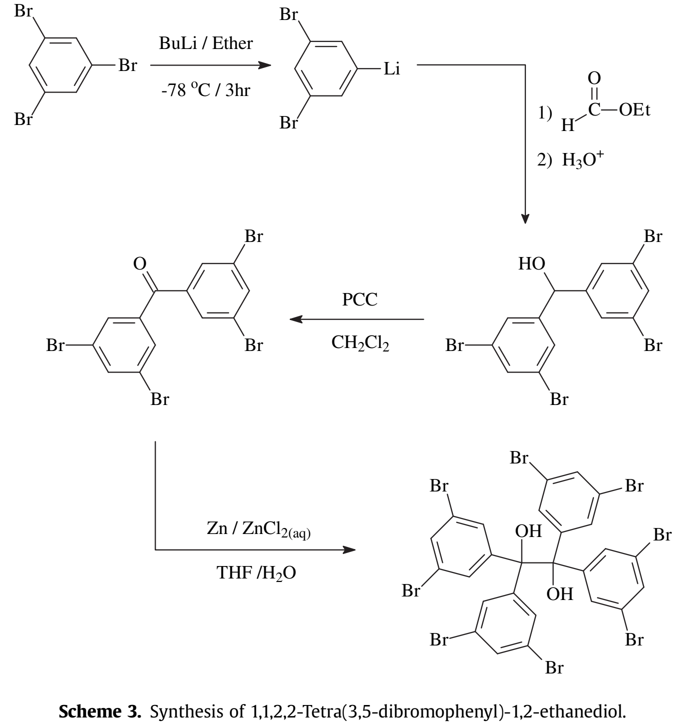


Fig. 1. Aromatic Region of the Carbon-13 NMR Spectrum of 2,2,4,4,5,5-Hexaphenyl-1,3-dioxa-2-silole.

2.3.2. Synthesis of 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 [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)



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