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Thermal decomposition of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

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Abstract Certain five-membered dioxaheterocyclic compounds (hetero atoms may be P, Si, S, etc.) contain a strained carbon–carbon bond which may undergo homolytic thermolysis at modest temperatures to generate a diradical capable of initiating vinyl polymerization. If substituents contain flame-retarding moieties this represents a convenient method for imparting flame retrdancy to a polymeric material. Of particular interest has been 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane. The thermal degradation of this compound has been studied using ^{13}C NMR spectroscopy. This may conveniently be done by monitoring the intensity of the signal for the benzylic carbon atom as a function of time and temperature. A simple transformation is the conversion of the cyclic compound to the linear polymer.

Keywords Phospholane stability · Radical initiators · Phosphorus flame retardants · Five-membered heterocycles

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-retarding 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, presumably, the linear polymer.

Experimental

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) was obtained from the Aldrich Chemical Company and used as-received. 1,1,2,2-Tetraphenyl-1,2-ethanediol (benzopinacol) was obtained by reductive coupling of benzophenone as previously described [8]. This is a white crystalline solid melting at 171 °C (Fig. 1). Spectral data for this compound are presented below (Figs. 2, 3, and 4).

The most useful spectral information for monitoring the formation of this compound and its transformation to phosphorus heterocycles is the absorption at δ 82.3 (benzylic carbon atom) in the carbon-13 NMR spectrum.

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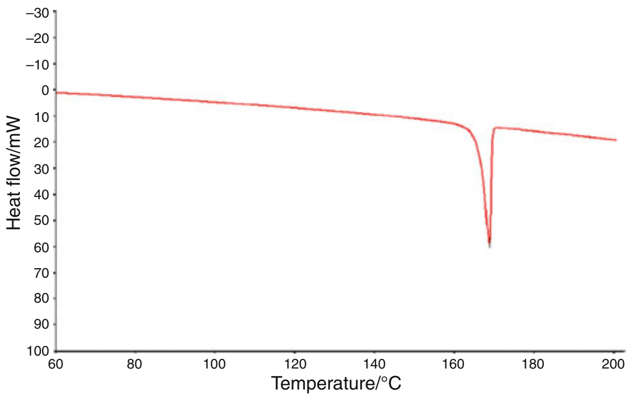


Fig. 1 DSC thermogram for 1,1,2,2-tetraphenyl-1,2-ethanediol (benzopinacol)

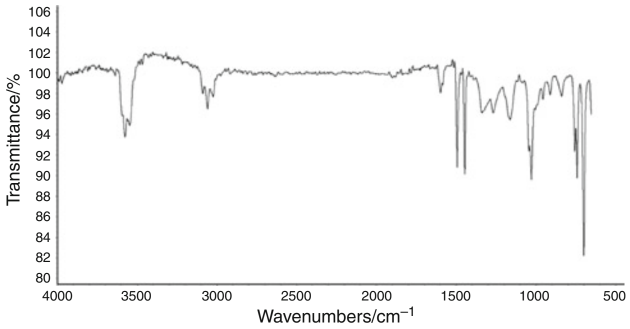


Fig. 2 IR spectrum for 1,1,2,2-tetraphenyl-1,2-ethanediol

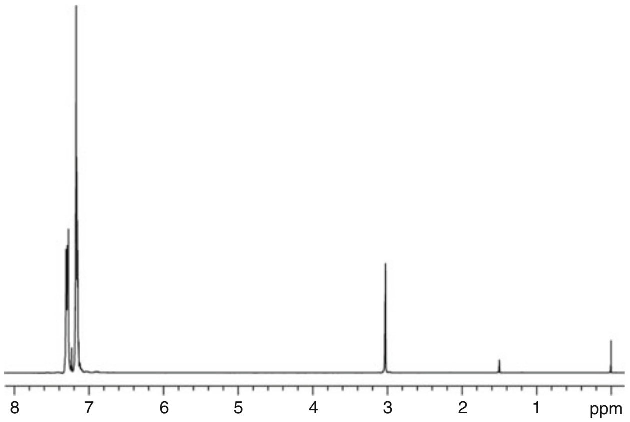


Fig. 3 Proton NMR spectrum for 1,1,2,2-tetraphenyl-1,2-ethanediol

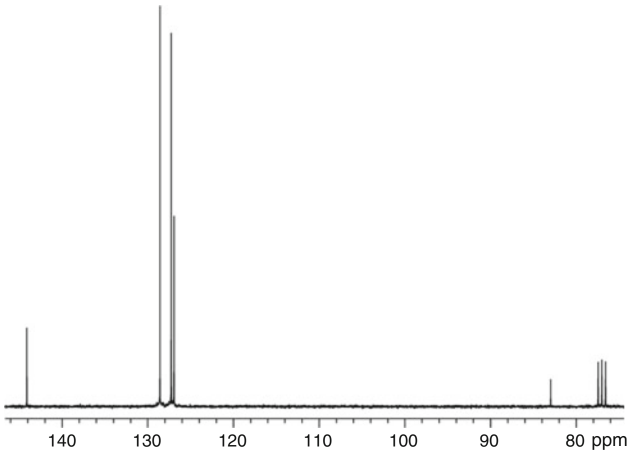


Fig. 4 ^{13}C NMR spectrum of 1,1,2,2-tetraphenyl-1,2-ethanediol

Instrumentation

Nuclear magnetic resonance (NMR) spectra were obtained using a 10–25% solution in deuterochloroform and a Varian Plus 300 MHz or Varian 500 MHz spectrometer. Proton and carbon chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane as internal reference ($\delta = 0$). Phosphorus chemical shifts are in δ with respect to triphenylphosphate as internal reference ($\delta = -18.0$). Melting points were determined by differential scanning calorimetry (DSC) using a TA Instruments 2910 MDSC at a heating rate of 5 °C min^{-1} in a constant nitrogen purge of 50 cm^3 min^{-1}. Thermal decomposition of the phospholane rearrangement product was examined by thermogravimetry using a TA Instruments 2950 Hi-Res TGA instrument interfaced with the Thermal Analyst 2100 control unit at a heating rate of 5 °C min^{-1}. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 cm^3 min^{-1} during analysis. 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 spectrophotometer.

Synthesis

2,4,4,5,5-Pentaphenyl-1,3,2-dioxaphospholane may be readily prepared by treating 1,1,2,2-tetraphenyl-1,2-ethanediol with (phenyl)dichlorophosphine in the presence of triethylamine. While it is difficult to isolate it in pure form, it has been characterized spectroscopically and it (or the linear polymer analog) has been utilized to initiate styrene polymerization to produce a polymer-containing phosphorus in the main chain [9, 10]. The conversion of the diol to the pospholane may be conveniently monitored using ^{13}C NMR spectroscopy. In a typical experiment, a solution of equimolar amounts of benzopinacol and dichloro(phenyl)phosphine (20 vol.%) in deuterochloroform was cooled to −20 °C. Triethylamine (two moles/mole of phosphine) was added, the mixture was mixed well, and a portion transferred to an NMR tube which was placed in the instrument cavity cooled to −20 °C. The sample was allowed to stand for 10 min for temperature equilibration and a spectrum was recorded. The temperature was increased to −10 °C, the sample allowed to stand for temperature equilibration, and a second spectrum was recorded. This procedure was repeated at 10° intervals until a temperature of 20 °C was reached. The spectra are displayed in Fig. 5. As may be seen, the initial mixture contains benzopinacol as noted by the absorption for the benzylic carbon atom at δ 82.3.

As the temperature is allowed to increase the absorption for the benzylic carbon atom of the diol (δ 82.3) diminishes in intensity while that for the phospholane (δ 92.7) increases in intensity as a function of time. The transformation to dioxaphospholane is also apparent in the corresponding phosphorus-31 spectra. As a function of time, the absorption for dichloro(phenyl)phosphine (δ −57.2) decreases in intensity and that for the dioxaphospholane (δ −40.6) increases. The ^{13}C NMR spectrum of the dioxaphospholane formed is shown in Fig. 6. The most noteworthy peak in the spectrum is the doublet ($J_{C\text{–}P} = 5\text{–}6$ Hz) at δ 92.7 corresponding to the benzylic carbon atoms of the compound. The phospholane is relatively stable in chloroform at low temperature.

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 [11, 12]. This is illustrated in Scheme 1. Similar compounds have been prepared from less highly functionalized 1,2-diols [13, 14].

The synthesis of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane is depicted in Scheme 2. As noted above, the preparation may be conveniently monitored using ^{13}C NMR spectroscopy.

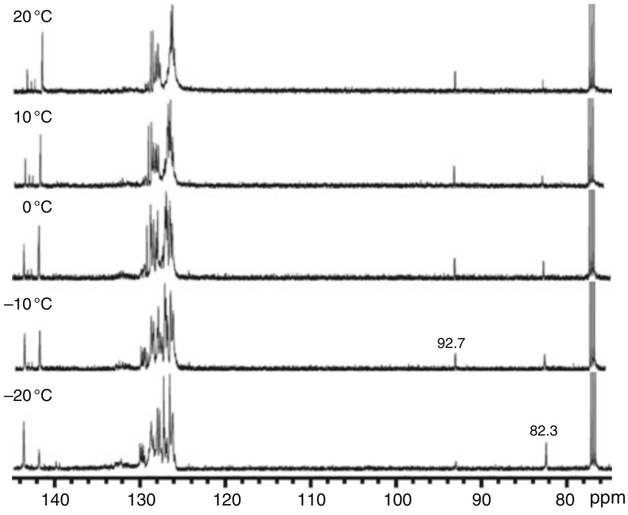


Fig. 5 ^{13}C NMR spectral changes which accompany the conversion of benzopinacol to the corresponding dioxaphospholane

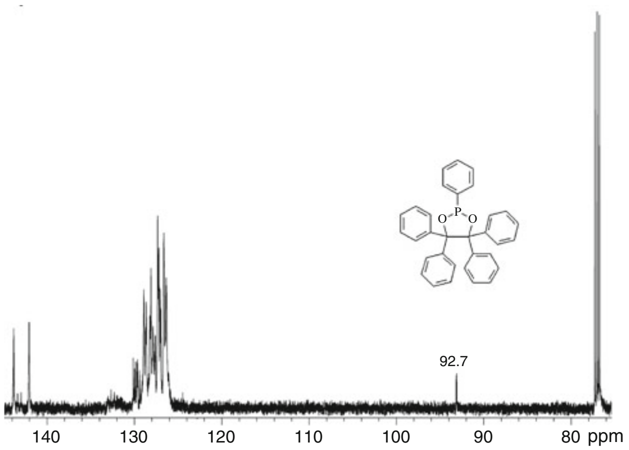
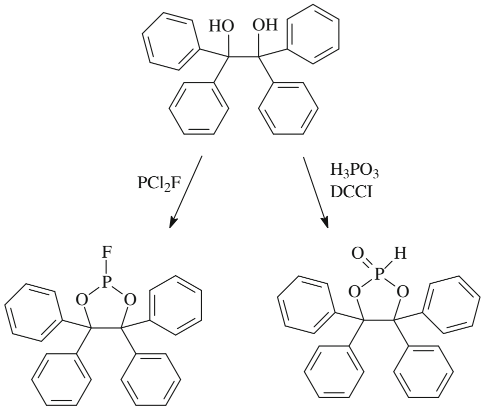
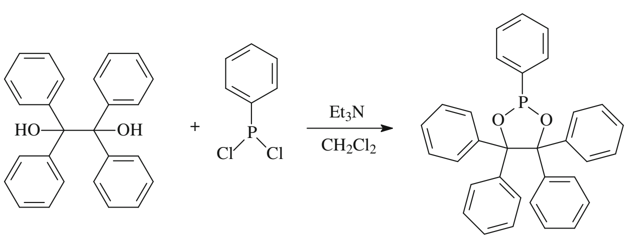


Fig. 6 ^{13}C NMR spectrum of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

The dioxaphospholane is relatively stable at low temperature but at room temperature and above it undergoes thermal degradation. This process may be conveniently monitored by either ^{13}C or ^{31}P NMR spectroscopy. As may be seen from the spectra collected in Fig. 7, the absorption for the benzylic carbon atoms of the dioxaphospholane (δ 92.7) decreases with time and increasing temperature while the intensity of a product peak at δ 97.8 increases. Ultimately, the transformation to the thermally rearranged



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



Scheme 2 Synthesis of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

product, presumably the linear polymer, is completed at 20 °C.

This is also apparent in the corresponding phosphorus-31 spectra. Absorption for the phosphorus atom of the dioxaphospholane (δ −40.6) decreases in intensity with time and temperature while that for the phosphorus atom of the product (δ 31.4) increases in intensity. The ^{13}C NMR spectrum for the thermal decomposition (rearrangement) of the dioxaphospholane is shown in Fig. 8. This spectrum contains a single absorption for benzylic carbon atoms at δ 97.8. Thus, the thermal degradation of the dioxaphospholane would seem to correspond to a clean rearrangement to a single new material which is depicted as the linear polymer.

The IR spectrum of this material (Fig. 9) contains P–O–C absorptions at 1159 and 1000 cm^{-1}.

This material is stable at room temperature and may be stored indefinitely. At higher temperature, it undergoes degradation (onset at 227 °C) in three steps. This may be readily observed using thermogravimetry. The thermogram is displayed in Fig. 10.

Conclusions

The cyclic heterocyclic compound, 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphopholane, has the potential to function as a radical initiator for vinyl polymerization. It may be prepared from a readily available diol precursor, 1,1,2,2-tetraphenyl-1,2-ethanediol. Its thermal stability may be conveniently monitored using ^{13}C or ^{31}P NMR

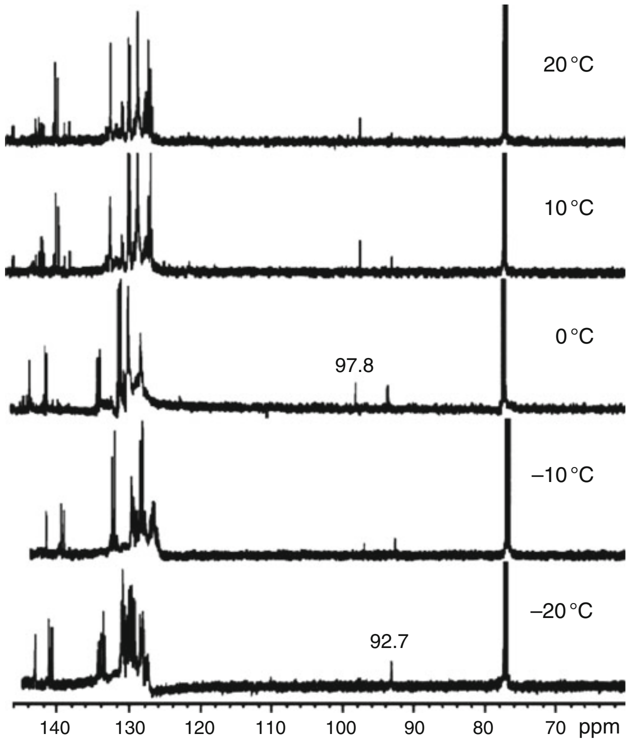


Fig. 7 ^{13}C NMR spectral changes as 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane undergoes thermal decomposition

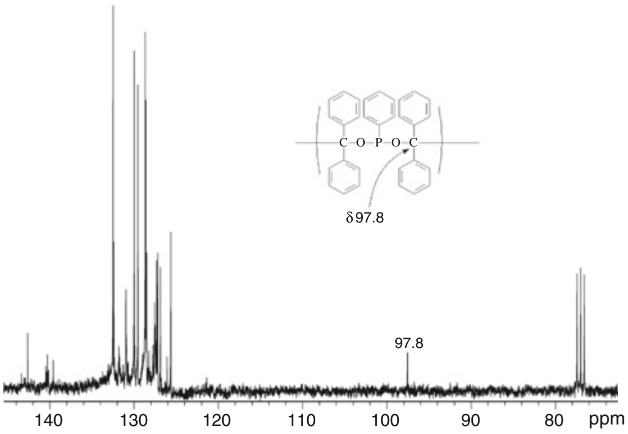


Fig. 8 ^{13}C NMR spectrum of the product of the thermal rearrangement of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

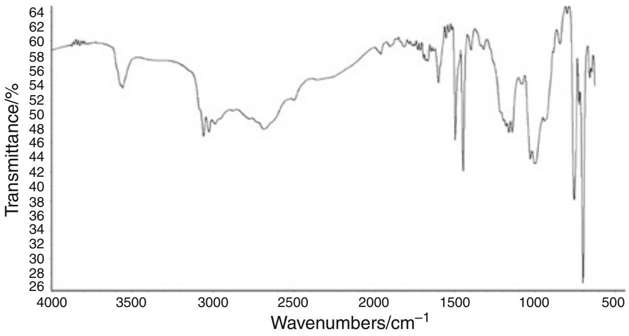


Fig. 9 IR spectrum of the product from the thermal rearrangement of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

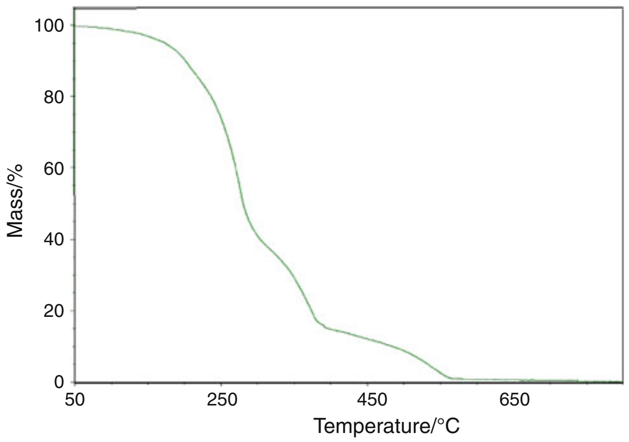


Fig. 10 Thermal decomposition of the 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane rearrangement product

spectroscopy. As the temperature is allowed to increase from −20 °C, it undergoes smooth rearrangement to a new compound, presumably the linear polymer.

References

1. Lewin M. Physical and chemical mechanisms of the flame retarding of polymers. In: LeBras M, Bourbigot S, Camino G, Delobel R, editors. Fire retardancy of polymers—the use of intumescence. Cambridge: The Royal Society of Chemistry; 1998. p. 1–32.
2. Gann RG. Flame retardants: our view. Vol. 10. Kirk-Othmer encyclopedia of chemical technology. New York: Wiley; 1993. p. 930–6.
3. Weil ED. Phosphorus-based flame retardants. In: Engel RE, editor. Handbook of organophosphorus chemistry. New York: Marcel Dekker; 1992.
4. Weil ED, Levchik SV, Ravey M, Zhu WM. A survey of recent progress in phosphorus-based flame retardants and some mode of action studies. Phosphorus Sulfur Silicon Relat Elem. 1999; 144–146:17–20.
5. Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. Prog Polym Sci. 2002; 27(8):1661–712.
6. Ciesielski M, Schafer A, Doering M. Novel efficient DOPO-based flame-retardants for PWB relevant epoxy resins with high glass transition temperatures. Polym Adv Technol. 2008; 19(6):507–15.
7. Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D, Artner J, Ciecielski M, Doering M, Balabanovich AJ, Knoll U, Braun U, Schartel B. Novel phosphorus-containing hardeners with tailored chemical structures for epoxy resins: synthesis and cured resin properties. J Appl Polym Sci. 2007;105(5):2744–59.
8. Howell BA, Feng ZR, Y-J Cho. Dioxaheteroatom cyclics as initiators for radical polymerization Macromol Symp. (in press).
9. Howell BA, Uzibor J. Impact of initiator characteristics on the thermal stability of poly(styrene). J Therm Anal Calorim. 2006; 85(1):45–51.
10. Howell BA, Uzibor J. Polymerization as a means of stabilization for poly(styrene). J Vinyl Addit Technol. 2006;12(4):192–7.
11. Meyer TG, Fischer A, Jones PG, Schmutzler R. Darstellung und Einkristall-Rontgenstrukturanalyse einiger Fluorphosphite und Phosphitester. Nautrforsch. 2003;486:659–71.
12. Munoz A, Hubert C, Luche JL. One-pot synthesis of phosphonic acid diesters. J Org Chem. 1996;61(17):6015–7.
13. Chauvin R. Preparation of 2-hydroxy-1,2-diphenylethyl phenylphosphinate: a chiral reagent for asymmetric reduction of ketones. Tetrahedron Asymmetry. 1990;1(10):737–42.
14. Brodesser B, Braun M. Synthesis of (R)-1,1,2-triphenyl-1,2-ethanediol derived phosphonates. Phosphorus Sulfur Silicon Relat Elem. 1989;44(3–4):217–21.