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Synthesis and photo-oxidative degradation of 2,6-bis-[ω-trimethylsiloxypolydimethylsiloxy-2′-dimethylsilylethyl]acetophenone

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Abstract

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) catalyzes the copolymerization of α,ω-divinylsiloxanes with aromatic ketones such as acetophenone to give polymers which have regularly alternating 2,6-diethylene-acetophenone and disiloxane units in the backbone. These copolymers absorb light in the UV $\lambda_{max} \sim 280$ nm, and are photochemically active. Monomeric model systems 2-(2′-trimethylsilylethyl)acetophenone (**III**), and 2-(3′,3′,5′,5′,5′-pentamethyl-3′,5′-disila-4′-oxaheptanyl)acetophenone (**IV**), as well as, 2,6-bis[ω-trimethylsiloxypolydimethylsiloxy-2′-dimethylsilylethyl]acetophenone (**II**) were prepared and their photochemistry in the presence and absence of oxygen studied. Photolysis of *alt*-copoly(2,6-diethylene-acetophenone/disiloxane) in the absence of oxygen results in recovered polymer whose molecular weight has not changed. On the other hand, photolysis in the presence of oxygen results in significant polymer degradation. Likewise, **III** was stable to irradiation in methanol-d_4 solution in the absence of oxygen. Deuterium was specifically incorporated into the benzylic methylene groups of recovered **III**. The photolysis of **III** in the presence of oxygen yields hexamethyldisiloxane and 1,2-diacetylbenzene. Mechanisms that accounts for these results are proposed.

Keywords: Ruthenium catalyzed; Photo-oxidative degradation of polymers; Photolysis

1. Introduction

The photo-degradation of polymers is a topic of considerable interest [1]. Commercially important synthetic polymers are often resistant to decomposition and degradation by water, air, sunlight, or microorganisms. Incineration is frequently not practical since combustion of some of these materials produces toxic fumes. Further, polymeric materials that contain flame resistant additives are difficult to incinerate. Elimination of such materials constitutes a major solid waste disposal problem. A potential solution to this lies in the development of photodegradable and/or biodegradable polymers [2]. Understanding the photo-degradation of polymers may permit design of materials with controlled lifetimes [3,4], which minimize environmental issues [5].

We have explored the scope of the dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) catalyzed copolymerization of α,ω-divinylsiloxanes with aromatic ketones such as acetophenone [6–9]. The backbone of these polymers contains regularly alternating 2,6-diethylene-acetophenone and disiloxane units. These copolymers absorb light in the UV $\lambda_{max} \sim 280$ nm. Neither photochemistry nor the photo-degradation of these materials has been reported.

Photolysis of closely related monomeric model systems 2′-alkylacetophenones and 2-alkylbenzophenones has been extensively studied. In summary, photolysis of these results in photoenolization and formation of 2-xylylenols via a Norrish type II process [10–14]. The OH group of such intermediates can undergo deuterium exchange with deuterated alcohols such as methanol-*O*-*d*. 2-Xylylenols have been trapped by dienophiles in Diels–Alder reactions [15,16], and undergo cheleotropic reactions with SO_2 [17].

2. Results

Photolysis of *alt*-copoly(2,6-diethylene-acetophenone/disiloxane) in the absence of oxygen results in recovered polymer whose molecular weight had not changed. On the other hand, photolysis in the presence of oxygen resulted in significant polymer degradation. We have carried out the following experiments to understand these results.

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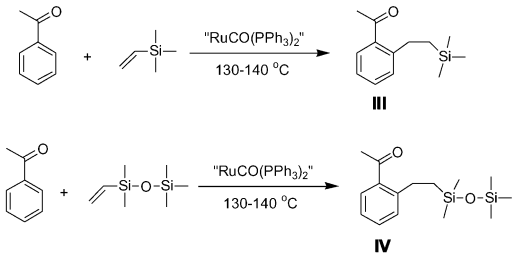

Fig. 1. Synthesis of **III** and **IV**.

Monomeric model systems 2-(2′-trimethylsilylethyl)acetophenone (**III**), and 2-(3′,3′,5′,5′,5′-pentamethyl-3′,5′-disila-4′-oxaheptanyl)acetophenone (**IV**), as well as, 2,6-bis[ω-trimethylsiloxypolydimethylsiloxy-2′-dimethylsilylethyl]acetophenone (**II**) were prepared and their photochemistry in the presence and absence of oxygen studied.

No change in the molecular weight of **II** was observed when methanol solutions of **II** were irradiated with either monochromatic (254 nm) or broad-spectrum ultra-violet light in the absence of oxygen. While **III** was stable to irradiation in methanol-d_4 solution in the absence of oxygen, deuterium was specifically incorporated into the benzylic methylene groups of recovered **III**. These results are consistent with those previously reported for 2′-alkylacetophenones [10–14].

On the other hand, photolysis of oxygen saturated THF or hexamethyldisiloxane solutions of **II** result in a 50% decrease in the molecular weight of **II**. The photolysis of **III** in the presence of oxygen yields hexamethyldisiloxane and 1,2-diacetylbenzene. Likewise, photolysis of **IV** gave 1,2-diacetylbenzene and decamethyltetrasiloxane as the major products. Mechanisms that accounts for these results are proposed.

3. Synthesis

The model compounds, **III** and **IV** were prepared by a Ru catalyzed Murai reaction between acetophenone and vinyltrimethylsilane or vinylpentamethyldisiloxane, respectively (Fig. 1). These Murai reactions involve the Ru catalyzed anti-Markovnikov addition of one of the ortho C–H bonds of acetophenone across the C–C double bond of the vinyl-Si functionality [18].

α-(Trimethylsiloxy)-ω-(vinyldimethylsiloxy)polydimethyl siloxane (**I**) was prepared by the reaction of monodispersed α-(trimethylsiloxy)-ω-(lithiodimethylsilanolate) polydimethylsiloxane with vinyldimethylchlorosilane. Monodispersed α-(trimethylsiloxy)-ω-(lithiodimethylsilanolate)polydimethylsiloxane was prepared by living anionic ring opening polymerization (AROP) of D_3 initiated by methyllithium. It is well known that AROP of D_3 yields narrow molecular weight polysiloxanes, because ring opening occurs faster than redistribution or equilibration [19,20]. **II** was prepared by Ru catalyzed

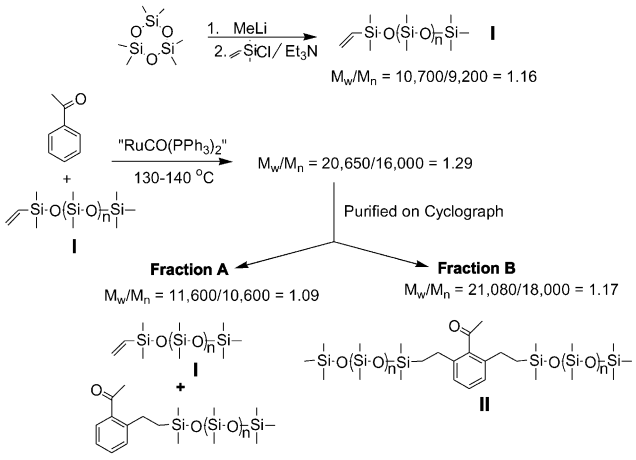

Fig. 2. Synthesis of **I** and **II**.

reaction of acetophenone with **I** (Fig. 2). In this reaction, 2-(ω-trimethylsiloxypolydimethylsiloxy-2′-dimethylsilylethyl)-acetophenone and unreacted **I** were obtained in addition to the desired product (**II**). The mixture was separated by preparative centrifugal partition chromatography on a Cyclograph instrument, using a silica gel rotor with gradient elution of methanol/toluene [21].

4. Experimental

4.1. NMR spectroscopy

^{1}H and ^{13}C NMR were obtained on a Bruker AMX-500 spectrometer. Four percent w/v solutions in $DOCD_3$, $CDCl_3$, C_6D_6 or a 60:40 solution of $C_6D_6/DOCD_3$ were used to obtain ^{1}H NMR spectra. ^{1}H and ^{13}C NMR spectra were internally referenced to residual $DOCH_3$, C_6H_6 or $CHCl_3$. ^{29}Si NMR spectra were externally referenced to TMS.

4.2. Gel permeation chromatography

GPC analysis for the molecular weight distribution of the polymers was performed on a Waters system, which comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a model 820 Maxima control system. Two 7.8 mm × 300 mm Styragel columns HR4 and HR2 in series were used for the analysis. HPLC grade THF or toluene at a flow rate of 0.6 ml min^{-1} was used as the eluent. The retention times were calibrated against those of monodispersed polystyrene standards ($M_w/M_n < 1.09$). GC-MS was performed on a Hewlett–Packard 4107 GLPC equipped with a Quadrupole mass detector and a 30 m DB-5 capillary column.

4.3. Photolysis

Photolysis was carried out either in a Rayonet photochemical reactor equipped with 16 low-pressure GE germicidal

lamps whose output is monochromatic at 254 nm, or with a medium pressure Hanovia 550 W lamp [22].

4.4. Materials

Acetophenone, 1,2-diacetylbenzene, toluene, methanol, styrene, triethylamine, and methyllithium were obtained from Aldrich. Vinyltrimethylsilane, vinyldimethylchlorosilane, hexamethyldisilazane, vinylpentamethyldisiloxane, hexamethyldisiloxane and D_3 were obtained from Gelest. Ru was prepared from ruthenium trichloride hydrate (Aldrich) [23]. All reactions were run in flame dried glassware equipped with a Teflon covered magnetic stir bar under an argon atmosphere (unless indicated otherwise).

4.5. Synthetic procedure

4.5.1. 2-(2′-Trimethylsilylethyl)acetophenone (*III*) [17]

Ru (69.6 mg, 68 μmol), 3.0 ml of toluene and styrene (7.8 μl, 68 μmol) were placed in an Ace pressure tube, sealed and heated for 3.0 min at 135°C to activate the catalyst [6]. After cooling, the tube was opened. Acetophenone (1.19 g, 9.98 mmol) and vinyltrimethylsilane (1.00 g, 9.98 mmol) were added. The tube was resealed and heated for 24 h at 135°C. After cooling, the tube was opened and the volatiles removed. The resulting oily brown liquid was distilled. A fraction, bp 119–122°C/15 mm, 1.31 g, 60% yield, was obtained; ^{1}H NMR δ: 0.064 (s, 9H), 0.81–0.85 (m, 2H), 2.59 (s, 3H), 2.84–2.88 (m, 2H), 7.23–7.65 (m, 4H). ^{13}C NMR δ: −1.84, 19.41, 28.31, 29.81, 125.38, 129.09, 130.45, 131.42, 137.34, 145.78, 201.97. ^{29}Si NMR δ: 1.57. UV λ_{max} nm (ε): 251 (23,600), 287 (13,360). IR ν: 1686 (C=O) cm^{-1}. GC-MS of **III** $(C_{13}H_{20}OSi)^{+\cdot}$ *m/e* (isotope ratio): $(M)^{+\cdot}$ 220 (100.00), 221 (18.75), 222 (5.00); $(M-15)^+$ 205 (100.00), 206 (17.85), 207 (5.00); 131; 73.

4.5.2. 2-(3′,3′,5′,5′,5′-Pentamethyl-3′,5′-disila-4′-oxaheptanyl)acetophenone (*IV*)

Acetophenone (2.4 g, 20.1 mmol) and vinylpentamethyldisiloxane (3.5 g, 20.1 mmol) were reacted as above to yield **IV**. A fraction bp 160–178 °C/15 mm, 3.4 g, 58% yield, was obtained. ^{1}H NMR δ: 0.09 (s, 9H), 0.6 (s, 6H), 0.80–0.83 (m, 2H), 2.56 (s, 3H), 2.83–2.86 (m, 2H), 7.25–7.79 (m, 4H). ^{13}C NMR δ: 0.16, 1.92, 20.89, 27.65, 29.72, 125.37, 129.0, 130.39, 131.35, 137.37, 145.48, 201.75. UV λ_{max} nm (ε): 241 (26,800), 279 (2250). GC-MS of **IV** *m/e*: $(M)^{+\cdot}$ 294, $(M-15)^+$ 279, 147, 77.

4.5.3. Synthesis of α-(Trimethylsiloxy)-ω-(vinyldimethylsiloxy)polydimethylsiloxane (*I*)

In a 50 ml round bottomed flask was placed D_3 (5.0 g). The flask was sealed with a rubber septum. To this was added 30 ml THF and 220 μl MeLi (1.4 M). The reaction mixture was stirred at room temperature for 4 h, and then quenched with vinyldimethylchlorosilane (600 μl) and triethylamine (600 μl). It was further stirred for 30 min, after which volatiles were removed and the polymer extracted using an ether/water mixture. The ether layer was washed twice with aqueous NaH_2PO_4 and twice with water. It was then dried over anhydrous $MgSO_4$, filtered and the ether removed under reduced pressure. The polymer **I** was obtained, 4.2 g, 84% yield, $M_w/M_n = 10,700/9200$. ^{1}H NMR δ: −0.15 (s), 5.48–5.92 (m). ^{13}C NMR δ: −0.46, 130.36, 138.03.

4.5.4. Reaction of *I* with acetophenone

In a 10.0 ml Ace pressure tube was placed Ru (27.5 mg, 30 μmol), styrene (3.12 mg, 3.45 μl, 30.0 μmol), and toluene (0.5 ml). The tube was sealed with a rubber O-ring and threaded Teflon seal, and stirred at 125–135°C for 10 min. The solution turned red, indicating catalyst activation [6]. The tube was cooled to room temperature, opened, and acetophenone (103 mg, 85.8 μmol) and **I** (2.7 g, 0.27 mmol) added. The tube was resealed and the contents stirred at 125–135°C for 30 h. The reaction mixture was cooled and the polymer precipitated from toluene/methanol. In this way a polymer, 2.6 g, with $M_w/M_n = 20,650/16,000$ was obtained. The GPC curve was bimodal; the ^{1}H NMR indicated the presence of unreacted **I**, monosubstituted material and disubstituted material (**II**) (Fig. 2).

The above mixture was separated using a Cyclograph silica gel rotor (6 mm) saturated with methanol. Then a solution of 1.5 g of the mixture in 15 ml toluene: methanol (1:1) was loaded onto the rotor. Fraction A was eluted by using 500 ml mixture of toluene:methanol (1:1). Fraction B was then eluted with 500 ml of toluene. The solvent was removed under reduced pressure and the fractions analyzed.

Fraction A. 350 mg, $M_w/M_n = 11,600/10,600$. ^{1}H NMR δ: 0.072 (s, trimethylsilyl protons); 0.826–0.95 (m, methylene protons); 2.48 (s, CH_3CO–); 2.46–2.56 (m, methylene protons); 5.65–6.2 (m, vinyl protons); 7.05–7.09, 7.50–7.55, 7.69–7.73 (m, aromatic protons). UV λ_{max} nm (ε): 273(1190), 228(5380). This data indicates that Fraction A is a mixture of **I**, and 2-[ω-trimethylsiloxypolydimethylsiloxy-2′-dimethylsilylethyl]acetophenone.

Fraction B (**II**). 870 mg, $M_w/M_n = 21,080/18,000$. ^{1}H NMR δ: 0.071 (s, trimethylsilyl protons); 0.82–0.89 (m, methylene protons); 2.47 (s, CH_3CO–); 2.48–2.54 (m, methylene protons); 7.04–7.09, 7.19–7.22 (m, aromatic protons). UV λ_{max} nm (ε): 274 (1000), 228 (2770). This data is consistent with **II**.

4.6. Photochemical reactions

4.6.1. Photolysis of *III* in CD_3OD

A 4% solution of **III** in $DOCD_3$ was prepared, degassed by a series of freeze-thaw cycles and divided into four aliquots. These were placed in quartz (Q) or Pyrex (P) NMR tubes, which were sealed with rubber septa. The first aliquot, **III-A**, was placed in a Q-NMR tube and purged with argon; the second, **III-B**, in a P-NMR tube purged with argon; the third, **III-C**, in a Q-NMR tube saturated with

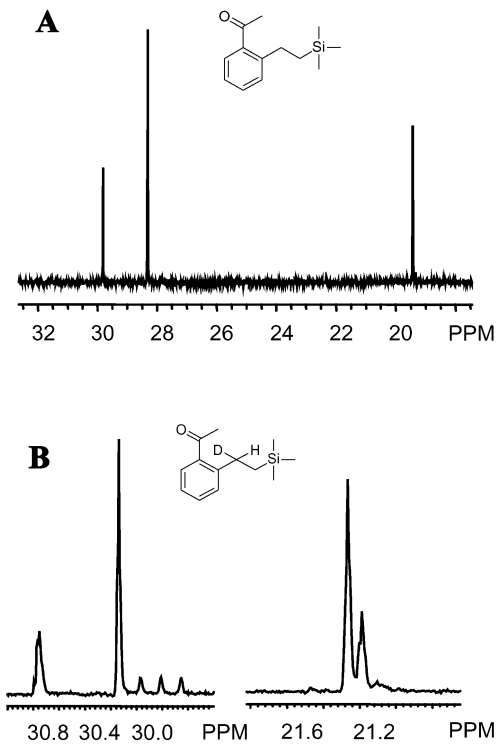

Fig. 3. ^{13}C NMR of the aliphatic region of **III**: (A) before and (B) after reaction in CD_3OD.

oxygen; and the fourth, **III-D**, in a P-NMR tube saturated with oxygen. The tubes were placed in a Rayonet reactor, and irradiated for 12 h.

The ^1H NMR spectra and GC-MS of **III-B** and **III-D** showed no change. In contrast, the ^1H NMR spectrum of both **III-A** and **III-C**, show a decrease in the intensity of the resonances associated with the benzylic protons (m, 2.84–2.88 ppm). For **III-A** a 50 % decrease was observed. In the ^{13}C NMR spectrum, new peaks were observed at 22.81, 31.274, 31.43, and 31.59 ppm (Fig. 3). A single major peak was detected in the GC/MS of **III-A** after irradiation. GC/MS showed a cluster of peaks at *m/e* (isotope ratio): $(M)^{+\cdot}$ 220 (100.00), 221 (71.40), 222 (24.11), 223 (4.46), 224 (0.89); $(M-15)^+$ 205 (100.0), 206 (60.00), 207 (17.85), 208 (3.6), 209 (0.71), Table 1. IR ν: 1688 (C=O) cm^{-1}.

4.6.2. Photolysis of *IV* in CD_3OD

A four percent solution of **IV** in CD_3OD was degassed by a series of freeze-thaw cycles. One aliquot, **IV-A**, was injected into a Q-NMR tube, which was sealed with a rubber septum and purged with argon. A second aliquot, **IV-B**, was injected into a P-NMR tube, which was sealed with a rubber septum and purged with argon. A third aliquot, **IV-C**, was pipetted into a P-NMR tube, which was sealed with a rubber septum and saturated with air.

^1H NMR spectra were taken of the three samples, these three were placed in a Rayonet reactor and irradiated with low-pressure mercury lamps. After 12 h, the ^1H NMR spectra of samples **IV-B** and **IV-C** showed no change. In contrast, the signals associated with the benzylic protons, (m, 2.83–2.86 ppm) in the ^1H NMR of **IV-A**, decrease by about 50%. GC analysis of **IV-A** after irradiation for 12 h had a single major peak 16.8 min (99%) whose retention time was identical to **IV**. The MS of this peak had a major cluster of peaks at *m/e* 279, which corresponds to $(M-15)^+$ ion for the mono-deuterated **IV** $(C_{15}H_{25}DO_2Si_2)^+$.

4.6.3. Photo-oxidative degradation of *II*

A solution of 265 mg of **II** in 50 ml of hexamethyldisiloxane was prepared. It was then irradiated using medium pressure Hanovia mercury lamp, while oxygen was bubbled through the solution. An aliquot was extracted after 8 h. The remaining solution was irradiated for an additional 15 h. The aliquot was analyzed by GPC, $M_w/M_n = 19,500/16,300$. The final reaction product, after 23 h of irradiation, was quenched with 20 ml of hexamethyldisilazane. The volatiles were removed; then the polymer extracted with ether/water; ether layer separated; dried over anhydrous $MgSO_4$, filtered and ether removed to give 245 mg, $M_w/M_n = 14,750/12,280$. This mixture was separated as above, to give two fractions (1 and 2) (Fig. 4).

Fraction 1. 112 mg, $M_w/M_n = 12,300/11,300$. ^1H NMR δ: 0.070 (s, trimethylsilyl protons); 0.82–0.89 (m, methylene

Table 1
Ratios for $P^{+\cdot}$ and $(P-15)^+$ peaks in MS of **III**

Peaks (*m/e*)	Calc.[a]	Before reaction in CD_3OD	After reaction in CD_3OD
P	100.00	100.00	100.00
$P+1$	18.30	18.75	71.40
$P+2$	3.40	5.00	24.11
$P+3$			4.46
$P+4$			0.89
$(P-15)$	100.00	100.00	100.00
$(P-15)+1$	17.20	17.85	60.00
$(P-15)+2$	3.40	5.00	17.85
$(P-15)+3$			3.6
$(P-15)+4$			0.71

[a] From Ref. [33].

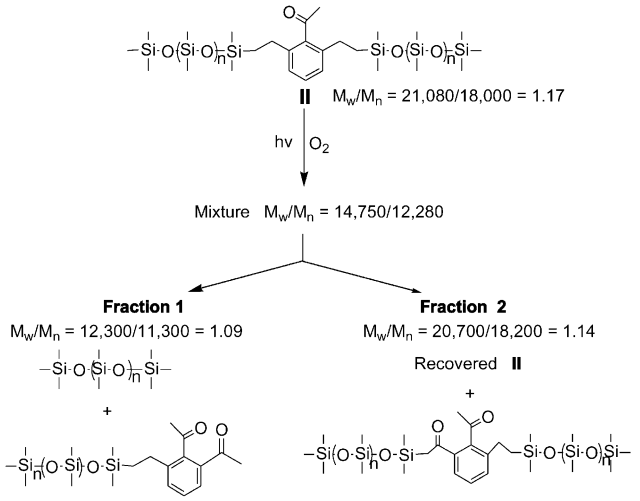

Fig. 4. Photo-oxidative degradation of **II**.

protons); 2.41 (s, CH_3CO–); 2.47 (s, CH_3CO–); 7.51–7.55, 7.69–7.73 (m, aromatic protons). UV λ_{max} nm (ε): 274 (7,380), 234 (15,330).

Fraction 2. 123 mg, $M_w/M_n = 20,700/18,200$. ^{1}H NMR δ: 0.083 (s, trimethylsilyl protons); 0.82–0.86 (m, methylene protons); 2.47 (s, CH_3CO–); 2.48–2.54 (m, methylene protons); 7.16–7.29 (m, aromatic protons). UV λ_{max} nm (ε): 273 (2880), 230 (6340).

*4.6.4. Photolysis of **III** in the presence of oxygen*

A: In a 1 ml quartz cuvette was placed 0.5 g of **III**, which was then dissolved in 0.5 ml of pentane. The cuvette was sealed with a rubber septum and oxygen was bubbled through the solution for 5 min. The cuvette was then placed at the center of a Rayonet photochemical reactor. The solution was irradiated for 9 h and then analyzed by GC-MS. Two product peaks were detected. Hexamethyldisiloxane and 1,2-diacetylbenzene were identified based on the agreement of their GC retention time and MS fragmentation patterns with those of authentic samples.

B: In a 1 ml quartz cuvette was placed 30.0 mg of **III**, which was then dissolved in 0.5 ml of C_6D_6. Activated 4 Å molecular sieves were added. The cuvette was sealed with a rubber septum and oxygen was bubbled through the solution for 5 min. The cuvette was then placed at the center of a Rayonet photochemical reactor. Oxygen was bubbled into the solution every 10 h, while the solution was irradiated for a total of 80 h. The reaction product was analyzed by GC-MS, and ^{1}H and ^{13}C NMR. Two peaks were observed in the GC having similar retention times of 25.46 and 25.75 min. Both had major peaks in the GC/MS at m/e = 219, 203, 145, 129, 73. In addition to the peak at m/e = 219(100), isotope peaks were detected at 220 (17.8), 221 (5.0) for the first peak and at 220 (16.0), 221 (4.5) for the second peak. In the ^{1}H and ^{13}C NMR spectra of the photolysis reaction product, new peaks were observed for: 1-trimethylsilylacetyl-2-acetylbenzene: ^{1}H (C_6D_6) δ: −0.03 (s, 9H), 0.3 (s, 2H),

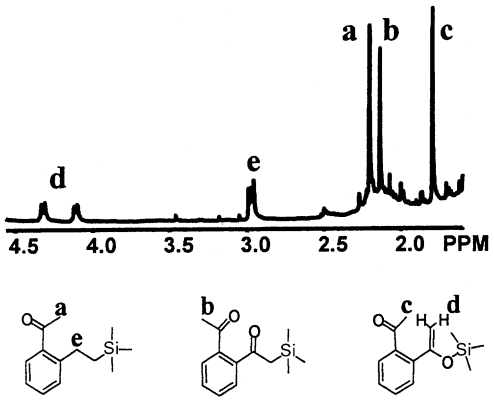

Fig. 5. ^{1}H NMR of the reaction products obtained in the presence of molecular sieves.

2.14 (s, 3H), 6.62–7.52 (4H). ^{13}C NMR ($CDCl_3$) δ: −1.34, 1.01, 29.87, 127.80, 127.95, 130.89, 130.96, 138.61, 139.86 and α-trimethylsiloxy-2-acetylstyrene: ^{1}H (C_6D_6) δ: 0.12 (s, 9H) 1.78 (s, 3H), 4.10 (d, 1H, J = 10 Hz), 4.32 (d, 1H, J = 10 Hz), 6.62–7.52 (4H) (Fig. 5). ^{13}C NMR ($CDCl_3$) δ: −1.05, 30.34, 124.70, 127.61, 127.68, 127.99, 129.11, 129.39, 145.81, 146.19. UV λ_{max} nm (ε): 275 (6067), 242 (15,000). IR ν: 1689 (C=O) cm^{-1}.

*4.6.5. Photolysis of **IV** in the presence of oxygen*

In a 1 ml quartz cuvette was placed 0.45 g of **IV** dissolved in 0.5 ml of pentane. The cuvette was sealed with a rubber septum and oxygen was bubbled through the solution for 5 min. The cuvette was then placed at the center of a Rayonet photochemical reactor. The solution was irradiated for a total of 12 h. It was then irradiated for 1.5 h using a Hanovia medium pressure lamp. The reaction was stopped at intervals and analyzed by GC-MS. A total of seven new peaks were observed during the course of the reaction. Five of these have been identified by comparison of their GC retention time and MS fragmentation pattern with known compounds [24,25]. These are pentamethyldisiloxanol, octamethyltrisiloxane (8%), decamethyltetrasiloxane (90%), 1,2-diacetylbenzene and dodecamethylpentasiloxane (2%) (Fig. 6).

5. Discussion of photochemical results

5.1. Deuterium exchange

On irradiation of **III-B**, **III-D**, **IV-B** or **IV-C** no change

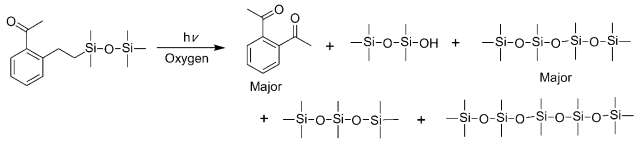

Fig. 6. Reaction of **IV** in the presence of oxygen.

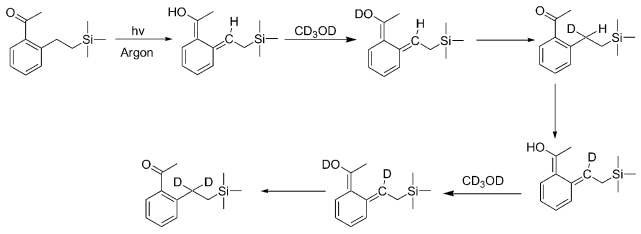

Fig. 7. Deuterium incorporation in **III**.

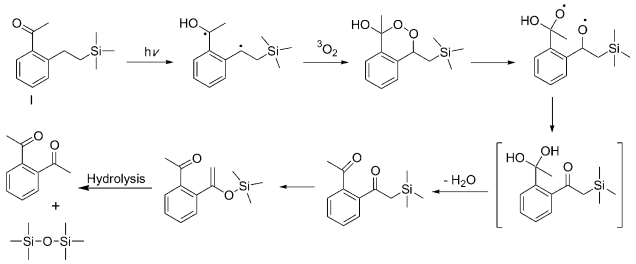

Fig. 8. Formation of α-trimethylsiloxy-2-acetylstyrene and 1,2-diacetylbenzene.

was observed when the reaction was carried out in P-NMR tubes. Since Pyrex cuts off at 300 nm [26], and **III** or **IV** do not have appreciable absorption at $\lambda > 300$ nm, this is expected. On the other hand, after irradiation of methanol-d_4 solutions of **III** or **IV** through quartz under argon (**III-A** or **IV-A**), the ^{1}H NMR indicates a decrease in the resonance associated with benzylic methylene protons by about 50%. For **III-A**, in the ^{13}C NMR, carbon-deuterium coupling is also observed for the α-carbon which gives a triplet (Fig. 3). This is consistent with the fact that the spectra was obtained under broadband proton–carbon decoupling conditions, but not deuterium–carbon decoupling. A second peak was observed for the β-carbon, due to the secondary deuterium-induced isotope effect (Fig. 3) [27]. In the MS, the cluster of peaks around 220 and 205, correspond to d_2, d_1 and d_0 — **III-A**. The decrease in the intensity of the resonance due to the benzylic protons of **III-C** is due to the oxidation of the methylene group.

III can incorporate deuterium by initial formation of an *o*-xylylenol intermediate, followed by OH/OD exchange with methanol-d_4 and finally tautomerization back to the ketone (Fig. 7) [10]. The molecules which have incorporated one deuterium can now undergo further reaction to incorporate a second deuterium.

5.2. Reaction with oxygen

When **III-C** was irradiated with a low pressure mercury lamp, in a Q-NMR or a quartz cuvette saturated with O_2, it showed a decrease of about fifty percent in the intensity of the resonance associated with the benzylic protons (2.80–2.84 ppm). Two new peaks corresponding to hexamethyldisiloxane and 1,2-diacetylbenzene were observed in the GC/MS when the reaction was performed in the absence of 4 Å molecular sieves. The peaks were identified based on their retention times (GC) and fragmentation patterns (MS). When the reaction was performed in the presence of 4 Å activated molecular sieves, two peaks with similar retention time, and $m/e = 219$ were observed. The intensity ratio of these peaks is consistent with the presence of one Si atom, $(C_{12}H_{15}O_2Si)^{+\cdot}$. These are $(M - 15)^+$ ions of 1-trimethylsilylacetyl-2-acetylbenzene and α-trimethylsiloxy-2-acetylstyrene, which arise by loss of a methyl radical from the silyl-center (Fig. 8). In the ^{1}H NMR spectrum a 65% decrease was observed for the resonances associated with the benzylic protons. New peaks were observed, which were assigned to 1-trimethylsilylacetyl-2-acetylbenzene and α-trimethylsiloxy-2-acetylstyrene based on comparison with 1,2-diacetylbenzene and α-trimethylsiloxystyrene [28], respectively. Molecular sieves apparently removed water, which prevented hydrolysis of the α-trimethylsiloxy-2-acetylstyrene to 1,2-diacetylbenzene and hexamethyldisiloxane.

In the case of **IV**, the expected reaction products (1,2-diacetylbenzene and decamethyltetrasiloxane) were observed. During the course of the reaction, pentamethyldisiloxanol was observed which later disappeared. Two other peaks were identified as octamethyltrisiloxane and dodecamethylpentasiloxane based on their mass fragmentation pattern. The remaining, very small, two peaks could not be identified but are presumed to be higher siloxanes formed as a result of secondary reactions.

5.3. Proposed mechanism

These observations may be explained by reaction of oxygen with the 1,4-triplet diradical of **III** (Fig. 8). Similar photochemically generated 1,4-diradicals or thermally generated 1,4-diradicals have been trapped by $^3O_2$ to yield cyclic peroxides [11,29]. The O–O bond of the cyclic peroxides can open to a pair of alkoxy radicals. Intramolecular α-hydrogen abstraction by the hydroxy alkoxy radical via a six-membered ring transition state yields trimethylsilylacetyl-2-(1′,1′-dihydroxyethyl)benzene, which loses water to give 1-trimethylsilylacetyl-2-acetylbenzene. Silyl tautomerization converts this to a silyl enol ether. α-Trimethylsilyl ketones are known to easily rearrange to isomeric trimethylsilyl enol ethers [30–32]. Finally, hydrolysis of the silyl enol ether, due to adventitious water and water generated in situ, leads to 1,2-diacetylbenzene and hexamethyldisiloxane. In the presence of molecular sieves, the water generated in the reaction is trapped, and hence 1-trimethylsilylacetyl-2-acetylbenzene and α-trimethylsiloxy-2-acetylstyrene are observed (Fig. 8).

A decrease in molecular weight by half was observed on irradiation of **II** through quartz in the presence of oxygen. The central acetophenone unit absorbs UV radiation, generates a 1,4-diradical by hydrogen abstraction. The 1,4-diradical reacts with oxygen to form cyclic peroxide. The cyclic peroxide undergoes further reaction, leading to cleavage of the polymer to half the initial molecular weight.

Water generated in situ plays an integral role in the hydrolysis of the silyl enol ether intermediate. The final reaction product is quenched with hexamethyldisilazane, which silylates the α-(trimethylsiloxy)-ω-(dimethylsiloxanol)polydimethylsiloxane which is formed as a result of polymer cleavage. The mechanism proposed for the photo-oxidative polymer degradation is similar to that outlined (Fig. 8).

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