Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Photoinitiators with Functional Groups. Part II. Silicon-Containing Photoinitiators

A. Kolar[a]; H. F. Gruber[a]; G. Greber[a]
[a] Institute of Chemical Technology of Organic Materials Vienna University of Technology, Vienna, Austria

To cite this Article Kolar, A. , Gruber, H. F. and Greber, G.(1994) 'Photoinitiators with Functional Groups. Part II. Silicon-Containing Photoinitiators', Journal of Macromolecular Science, Part A, 31: 3, 305 — 318
To link to this Article: DOI: 10.1080/10601329409351520
URL: http://dx.doi.org/10.1080/10601329409351520

J.M.S.—PURE APPL. CHEM., A31(3), pp. 305–318 (1994)

PHOTOINITIATORS WITH FUNCTIONAL GROUPS. PART II. SILICON-CONTAINING PHOTOINITIATORS†

A. KOLAR, H. F. GRUBER,* AND G. GREBER‡

Institute of Chemical Technology of Organic Materials
Vienna University of Technology
Getreidemarkt 9/162, 1060 Vienna, Austria

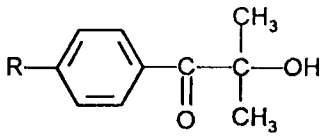
ABSTRACT

The new photoinitiators (PIs) 1-(4-dimethylsilyl)phenyl-2-hydroxy-2-methyl-propan-1-one (**8a**) and 1-(4-dimethylsilyl)phenyl-2-methoxy-2-methyl-propan-1-one (**8b**) have been synthesized by Grignard reaction of 4-dimethylsilylphenylmagnesium chloride (**5**) with protected acetone cyanohydrins. The photoactivity of **8a** was similar to the most efficient commercial hydroxyalkylphenone 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) whereas **8b** exhibits even higher efficiency. **8a** and **8b** were reacted with allyl alcohol, allyl amine, vinyl acetic acid, 3-allyloxypropane-1,2-diol, allyl glycidyl ether, polybutadiene, and a vinyl polysiloxane to yield new functional PIs of high activity. Thus, hydrosilation reactions of the new PIs enable the preparation of a variety of functional derivatives usable in different UV-curable systems.

INTRODUCTION

The synthesis of new, highly efficient photoinitiators (PIs) has received growing interest in recent years, stimulated by the increased industrial application of UV curing as well as by the development of new UV-curable resin systems [1–5].

†For Part I, see this Journal, A28(9), 925 (1991).
‡Deceased February 1993.



R = H (DAROCUR 1173), $(CH_3)_2CH$-, $(CH_3)_3C$, $C_{12}H_{25}$-, HO-, CH_3O-, $HOCH_2CH_2O$- (DAROCUR 2959), $(CH3)_2N$-, CH_3S-

SCHEME 1.

We recently reported the preparation and characterization of new polymerizable and polymer PIs exhibiting excellent reactivity and high migration stability [6]. In continuation of this work we were interested in new PIs containing functional groups capable of reacting with resin components, thus enabling covalent incorporation into the cured coating. Besides, the compatibility of functional PIs with various photocurable compositions can be adjusted easily by introduction of appropriated residues.

Among the industrially important PIs, α-hydroxyalkylphenones enjoy widespread usage in many applications due to their exceptional reactivity, storage stability, and low yellowing of the cured coatings. The basic compound 2-hydroxy-2-methyl-1-phenyl-propanon-1-one (HMPP, Darocur 1173, Ciba Geigy Co., Scheme 1) was shown to be one of the most efficient PIs of this class. In addition, substituted HMPPs have been described but only a few of them are commercially available [5, 7–11]. Substituents in the 4-position of the phenyl residue influence the solubility and the photoactivity in various formulations. Generally, the efficiency of HMPP derivatives containing alkyl substituents such as isopropyl, *tert*-butyl, and *n*-dodecyl residues or methoxy groups was found to be slightly diminished, whereas the introduction of functional groups such as HO—, $HOCH_2CH_2O$— (Darocur 2959), CH_3S—, or $(CH_3)_2N$— resulted in a drastic decrease of the photoinitiating efficiency [7, 12–15]. So far, no improvement of the photoactivity of HMPP has been achieved by any substituent.

Other coreactive PIs based on α-hydroxyalklphenones, benzildimethylketals, and thioxanthones containing functionalities such as allyloxy, epoxy, amino, or isocyanate groups have also been claimed, but only a few experimental details concerning the synthesis and reactivity of these PIs are available [16].

In this paper we describe the synthesis and characterization of α-hydroxyalkylphenones containing H—Si groups. This functional group is of special interest with respect of its influence on the photoinitiating activity of the basic structure. In addition, it enables versatile derivatizations by hydrosilation reactions of unsaturated compounds, resulting in new functional PIs as well as covalent incorporation into silicone-based resins.

EXPERIMENTAL

The solvents were dried and purified by common methods. A solution of 0.25 mol/L H_2PtCl_6 in 2-propanol was used as catalyst for the hydrosilation reactions.

2-Methyl-2-(2-tetrahydropyranyloxy)propionitril (**6a**)[18] and 2-methoxy-2-methylpropionitril (**6b**) [19] were prepared by known procedures.

4-Chlorophenyldimethylsilane (4)

From 4-chlorophenyldimethyl-chlorosilane (**3**) [17]: A solution of 59 g (0.4 mol) 1,4-dichlorobenzene (**1**) in 170 mL THF was added slowly under nitrogen to a stirred mixture of 12 g (0.49 mol) Mg, 1 mL 1,2-dibromoethane, and 30 mL THF, keeping the reaction mixture under reflux. After 6 hours the solution was filtered under nitrogen and the yield was evaluated by hydrolysis and titration of a 1-mL aliquot with 0.1 N HCl. Yield: 0.35 mol **2**/200 mL THF.

The Grignard-solution **2** was dropped under nitrogen within 2 hours to a solution of 51.2 g (0.40 mol) dichlorodimethylsilane in 200 mL THF at 0°C. The mixture was heated to room temperature and refluxed for 4 hours. The mixture was filtered, the solvent was removed under reduced pressure, and the residue was fractionated. Yield: 35.8 g (0.18 mol) **3** (50%); bp 102–104°C/12 mm.

A solution of 4.2 g (0.11 mol) $LiAlH_4$ in 100 mL THF was added to a solution of 80 g (0.39 mol) **3** in 50 mL THF at reflux temperature and stirred for 1 hour. The mixture was cooled and poured into dilute H_2SO_4 at 0°C. The organic phase was separated, washed with water, and dried over NA_2SO_4. The solvent was removed under reduced pressure and the residue was fractionated. Yield: 54.6 g (0.32 mol) **4** (82%); overall yield based on **2**, 40%; bp 42–43°C (0.03 mm).

From 4-chlorophenylmagnesium chloride (**2**): A solution of 0.315 mol **2** in 200 mL THF was added to a solution of 33.1 g (0.35 mol) chlorodimethylsilane in 300 mL THF at 0°C. The reaction mixture was then stirred at 20°C and refluxed for 4 hours. The salts were filtered and the solvent removed under reduced pressure. The residual product was distilled. Yield: 40.3 g (0.236 mol) **4** (75%); bp 42–43°C (0.03 mm).

4-Dimethylsilylphenylmagnesium Chloride (5)

A solution of 40 g (0.234 mol) **4** in 170 mL THF was added slowly to a stirred mixture of 6.6 g (0.271 mol) Mg, 1 mL dibromoethane, and 30 mL THF at a rate to maintain gentle boiling of the reaction mixture. The mixture was stirred 6 hours under reflux and filtered under nitrogen. The yield was evaluated by hydrolysis and titration of a 1-ml aliquot with 0.1 N HCl. Yield: 0.233 mol **5** (98%).

2-Hydroxy-2-methyl-1-(4-dimethylsilyl)phenyl-propan-1-one (8a)

To a precooled solution (−15 to −20°C) of 39.6 g (0.234 mol) **6a** in 200 mL THF a Grignard solution of 0.211 mol **5** in 200 mL THF was added slowly and stirred for 4 hours with cooling. The reaction mixture was refluxed for 3 hours, cooled, and poured into 300 mL ice water. After adjusting the pH to 3 with 50%

HCl, the mixture was stirred at 45°C for 30 hours. The phases were separated, and the aqueous phase was extracted several times with diethylether. The combined organic phases were washed with water and dried over Na_2SO_4. The solvents were removed under reduced pressure, and the residual oil was purified by distillation. Yield: 16.6 g (0.075 mol) **8a** (35%); bp 100–102°C/0.03 mm.

IR (cm^{-1}): 879 (Si—C), 1630, 2112 (H—Si), 2870–2964, 3083, 3462.

^1H NMR ($CDCl_3$, ppm): 0.2–0.5 (d, 6H, Si—CH_3), 2.4–2.8 (s, 6H, CH_3), 4.3–4.6 (m, 1H, H—Si), 4.8 (s, 1H, OH), 7.5–8.3 (m, 4H, Ar—H).

Elemental analysis. Calculated C, 64.82%; H, 8.14%. Found: C, 65.05%; H, 8.24%.

2-Methoxy-2-methyl-1-(4-dimethylsilyl)phenyl-propan-1-one (8b)

To a precooled solution (−15 to −20°C) of 25.0 g (0.252 mol) **6b** in 100 mL THF Grignard solution of 0.226 mol **5** in 200 mL THF was added slowly within 2 hours. The reaction mixture was stirred at 60°C for 6 hours, cooled, and poured into 300 mL ice water. After adjusting the pH to 3 with 50% HCl, the mixture was stirred for 30 minutes. The phases were separated, and the aqueous phase was extracted several times with diethylether. The combined organic phases were washed with water and dried over Na_2SO_4. The solvents were removed under reduced pressure, and the residual oil was purified by distillation. Yield: 19 g (0.080 mol) **8b** (36%); bp 78–80°C/0.007 mm.

IR (cm^{-1}): 879 (Si—C), 1676, 2123 (H—Si), 2827–2988, 3057–3070.

^1H NMR ($CDCl_3$, ppm): 0.4 (d, 6H, Si—CH_3), 1.5 (s, 6H, C—CH_3), 3.2 (s, 3H, OCH_3), 4.5 (m, 1H, H—Si), 7.6–8.3 (m, 4H, Ar—H).

Elemental analysis. Calculated C, 66.09%; H, 8.53%. Found: C, 66.42%; H, 8.61%.

Allyloxytrimethylsilane (10a), 3-Allyloxy-bis(1,2-trimethylsilyloxy)-propandiol (10b) and Vinyl Acetic Acid Trimethylsilylester (10d)

The TMS protected derivatives **10a**, **10b**, and **10d** were prepared according to general procedures for the silylation of alcohols [20–22]. A solution of trimethylchlorosilane in *n*-hexane was added slowly with stirring at 40°C to a solution of the alcohol or acid in formamide and pyridine. The mixture was stirred for 6 hours, and then the hexane phase was separated and distilled.

10a: 30 g (0.52 mol) allylalcohol (**9a**), 61.6 g (0.57 mol) trimethylchlorosilane, 100 mL *n*-hexane, 100 mL formamide, 40 mL pyridine. Yield: 41.3 g (0.32 mol) **10a** (62%); bp 98–99°C.

10b: 50 g (0.38 mol) 3-allyloxy-1,2-propandiol (**9b**), 82.2 g (0.75 mol) trimethylchlorosilane, 150 mL *n*-hexane, 100 mL formamide, 60 mL pyridine. Yield: 80.4 g (0.29 mol) **10b** (77%); bp 80–81°C/3 mm.

10d: 34.4 g (0.4 mol) vinylacetic acid (**9d**), 45.6 g (0.42 mol) trimethylchlorosilane, 100 mL *n*-hexane, 100 mL formamide, 33 mL pyridine. Yield: 45.4 g (0.29 mol) **10d** (72%); bp 43–44°C/12 mm.

N-Allyltrimethylsilylamine (10c)

A mixture of 28.6 g (0.50 mol) allylamine (**9c**), 40.35 g (0.25 mol) bis-(trimethylsilyl)amine, and 0.5 g ammonium sulfate was refluxed for 6 h. The precipitate was filtered under nitrogen, and the product was obtained by fractional distillation. Yield: 35.6 g (0.28 mol) **10c** (55%); bp 113–115°C.

2-Methoxy-2-methyl-1-[4-(3-hydroxypropyl)dimethylsilyl]-phenyl-propan-1-one (11a)

A mixture of 5 g (0.02 mol) **8b**, 20 g **10a**, and 30 μL of H_2PtCl_6 solution was heated to 110°C in an autoclave for 6 hours. The excess of **10a** was distilled, yielding a residue that contained 28% of the hydrosilation product (GC analysis). The residue was stirred with a mixture of 10 mL methanol and 1 mL water at 45°C for 4 hours. The solvent was removed by distillation, and the product was purified by column chromatography on silica gel 60 using petrol ether/ethyl acetate 2:1 as eluent. Yield: 0.97 g (0,003 mol) **11a** (25%).

IR (cm^{-1}): 1676, 2831–2937, 3057–3070, 3375.

^1H NMR ($CDCl_3$, ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H CH_2—Si)1.5 (s, 6H, C—CH_3), 1.6 (m, 2H, C—CH_2—C), 1.8 (s, 1H, OH), 3.2 (s, 3H, OCH_3), 3.6 (t, 2H—CH_2—OH), 7.6–8.3 (m, 4H, Ar—H).

Elemental analysis. Calculated: C, 65.25%; H, 8.90%. Found: C, 65.52%; H, 9.06%.

2-Methoxy-2-methyl-1-[4-(2,3-dihydroxy-1-propoxy)propyl-dimethylsilyl]phenyl-propan-1-one (11b)

30 μL H_2PtCl_6 solution was added to a solution of 5 g (0.021 mol) **8b** and 6.36 g (0.023 mol) **10b** in 30 mL toluene, and the reaction mixture was refluxed for 6 hours. The solvent was removed under reduced pressure, yielding a residue that contained 84% hydrosilation product (GC analysis). The residue was stirred with a mixture of methanol/water 10:1 at 45°C for 4 hours. After filtration the solvent was distilled under reduced pressure, yielding 4.35 g (76%) **11b** as a raw product.

Purification of crude **11b** by column chromatography (silica gel 60, acetone/chloroform 3:1) gave **11b** and the ketal **12**. 0.3 g of **12** was stirred with 3 mL 50% HCl at 20°C for 1 hour. The reaction mixture was extracted with diethylether. The organic phase was washed with water and dried over Na_2SO_4. The solvent was removed by distillation. Yield: 0.22 g **11b** (82%).

IR (cm^{-1}): 1676, 2827–2984, 3057–3070, 3422.

^1H NMR ($CDCL_3$, ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H, CH_2—Si), 1.3 (s, 2H, OH), 1.5 (s, 6H, C—CH_3), 1.6 (m, 2H, C—CH_2—C), 3.2 (s, 3H, OCH_3), 3.4 (m, 4H, CH_2—O—CH_2), 3.7 (m, 2H, HO—CH_2), 3.8 (m, 1H, CH_2—CHOH), 7.6–8.3 (m, 4H, Ar—H).

Ketal **12**: ^1H NMR (ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H, CH_2—Si), 1.3 + 1.4 (s, 6H, CH_3—C—CH_3), 1.5 (s, 6H, C—CH_3), 1.6 (m, 2H, C—CH_2—C), 3.2 (s, 3H, OCH_3), 3.4 (m, 4H, CH_2—O—CH_2), 3.7 + 4.0 (t, 2H, O—CH_2—CH—), 4.3 (m, 1H, CH_2—CH—O), 7.6–8.3 (m, 4H, Ar—H).

2-Methoxy-2-methyl-1-[4-(3-amino-1-propyl)dimethylsilyl]-phenyl-propan-1-one (11c)

30 μL H_2PtCl_6 solution was added to a solution of 5 g (0.021 mol) **8b** and 3.0 g (0.023 mol) **10c** in 30 ml toluene, and the reaction mixture was refluxed for 15 hours. The solvent was removed under reduced pressure, yielding 3.65 g crude hydrosilation product **11c** which was stirred with 22 mL of a mixture of methanol/water 10:1 at 50°C for 6 hours. The amine was treated with 2 N HCl and, after neutralization with $NaHCO_3$, **11c** was extracted with ethyl acetate. The solvent was removed under reduced pressure. Yield: 2.24 g **11c** (76%).

IR (cm^{-1}): 1676, 2831-2984, 3057-3070, 3402, 3495.

^1H NMR ($CDCl_3$, ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H, CH_2—Si), 1.5 (s, 6H, C—CH_3), 1.5 (m, 2H, C—CH_2—C), 2.0 (t, 2H, CH_2—NH_2), 2.7 (s, 2H, NH_2), 3.2 (s, 3H, OCH_3), 7.6-8.3 (m, 4H, Ar—H).

1 g **11c** was dissolved in 20 mL diethylether and treated with HCl gas at 30°C. On cooling to 0-5°C, the hydrochloride **13** crystallized. Yield: 0.83 g **13** (74%).

Elemental analysis. Calculated (2.2% HCl): C, 56.9%; H, 8.43%; N, 4.15%. Found: C, 57.04%; H, 8.37%; N, 4.38%.

4-[4-(2-Methoxy-2-methyl-1-oxo-propyl)phenyl-dimethylsilyl]butanoic Acid (11d)

30 μL H_2PtCl_6 solution was added to a solution of 5 g (0.021 mol) **8b** and 3.64 g (0.023 mol) **10d** in 25 mL toluene, and the reaction mixture was refluxed for 6 hours. The solvent was removed under reduced pressure, yielding a residue that contained 68% hydrosilation product (GC analysis). 5.89 g (0.015 mol) of the residue was stirred with a mixture of methanol/water 10:1 at 50°C for 1 hour. After filtration the solvent was distilled under reduced pressure, yielding an oil which crystallized at 20°C. Yield: 4.25 g (0.013 mol) **11d** (88%); mp 62-63°C.

IR (cm^{-1}): 1680, 1712, 2798-2987, 3057-3070, 3200.

^1H NMR ($CDCl_3$, ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H, CH_2—Si), 1.5 (s, 6H, C—CH_3), 1.7 (m, 2H, C—CH_2—C), 2.4 (t, 2H, CH_2—COOH), 3.2 (s, 3H, OCH_3), 7.6-8.3 (m, 4H, Ar—H).

Elemental analysis. Calculated: C, 62.27%; H, 8.18%. Found: C, 62.19%; H, 8.06%.

2-Methoxy-2-methyl-1-[4-(3-oxiranylmethoxy-1-propyl)-dimethylsilyl]phenyl-propan-1-one (15)

30 μL H_2PtCl_6 solution was added to a solution of 5 g (0.021 mol) **8b** and 2.7 g (0.023 mol) **14** in 30 mL toluene, and the reaction mixture was refluxed for 6 hours. After filtration the solvent was distilled under reduced pressure, yielding a yellow oil. Yield: 7.06 g **15** (98%).

IR (cm^{-1}): 1676, 2827-2937, 3057-3070.

^1H NMR ($CDCl_3$, ppm): 0.4 (s, 6H, Si—CH_3), 0.8 (t, 2H, CH_2—Si), 1.5 (s, 6H, C—CH_3), 1.6 (m, 2H, C—CH_2—C), 2.6 (t, 1H, CH_2—oxirane), 2.8 (t, 1H, CH_2—oxirane), 3.1-3.7 (m, 3H, CH—oxirane, CH_2—oxirane), 3.2 (s, 3H, OCH_3), 3.4 (t, 2H, O—CH_2—CH_2), 7.6-8.3 (m, 4H, Ar—H).

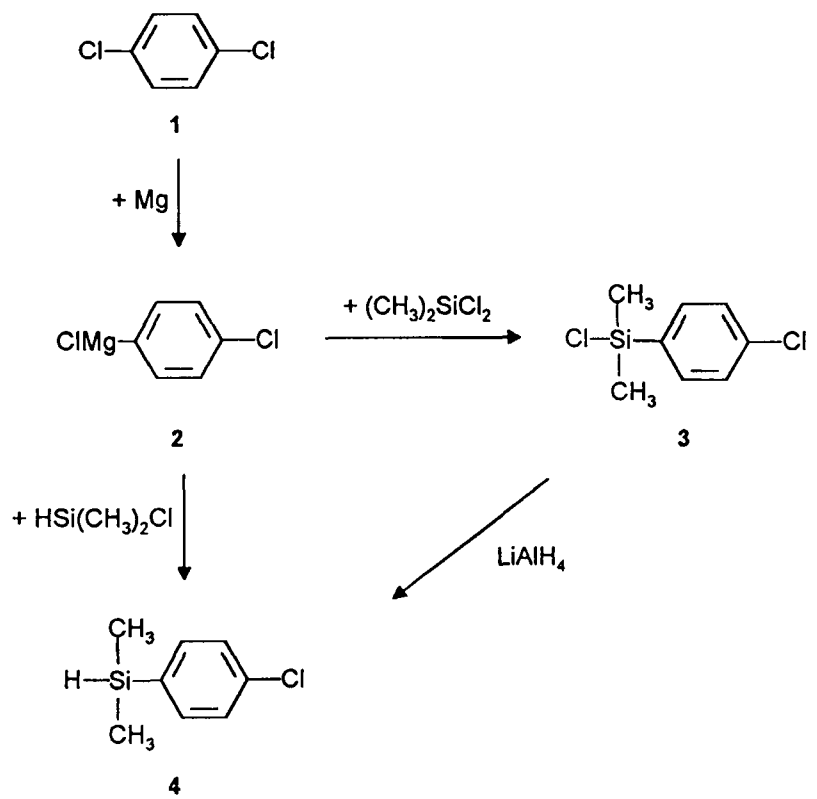
TABLE 1. Photoinitiating Activity of the PIs[a]

	Hardness [s][b] at speed of band conveyer (m/min)[a] of					
	2.5	3.75	5.0	7.5	10.0	15.0
Darocur 1173	209	207	204	198	190	188
8a	210	211	208	206	200	202
8b	216	213	214	209	209	204
11a	208	–	206	–	193	–
11b	203	–	205	–	198	–
11c[c]	190	–	183	–	175	–
11d[c]	183	–	174	–	168	–
15	213	–	211	–	208	–
17[c]	153	–	108	–	96	–
19[c]	180	–	175	–	103	–

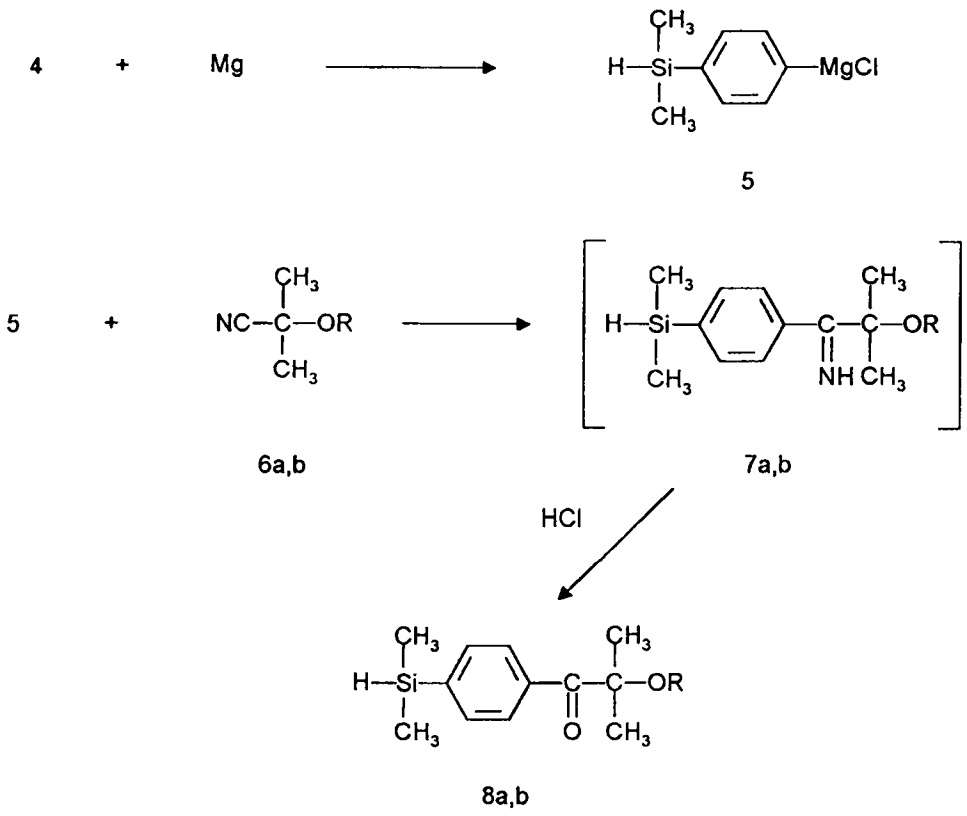
[a]Films were cured on glass slides passing the radiation source on a conveyer band at various speeds, thus varying the dose of radiation.

[b]Hardness (DIN 53157) of cured films based on 2.5% PI in Epoxyacrylate Laromer EA 81 (BASF), UV-radiation 80 W/cm.

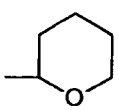
[c]PI not completely soluble in the test mixture.



SCHEME 2.



6a, 7a R =



6b, 7b, 8b R = CH3

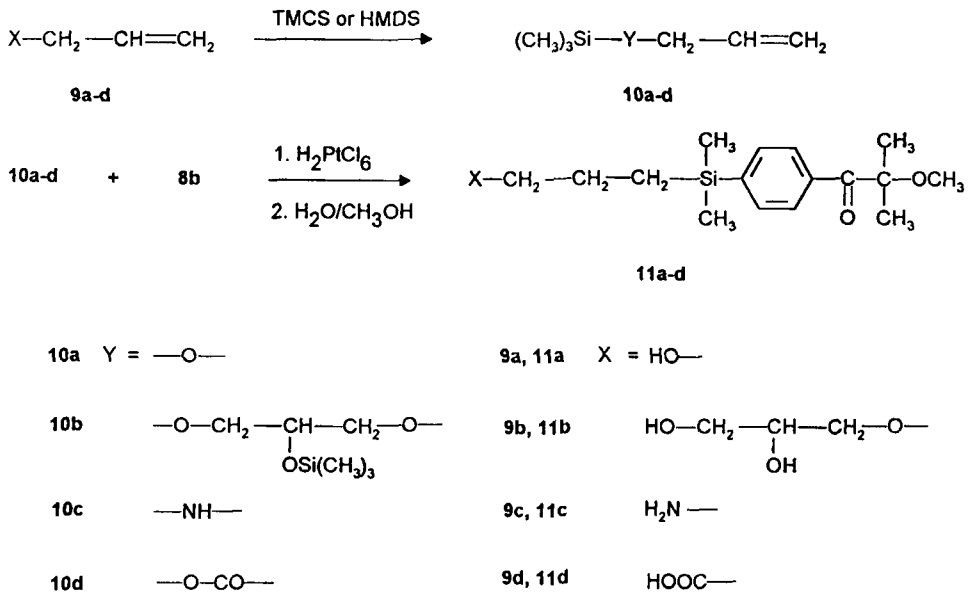
8a R = H

SCHEME 3.

Elemental analysis. Calculated: C, 65.10%; H, 8.62%. Found: C, 65.50%; H, 8.76%.

Hydrosilation of Polybutadiene

1 g (0.018 mol) polybutadiene (Buna France CB 35 NF) and 4.7 g (0.022 mol) **8a** in 40 mL xylene were heated to 100°C. After addition of 0.16 mL H_2PtCl_6 solution, the mixture was heated to 130°C. Within 55 hours 0.3 mL H_2PtCl_6 solution was added in three portions. The solution was filtered precipitated two times in an excess methanol. Yield: 1.8 g **17**.



SCHEME 4.

IR (cm^{-1}): 881 (Si—CH), 1674 (C=O), 3474 (OH).

5.5 g (0,093 mol) polybutadiene was reacted with 3.9 g (0.018 mol) **8a** in a similar manner and precipitated in excess tetrahydrofurane, yielding 6.9 g **17**.

Preparation of Poly(Dimethyl/methylvinyl)siloxane (18)

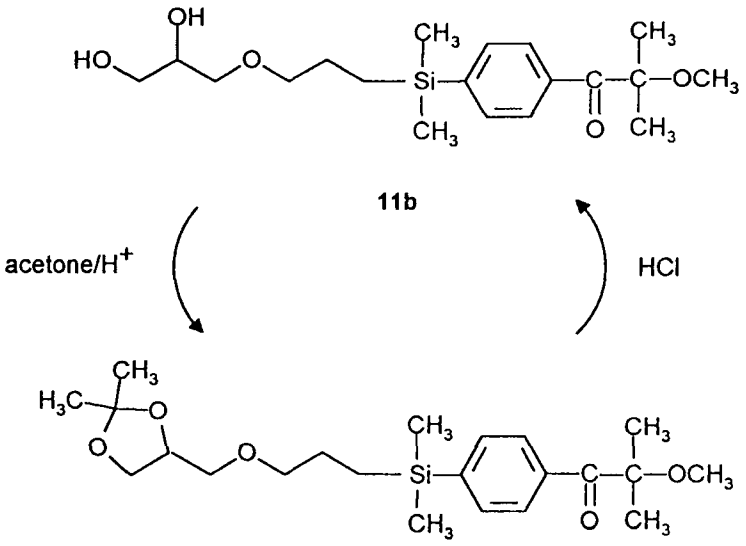
A mixture of 32.3 g (0.25 mol) dimethyldichlorosilane and 35.3 g (0.25 mol) methylvinyldichlorosilane was dropped at 20°C into 125 mL water with stirring. The organic phase was extracted with diethylether, washed with water, and dried over Na_2SO_4. The solvent was removed under reduced pressure, yielding 38 g crude oligosiloxanes. The residue was mixed with 1.2 g hexamethyldisiloxane, 3 g acid-treated clay, and stirred at 20°C for 14 hours and at 140°C for 8 hours. After filtration the poly(dimethyl/methylvinyl)siloxane **18** was extracted with methanol and dried under reduced pressure. Yield: 31.5 g **18**, 0.0076 mmol vinyl groups/g.

Hydrosilation of 18

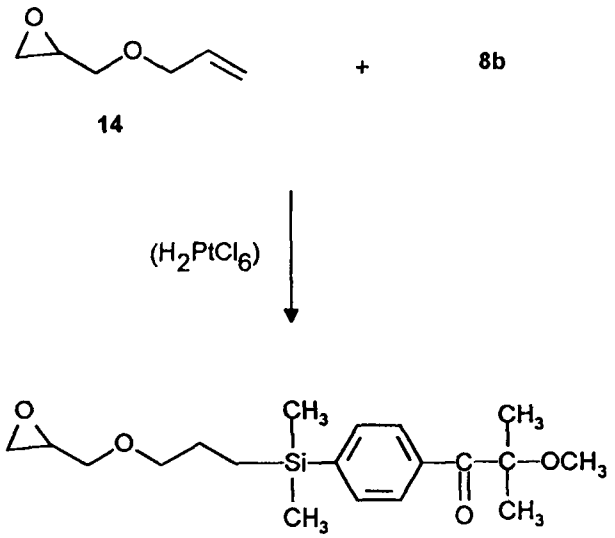
A mixture of 2 g (0.015 mol) **18**, 1.7 g (0.0076 mol) **8a**, 0.1 mL H_2PtCl_6 solution, and 8 mL toluene was stirred at 90°C for 1 hour. After filtration the reaction mixture was dissolved in chloroform and precipitated two times in an excess of petroleum ether. Yield: 1.9 g **19**.

IR (cm^{-1}): 810 and 1080 (Si—O), 1616 (C=C), 1668 (C=O), 3474 (OH).

Elemental analysis. Calculated: C, 48.75%; H, 9.80%. Found: C, 48.44%; H, 9.63%.



SCHEME 5.



SCHEME 6.

Test Methods

The PIs were tested by Merck Co. using a standard method and compared with Darocur 1173. Films (50 μm) on glass plates were prepared using a solution of 2.5% PI in a resin based on epoxacrylates (Laromer EA 81, BASF) and 1,6-hexanedioldiacrylate. The glass plates were placed on a conveyor belt and the coatings were hardened by two 80 W/cm lamps. The radiation dose could be regulated by the speed of the conveyor belt. The hardness of the cured films (DIN 53157) is a measure of the photoactivity. The results are summarized in Table 1.

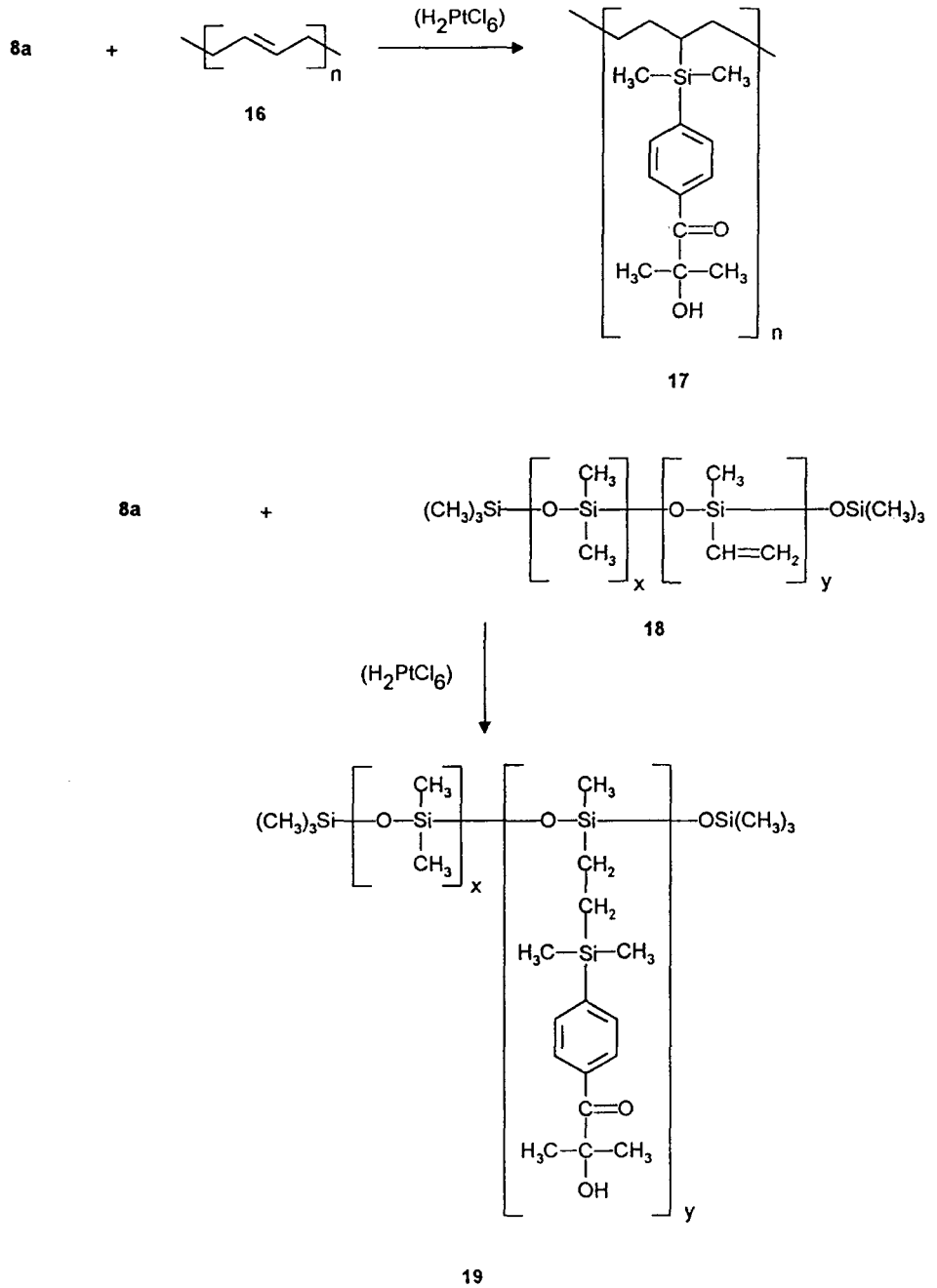
In addition, photo-DSC was used to test **8a** and **8b** in a silicone acrylate resin (Tego RC 300) by measuring the maximum heat flow upon irradiation with a Perkin-Elmer photocalorimeter DPA 7. Irradiation was started after 1.0 minutes, and the onset of heat flow was found to be at 1.017 and 1.015 minutes for **8a** and **8b** and 1.023 minutes for HMPP. The peak shape was almost identically in all cases.

Analysis

^{1}H-NMR spectra were recorded on a Jeol JNM-PX 60 spectrometer using TMS as internal standard. IR spectra were recorded on a Nicolet FT-IR-5 spectrometer.

RESULTS AND DISCUSSION

4-Chlorophenyldimethylsilane (**4**) was prepared by reaction of 4-chlorophenylmagnesium chloride (**2**) with dimethylchlorosilane and subsequent reduction of 4-



SCHEME 7.

chlorophenyldimethylchlorosilane (**3**) with lithium aluminium hydride [17]. By a new one-step reaction of **2** with chlorodimethylsilane, **4** was obtained in a nearly twofold overall yield of 75% (Scheme 2).

Grignard reaction of **4** gave 4-dimethylsilylphenylmagnesiumchloride (**5**) which was reacted with dihydropyran-protected acetone cyanohydrine (**6a**) to yield the imine **7a**. By hydrolysis of **7a**, the PI 2-hydroxy-2-methyl-1-(4-dimethylsilyl)-phenyl-propan-1-one (**8a**) was obtained without isolation of **7a**. Another PI, 2-methoxy-2-methyl-1-(4-dimethylsilyl)phenyl-propan-1-one (**8b**) was synthesized by a similar procedure using the methyl ether of acetone cyanohydrin **6b** (Scheme 3).

Based on **8b** as a reactive H—Si-containing PI, some other functional PIs were synthesized by hydrosilation of allyl alcohol (**9a**), 3-allyloxypropane-1,2-diol (**9b**), allylamine (**9c**), and vinyl acetic acid (**9d**). **9a–d** were reacted first with trimethylchlorosilane or bis-(trimethylsilyl)amine to give the protected derivatives **10a–d**. Hydrosilation of **10–d** with **8b** in the presence of H_2PtCl_6 solution as catalyst yielded the trimethylsilyl (TMS) derivatives which were converted without isolation to the functional PIs **11a–d** by hydrolysis with methanol/water (Scheme 4).

The alcohol **11a** was purified by column chromatography, and the carboxylic acid **11d** by crystallization. Purification of the diol **11b** could be achieved only by column chromatography with chloroform/acetone as eluent, yielding the ketal **12** which was separated and hydrolyzed with dilute HCl to give pure **11b**. The amine **11c** was purified by crystallization of its hydrochloride **13** which was subsequently reconverted to the amine by treatment with alkali (Scheme 5).

The epoxide PI 2-methoxy-2-methyl-1-[4-(3-oxiranylmethoxy-1-propyl)dimethylsilyl]phenyl-propan-1-one (**15**) was obtained in 98% yield by hydrosilation of allyl glycidyl ether (**14**) with **8b** (Scheme 6).

Polymers containing PI residues were prepared by addition of **8a** to polybutadiene (**16**) as well as to a poly(dimethyl/vinyl-methyl)siloxane (**18**) yielding **17** and **19**, respectively (Scheme 7). The addition of **8a** to **16** required long reaction times due to steric hindrance of the C=C double bonds in the main chain.

The photoinitiating activity of the new PIs has been compared by a standard method with 2-hydroxy-2-methyl-1-phenyl-propan-1-one (HMPP, Darocur 1173, Ciba Geigy Co.) [5, 9]. Films based on mixtures of the PIs with epoxyacrylates were irradiated under standard conditions, and the curing efficiency was estimated by measuring the hardness of cured films after various irradiation times. In addition, **8a** and **8b** were tested by measuring the maximum heat flow upon irradiation (Photo-Differential-Scanning-Calorimetry).

The tests demonstrated similar efficiencies of **8a** and HMPP, whereas **8b** exhibited even higher photoactivity than the standard PI (Table 1), presumably because of the higher activity of the basic methyl ether of HMPP [15]. Similar high efficiencies were obtained with **11a**, **11b**, and **15**. The functional PIs **11c** and **11d** as well as the polymer PIs **17** and **19** exhibited somewhat less photoactivity due to less solubility in the resins. Preliminary photo-DSC tests in silicone-acrylate compositions indicated that both **8a** and **8b** were more effective than HMPP.

These results demonstrate that the H—Si-containing PIs **8a** and **8b** are characterized by high photoinitiating activity, surpassing some of the most efficient PIs based on hydroxyalklyphenones. Advantageously, these PIs can be incorporated covalently into silicones as well as in other formulations containing C=C double bonds by hydrosilation. In addition, hydrosilation reactions of these PIs enable the preparation of a variety of functional derivatives usable in different UV-curable systems.

ACKNOWLEDGMENT

Support for this work by Merck Co., Darmstadt, is gratefully acknowledged.

REFERENCES

[1] R. K. Dietliker, *Chemistry & Technology of UV and EB Formulation for Coatings, Inks & Paints, Vol. 3, Photoinitiators for Free Radical and Cationic Polymerisation*, SITA Technology Ltd., Gardiner House, Broomhill Road, London, UK, 1991, p. 141.
[2] H. F. Gruber, *Prog. Polym. Sci., 17*, 953 (1992).
[3] P. P. Fouassier, *Prog. Org. Coat., 18*, 229 (1990).
[4] N. S. Allan and M. Edge, *J. Oil Colour Chem. Assoc., 73*, 438 (1990).
[5] J. Ohngemach, K. H. Neisius, J. Eichler, and C. P. Herz, *Merck Kontakte, 3/79*, 37 (1979).
[6] R. Klos, H. Gruber and G. Greber, *J. Macromol. Sci.—Chem., A28*(9, 925 (1991).
[7] J. Ohngemach, K. H. Neisius, J. Eichler, and C. P. Herz, *Merck Kontakte (Darmstadt), 3/80*, 15 (1979).
[8] R. Kirchmayr, G. Berner, R. Huesler, and G. Rist, *Farbe Lack, 88*, 910 (1982).
[9] C. P. Herz and J. Eichler, *Ibid., 85*, 933 (1979).
[10] M. Köhler, J. Ohngemach, and G. Wehner, DE 3,512,179 (1986), assigned to Merck GmbH.
[11] M. Köhler, J. Ohngemach, G. Wehner, and J. Gehlhaus, EP 216,884 (1985), assigned to Merck GmbH.
[12] W. Bäumer, *Merck Kontakte (Darmstadt), 42*(3) (1989).
[13] J. P. Fouassier, D. J. Lougnot, G. Li Bassi, and C. Nicora, *Polym. Commun., 30*, 245 (1989).
[14] J. Ohngemach, M. Köhler, and G. Wehner, *Proc. Conf. RadTech Europe; Florence, Italy*, p. 639 (1989).
[15] L. Felder, R. Kirchmayr, and R. Hüsler, U.S. Patent 4,321,118 (1982), assigned to Ciba Geigy Corp.
[16] M. Köhler, J. Ohngemach, E. Poetsch, R. Eidenschink, G. Greber, D. Dorsch, J. Gehlhaus, K. Dorfner, and H. Hirsch, EP 281,941, assigned to Merck GmbH.
[17] A. Balciunas, *Makromol. Chem., 71*, 62 (1964).
[18] I. Elphimoff-Felkin and M. Verrier, *Bull. Soc. Chim. France 3*, 1047 (1967).
[19] R. A. Navolokina and E. N. Zil'bermann, *J. Org. Chem. USSR, 16*(2), 1382 (1980).
[20] F. A. Henglein and K. Scheinost, *Makromol. Chem., 21*, 59 (1956).
[21] F. A. Henglein, G. Abelsnes, H. Henika, K. Lienhard, P. Nakhre, and K. Scheinost, *Ibid., 24*, 1 (1967).
[22] J. L. Speier, R. Zimmermann, and J. Webster, *J. Am. Chem. Soc., 178*, 2278 (1956).

Received April 26, 1993
Revision received June 21, 1993