Thermal decomposition of 1,1,2,2-tetraaryl-1,2-ethanediols

B. A. Howell · Y.-J. Cho · Z.-R. Feng

Abstract The thermal degradation of a series of 1,1,2, 2-tetraaryl-1,2-ethanediols has been examined using thermogravimetry (TG) and gas chromatography/mass spectrometry (GC/MS). These compounds are smoothly converted to the corresponding diaryl ketone and diaryl carbinol, i.e., the compounds undergo disproportionation arising from homolytic cleavage of the central carbon–carbon bond. Presumably, cleavage of the carbon–carbon bond generates a radical pair which disproportionates to provide the observed products.

Keywords Disproportionation · Radical pair decomposition by hydrogen atom transfer · Thermally labile carbon–carbon bonds · Pyrolysis · Pinacol decomposition

Introduction

1,1,2,2-Tetraaryl-1,2-ethanediols are useful precursors for five-membered dioxaheterocycles [1, 2]. The heterocycles contain a strained carbon–carbon bond which will undergo homolytic thermolysis at modest temperatures to generate a diradical [2, 3]. If the aryl groups are properly substituted, this provides a ready means of introducing a flame-retarding unit into the main chain of a vinyl polymer [4]. The diols may be readily prepared by reductive coupling of the corresponding phenones [5–7]. The simplest diol, 1,1,2,2-tetraphenyl-1,2-ethanediol, may be prepared by photoreduction in isopropanol as a hydrogen atom source using either an ultraviolet lamp or sunlight for irradiation [1]. More complex tetraaryl-1,2-ethanediols are usually prepared by metal-promoted reductive coupling [5–7]. A series of tetraaryl-1,2-ethanediols have been prepared, characterized, and subjected to thermal degradation. The degradation may be examined using thermogravimetry (TG), gas chromatography/mass spectrometry (GC/MS), or simple pyrolysis.

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 (Thermo-Fisher 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

B. A. Howell (✉) · Y.-J. Cho · Z.-R. Feng
Center for Applications in Polymer Science and Department
of Chemistry, Central Michigan University,
Mount Pleasant, MI 48859-0001, USA
e-mail: bob.a.howell@cmich.edu

(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-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 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 programed 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. Precursor phenones were prepared as previously reported [2, 4].

Synthesis

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

A solution of 120 g (0.66 mol) of benzophenone in 1,000 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 as white crystalline solid (89.25 g, 97.3% yield), mp 198 °C (DSC), decomposition onset 200 °C (TG); ^{1}H-NMR (δ, CDCl$_3$) 3.03 (s, 2H, exchangeable protons), 7.10–7.60 (m, 20H, aromatic protons); ^{13}C-NMR (δ, CDCl$_3$) 83.3 (tertiary carbon atoms bearing hydroxyl groups), 127.2 (substituted aromatic carbon atoms), 127.5 (aromatic carbon atoms at *ortho* positions), 128.4 (aromatic carbon atoms at *meta* positions), 144.4 (aromatic carbon atoms at *para* positions).

1,2-(4-Bromophenyl)-1,2-{4-[t-(butyl)dimethylsilyloxy]phenyl}-1,2-ethanediol

A mixture of 10.02 g (0.03 mol) of 4-bromophenyl-{4-[t-(butyl)dimethylsilyloxy]phenyl}methanone, 10.0 g (0.07 mol) of zinc chloride, and 100 mL of 50% (v/v) aqueous THF was stirred as 50.0 g (0.82 mol) of zinc powder was added portionwise over a period of 0.25 h. The resulting mixture was stirred 0.5 h. Aqueous 3 N hydrochloric acid solution (50 mL) was added with stirring. The mixture was filtered through a short silica gel column to remove zinc and the filtrate was extracted with three 40-mL portions of toluene. The combined toluene layers were washed with two 40-mL portions of saturated aqueous bicarbonate solution and 40 mL of saturated aqueous sodium chloride solution. The toluene solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford the crude product as a white solid. This material was purified by chromatography on silica gel using ethyl acetate/hexane (5/95 to 20/80) as eluent. The fractions containing product (TLC) were combined and the solvent removed by rotary evaporation at reduced pressure to provide 9.38 (79.6% yield) of 1,2-(4-bromophenyl)-1,2-{4-[t-(butyl)dimethylsilyloxy]phenyl}-1,2-ethanediol as a white solid: mp 52 °C (DSC); decomposition 125 °C (TG); ^{1}H-NMR (δ, CDCl$_3$) 0.17 (s, 12H, protons of methyl groups attached to silicon), 0.87 (s, 18H, protons of *t*-butyl methyl groups), 2.95 (broad s, 1H, hydroxyl proton), 6.63–7.31 (m, 16H, aromatic protons); ^{13}C-NMR (δ, CDCl$_3$) −4.42 (carbon atoms of methyl groups attached to silicon), 18.28 (quaternary carbon atom of *t*-butyl groups), 25.67 (carbon atoms of the *t*-butyl methyl groups), 82.56 (benzylic carbon adjacent to oxygen), 119.06, 130.19, 143.35, 154.78 (carbon atoms of the silyloxyphenyl group), 121.15, 125.28, 128.21, 135.55 (carbon atoms of the bromophenyl group); FTIR (cm^{-1}, KBr) 3562 (m-broad) hydroxyl group, 3120 (w), 3059 (w) C$_{sp^2}$−H, 2956 (s), 2930 (s), 2886 (m), 2858 (s) C$_{sp^3}$−H, 1605 (s), 1507 (s) aromatic nucleus, 1265 (vs), 913 (vs) Si–O; mass spectrum *m/z* (% of base), 392 (8.3), 183 (100), 151 (66.3), 77 (81.3), 394 (6.3), 335 (23.8), 185 (24.1), 151 (97.1), 77 (100).

1,1,2,2-Tetra(3,5-dibromophenyl)-1,2-ethanediol

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. 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, mp 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.

Product characterization

4-Bromophenyl-4-{[t-(butyl)dimethylsilyloxy]phenyl}methanol

A clear colorless oil, TG decomposition onset temperature, 365 °C; ^{1}H-NMR (δ, CDCl$_3$) 0.20 (s, 6H), protons of methyl groups attached to silicon, 0.37 (s, 9H), t-butyl protons, 2.23 (broad, s, 1H), hydroxyl proton, 5.73 (s, 1H), benzylic proton adjacent to oxygen, 6.98 (AB pattern, J_{AB} = 8.5 Hz, $\Delta\nu_{AB}$ = 111.4 Hz, 4H, protons of the silyloxyphenyl group), 7.28 (AB pattern, J_{AB} = 8.5 Hz, $\Delta\nu_{AB}$ = 63.3 Hz, 4H, protons of the bromophenyl group; ^{13}C-NMR (δ, CDCl$_3$) −4.17 (carbon atoms of methyl groups attached to silicon), 18.4 (quaternary carbon atom of t-butyl group), 25.9 (carbon atoms of the t-butyl methyl group), 75.5 (benzylic carbon atom attached to oxygen), 120.4, 121.5, 128.1, 136.5 (carbon atoms of the bromophenyl group), 126.3, 131.7, 143.2, 155.6 (carbon atoms of the silyloxyphenyl group); FTIR (cm^{-1}, NaCl) 3334 (s-broad, hydroxyl group), 3120 (w), 3062 (w), 3031 (w) C$_{sp^2}$−H, 2930 (s), 2886 (m), 2858 (s) 2156 (s), C$_{sp^3}$−H, 1608 (s), 1509 (s) aromatic C–H, 1472 (vs), 1255 (vs), 916 (vs) Si–O; mass spectrum, m/z (% of base), 394 (6.3), 335 (23.8), 185 (24.1), 151 (97.1), 77 (100).

4-Bromophenyl-4-[t-(butyl)dimethylsilyloxy]phenylmethanone

White needles, mp 61 °C (DSC); decomposition onset 162 °C (TG); ^{1}H-NMR (δ, CDCl$_3$) 0.25 (s, 6H, protons of methyl groups attached to silicon), 1.00 (s, 9H, protons of t-butyl groups), 6.89 (AB pattern, J_{AB} = 8.5 Hz, $\Delta\nu_{AB}$ = 113.4 Hz, 4H, protons of the silyloxyphenyl group), 7.72 (AB pattern, J_{AB} = 8.5 Hz, $\Delta\nu_{AB}$ = 63.3 Hz, 4H, protons of the bromophenyl group; ^{13}C-NMR (δ, CDCl$_3$) −4.04 (carbon atoms of methyl groups attached to silicon), 10.5 (quaternary carbon atom of t-butyl group), 25.8 (carbon

atoms of the t-butyl methyl group), 75.5 (benzylic carbon atom attached to oxygen), 120.1, 131.5, 131.7, 160.4 (carbon atoms of the silyloxyphenyl group), 127.1, 130.5, 131.6, 131.7, 137.8 (carbon atoms of the bromophenyl group), 194.8 (carbonyl carbon atom); FTIR (cm^{-1}, KBr) 3229 (w), 3066 (w), C$_{sp^2}$−H, 2930 (s), 2886 (m), 2885 (s) 2858 (s), C$_{sp^3}$−H, 1657 (vs), conjugated carbonyl group, 1598 (s), aromatic nucleus, 1269 (vs), 916 (vs) Si–O; mass spectrum, m/z (% of base), 392 (8.3), 183 (100), 151 (66.3), 77 (81.1).

Di(3,5-dibromophenyl)methanol

White crystalline solid, mp 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$_{sp^2}$−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

White crystalline solid mp 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$_{sp^2}$−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).

Results and discussion

Tetraaryl-1,2-ethanediols are useful starting materials for the synthesis of a variety of dioxaheterocyclic compounds. These heterocycles contain a strained carbon–carbon bond which readily undergoes thermolysis to generate a diradical capable of initiating vinyl polymerization. If the aryl groups bear appropriate substituents, the use of these heterocycles for the initiation of polymerization serves to

Fig. 1 Strained dioxaheterocycle containing flame-retarding moieties
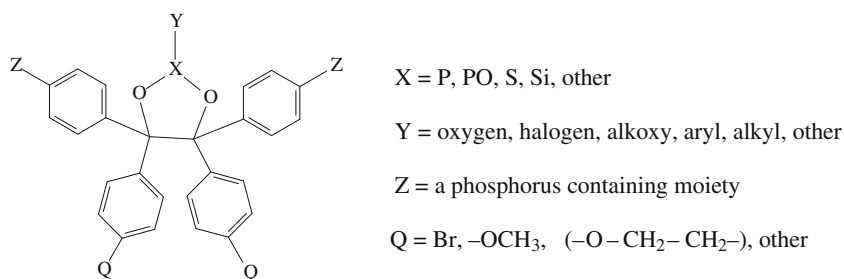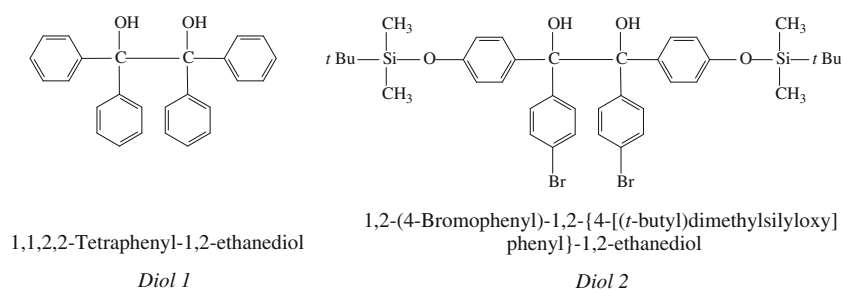
X = P, PO, S, Si, other

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

Z = a phosphorus containing moiety

Q = Br, –OCH₃,   (–O – CH₂ – CH₂–), other

Fig. 2 Structures of tetraarylethane-1,2-diols

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

Diol 1

1,2-(4-Bromophenyl)-1,2-{4-[(*t*-butyl)dimethylsilyloxy]phenyl}-1,2-ethanediol

Diol 2

1,1,2,2-Tetra(3,5-dibromophenyl)-1,2-ethanediol

Diol 3

introduce a flame-retarding unit into the polymer main chain (Fig. 1).

In fact, the diols themselves are thermally labile and undergo decomposition at relatively low temperatures. The thermal decomposition of three of these diols (structures in Fig. 2) have been examined in detail using thermogravimetry and, in particular, GC–MS. The diols are all
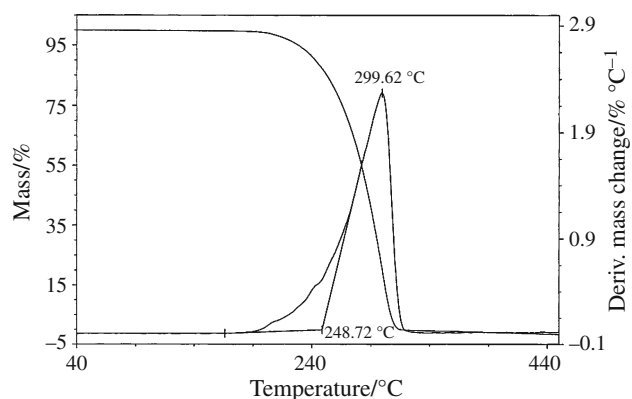
Fig. 3 Thermal decomposition of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol

thermally well-behaved and undergo smooth decomposition at modest temperatures. The decomposition of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol is depicted in Fig. 3 (Table 1).

Decomposition of the diols with the more highly substituted aryl groups occurs at lower temperature than does that of the tetraphenyl diol containing unsubstituted aryl groups. In all cases, the products of decomposition are diaryl ketone and diarylcarbinol, i.e., the diols undergo simple disproportionation under thermal stress. Cleavage of the aliphatic carbon–carbon bond generates a radical pair which undergoes hydrogen atom transfer more rapidly than diffusion. This is illustrated in Scheme 1.

Table 1 Thermal properties of tetraaryl-1,2-ethanediols

Diol	Melting point/°C (DSC)	Decomposition-extrapolated onset temperature (TG)
1	197	200
2	152	225
3	167	248

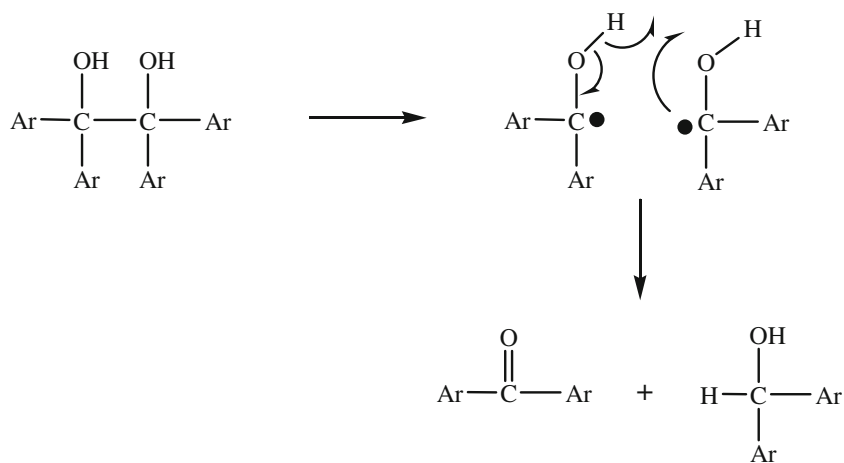**Scheme 1** Mode of thermal decomposition of tetraaryl-1,2-ethanediols

Fig. 4 Gas chromatogram of the product mixture from pyrolysis of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol
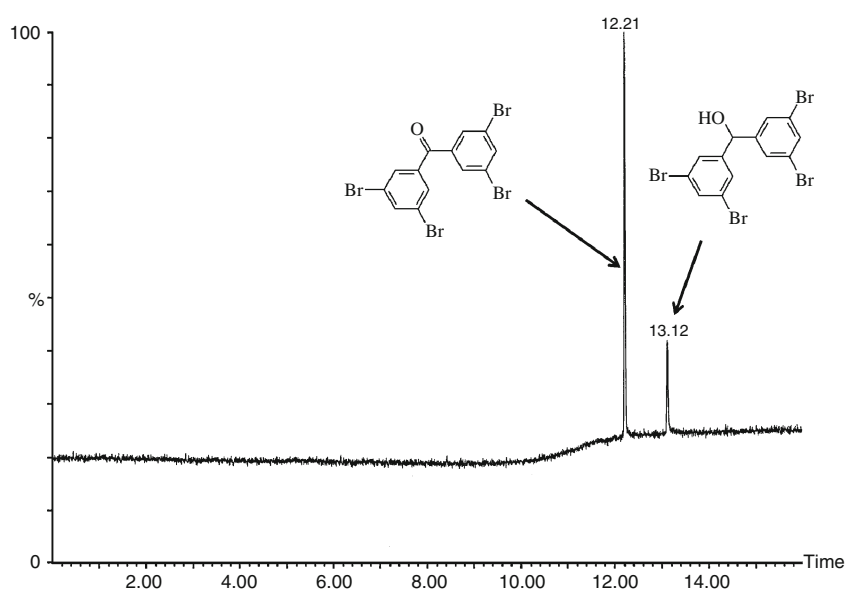

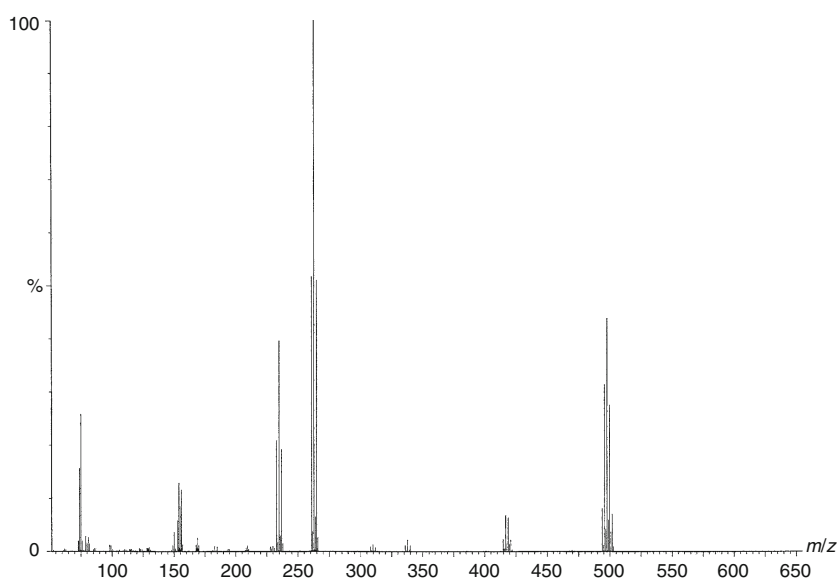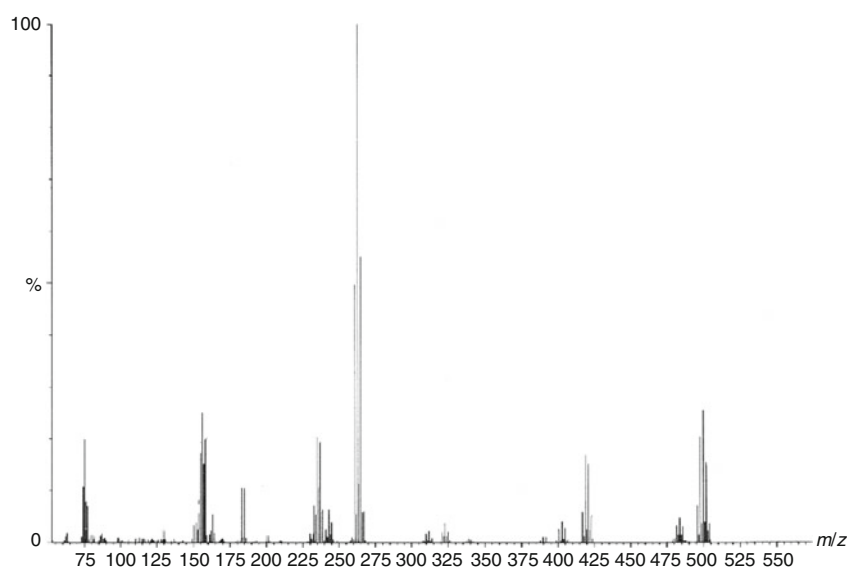**Fig. 5** Mass spectrum of di(3,5-dibromophenyl)-methanone

Fig. 6 Mass spectrum of di(3,5-dibromophenyl)methanol

This may be most readily observed using GC–MS. Injection of any of the diols leads to a chromatogram containing two peaks (and only two peaks, i.e., there are no side products formed) (Fig. 4). The corresponding mass spectra clearly identify the compounds giving rise to the two peaks as the ketone and the alcohol. Apparently, the diols undergo decomposition in the injection port of the GC to form the disproportionation products. This is illustrated below for the decomposition of 1,1,2,2-tetra(2,5-dibromophenyl)-1,2-ethanediol.

The mass spectrum of the material eluting at 12.2 min is displayed in Fig. 5. It contains a molecular ion peak at m/z 494 with an isotopic cluster (m/z 494, 496, 498, 500, 502) indicative of a compound containing four bromine atoms. It contains a base peak at m/z 261 (with isotopic ion peaks at m/z 263, 265 indicative of a fragment containing two bromine atoms) corresponding to the dibromophenacyl cation (loss of dibromophenyl). The mass spectrum clearly identifies this fragment as di(3,5-dibromophenyl)-methanone.

The mass spectrum of the material eluting at 13.1 min is displayed in Fig. 6. The spectrum contains a molecular ion peak at m/z 496 with an isotopic cluster (m/z 496, 498, 500, 502, 504) indicative of a compound containing four bromine atoms. It contains a base peak at m/z 261 (with iso-
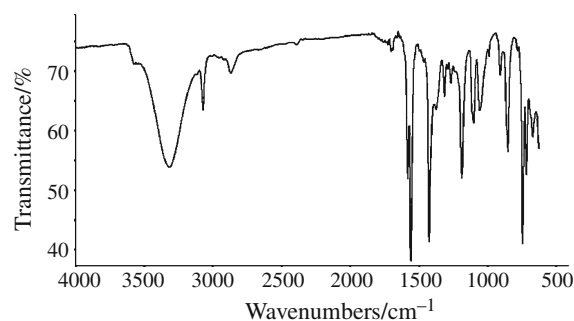

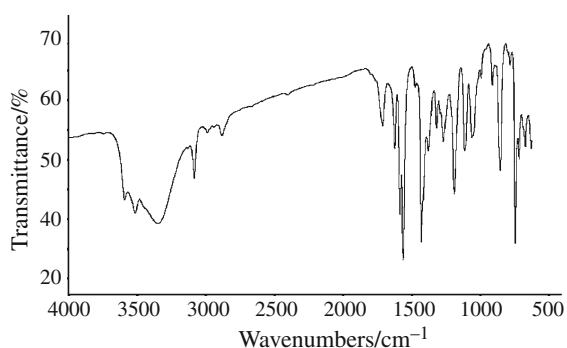Fig. 8 Infrared spectrum of di(3,5-dibromophenyl)methanol

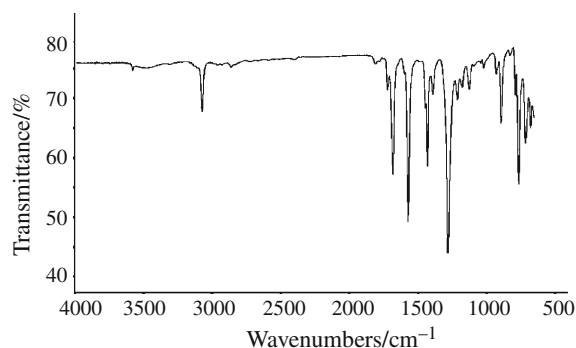Fig. 7 Infrared spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol
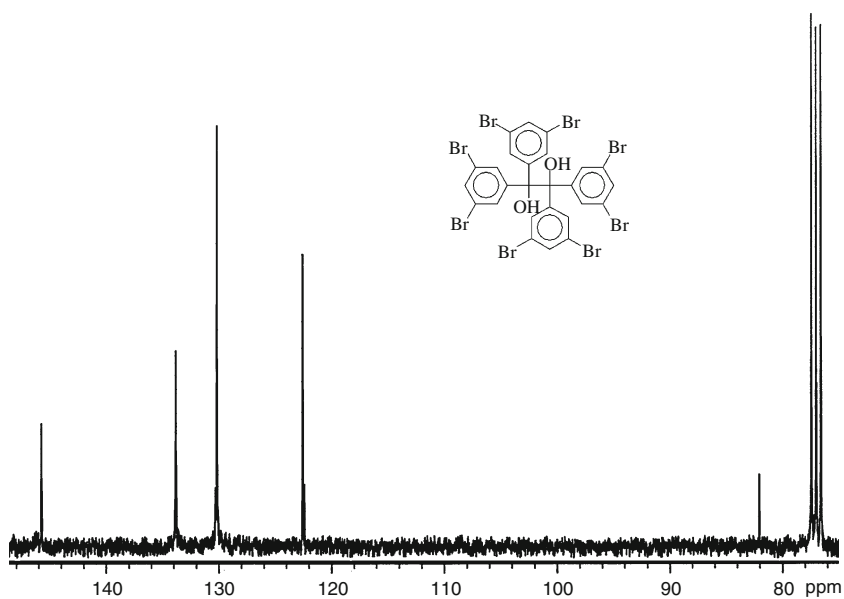

Fig. 9 Infrared spectrum of di(3,5-dibromophenyl)methanone

Fig. 10 Carbon-13 NMR spectrum of 1,1,2,2-tetra(3,5-dibromophenyl)-1,2-ethanediol

topic ion peaks at *m/z* 263, 265 indicative of a fragment containing two bromine atoms) corresponding to the loss of a dibromophenyl fragment. This compound is clearly di(3,5-dibromophenyl)methanol.
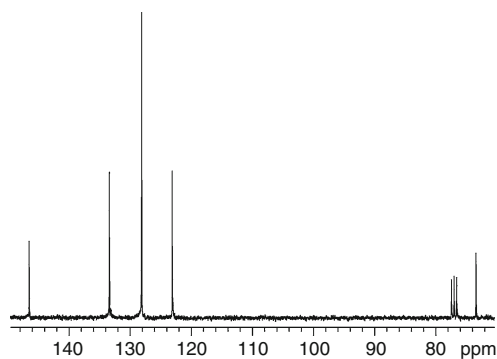

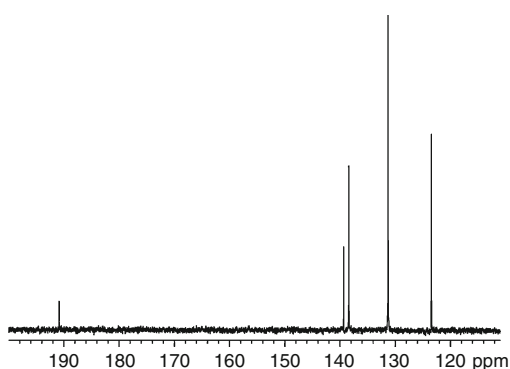**Fig. 11** Carbon-13 NMR spectrum of di(3,5-dibromophenyl)-methanol

**Fig. 12** Carbon-13 NMR spectrum of di(3,5-dibromophenyl) methanone

The identity of the products and the nature of the transformation is also readily apparent from other spectral data as well.

The infrared spectrum for the starting diol is shown in Fig. 7. The infrared spectra of the corresponding disproportionation products are contained in Figs. 8 and 9. Both the diol and alcohol spectra contain hydroxyl absorption, but it is more complex in the diol spectrum as would be
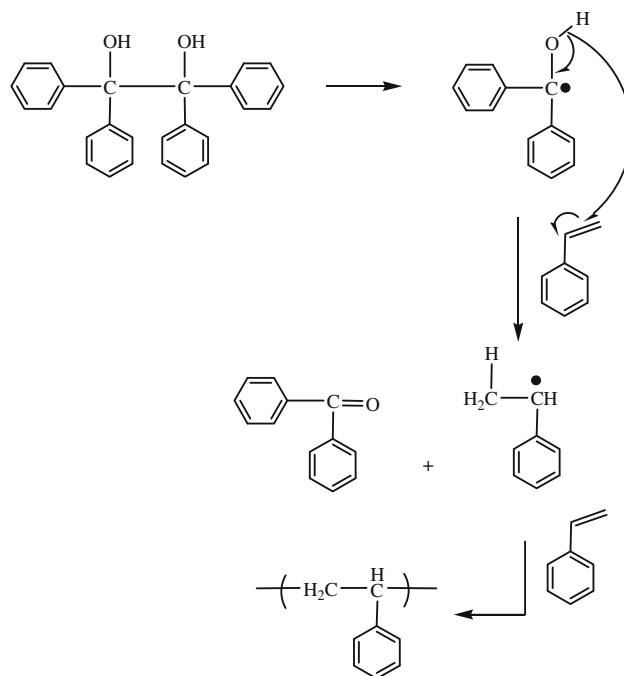
Scheme 2 Tetraaryl-1,2-ethanediol initiation of styrene polymerization by hydrogen atom transfer

Scheme 3 Initiation of styrene
polymerization by tetraaryl-1,2-
dimethoxyethane
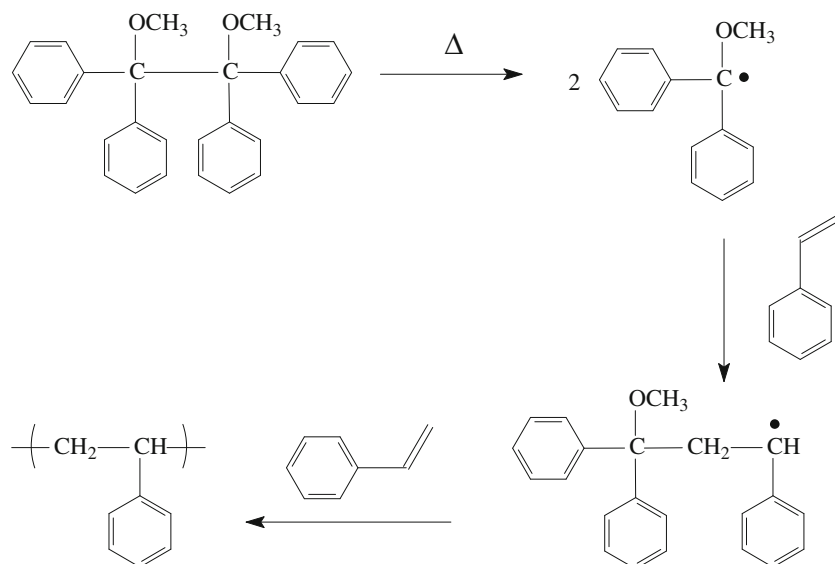
expected due to intramolecular hydrogen bonding. The
hydroxyl absorption is absent in the spectrum of the ketone.
This spectrum contains conjugated carbonyl absorption at
$1,662 \ cm^{-1}$.

The changes are also apparent in the corresponding
carbon-13 NMR spectra. The most notable change is in the
chemical shift for the benzylic carbon atom. This absorp-
tion appears at δ 73.8 for the alcohol, and at δ 190.9 for the
ketone (Figs. 10, 11, 12).

This mode of decomposition is completely consistent
with the earlier observation that diols of this type undergo
thermally induced homolysis of the central carbon–carbon
bond to generate radicals which initiate vinyl polymeriza-
tion by hydrogen atom transfer [8–11]. This is illustrated
below (Scheme 2).

The polymer chain ends in this case were methyl
groups rather than diphenyl(hydroxy)methyl. Interestingly,
when the hydroxyl groups were converted to alkoxy
groups initiation occurred as expected (Scheme 3) to
generate polymer containing diphenyl(methoxy)methyl
chain ends [10].

Conclusions

The thermal decomposition of a series of tetraaryl-1,2-
ethanediols has been investigated using a variety of tech-
niques. These compounds degrade smoothly by thermolytic
cleavage of the aliphatic carbon–carbon bond to generate a
radical pair which undergoes disproportionation by
hydrogen atom transfer to generate the corresponding
phenone and carbinol.

References

1. Howell BA, Uzibor J. Thermal stability of poly(styrene) con-
   taining phosphorus in the main chain. J Therm Anal Calorim.
   2006;85:45–51.
2. Howell BA, Feng Z-R, Cho Y-J. Dioxoheteroatom cyclics as
   initiators for radical polymerization. Macromol Symp. 2010;
   297:33–42.
3. Howell BA, Cho Y-J. Halogenated dioxasilates as precursors to
   flame retardant polymers, Chap. 10. Proceedings, 21st annual
   conference on recent advances in flame retardancy of polymeric
   materials. BCC Research 2010. Wellesley.
4. Crivello V, Lee JL, Conlon DA. Cyclic silyl pinacol esters.
   A new class of multifunctional free radical initiators. Polym Bull.
   1986;16:95–102.
5. McMurry JE. Carbonyl-coupling reactions using low-valent
   titanium. Chem Rev. 1989;89:1513–24.
6. Tanaka K, Kishigam S, Toda F. A new method for coupling
   aromatic aldehydes and ketones to produce glycols using
   Zn–ZnCl2 and sunlight in aqueous solution and in the solid state.
   J Org Chem. 1990;55:2981–3.
7. Hekmatshoar R, Yavar I, Beheshtiha YS, Heravi MM. Reductive
   coupling of carbonyl compounds to pinacols with zinc in THF-
   saturated aqueous ammonium chloride. Mon Chem. 1969;6:
   186–9.
8. Braun D, Becker KH. Aromatische pinakole als polymerisatio-
   ninitatoren. Angew Makromol Chem. 1989;89:1513–24.
9. Braun D, Becker KH. Kinetic der polymerizationsauslosung mit
   aromatischen pinakolen. Makromol Chem. 1971;147:91–9.
10. Braun D, Becker KH. Aromatic pinacols as polymerization ini-
    tiators. Ind Eng Chem Prod Res Dev. 1971;10:386–8.
11. Braun D. Origins and development of initiation of free radical
    polymerization processes. Int J Polym Sci. 2009;1–10.