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PHOTOCHEMICALLY GENERATED SILICON—CARBON DOUBLE-BONDED INTERMEDIATES

V *. PHOTOLYSIS OF ARYLPENTAMETHYLDISILANES IN THE PRESENCE OF CARBONYL COMPOUNDS

MITSUO ISHIKAWA, TAKAMASA FUCHIKAMI and MAKOTO KUMADA
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University Kyoto 606 (Japan)

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Summary

The reaction of silicon—carbon double-bonded intermediates (A) generated by photolysis of arylpentamethyldisilanes (aryl = Ph, *p*-tolyl or *p*-t-butylphenyl) with a variety of carbonyl compounds has been studied. Both enolizable and non-enolizable ketones reacted with A to give 2-trimethylsilyl(alkoxydimethylsilyl)benzene derivatives as the sole volatile product. α,β-Unsaturated carbonyl compounds, such as methyl vinyl ketone and acrolein, also reacted with A to afford the same type of products. However, reaction with methyl methacrylate proceeded to give a product resulting from an addition of A to the carbon—carbon double bond.

Introduction

In spite of recent activity in the chemistry of silicon—carbon double-bonded intermediates only limited information is available concerning the chemical behavior of these interesting species toward organic substrates [1—6].

Sommer and his co-workers [7] recently have shown that the reaction of the silicon—carbon double-bonded intermediates generated by thermolysis of the corresponding silacyclobutane with carbonyl compounds proceeds by two major reaction pathways: One involves olefin formation which is postulated to occur via a pseudo-Wittig reaction, and the other comprises the formation of silyl-enol ethers.

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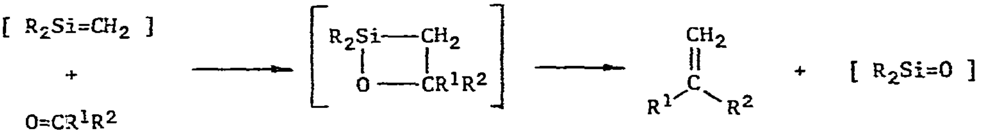
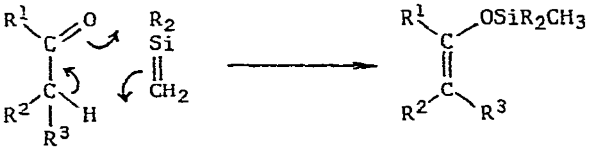
[*] For Part IV, see ref. 6.





These findings prompted us to investigate the reaction of the silicon—carbon double-bonded intermediates generated by photolysis of aryldisilanes in the presence of carbonyl compounds. As we reported previously [1,8], the chemical properties of such photochemically generated reactive intermediates are apparently different from those of the thermally generated ones. The most significant difference between both types of intermediate lies in the fact that the thermally generated intermediates undergo dimerization to give 1,3-disilacyclobutanes in the absence of a trapping agent, whereas those generated photochemically from aryldisilanes never afford any volatile product in the absence of a suitable substrate, always giving non-volatile substances. Therefore, we might expect that the reaction of our reactive intermediates with carbonyl compounds proceeds in a different fashion from that of those produced by other means.

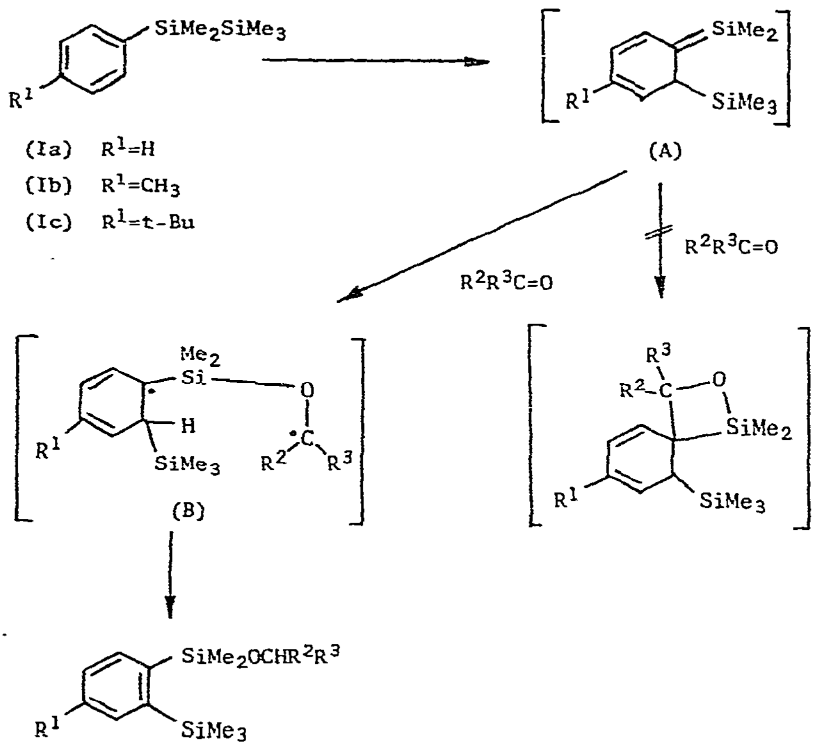
Results and discussion

In marked contrast to copyrolysis of silacyclobutanes [7] or silylphenyldiazomethanes [2] with ketones at high temperature, our results indicated that all reactions of the silicon—carbon double-bonded intermediates (A) generated via aryldisilanes with either enolizable or non-enolizable ketones lead to the formation of 2-trimethylsilyl(alkoxydimethylsilyl)benzene derivatives as shown in Scheme 1.

When photolysis of phenylpentamethyldisilane (Ia) was carried out in a large excess of acetone (12-fold molar excess), no photochemical isomerization of Ia to the silicon—carbon double-bonded intermediate A was observed, the starting disilane Ia being recovered unchanged. Recently, Valkovich and Weber have reported that the photolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene in acetone gives 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-sila-3-cyclohexene [9]. However, in our case, the acetone molecule undoubtedly absorbs most of the incident radiation, thus preventing photoisomerization of Ia to the silicon—carbon double-bonded intermediate. Similar results were observed when a large excess of any other carbonyl compound was used as a quencher. Therefore, we carried out the photolysis of an arylpentamethyldisilane in the presence of an approximately equimolar amount of a quencher.

Thus a solution of Ia (4.75 mmol) and acetone (5.50 mmol) in dry benzene was irradiated for 10 h. 2-Trimethylsilyl(isopropoxydimethylsilyl)benzene (II) was obtained in 59% yield as the sole volatile product, but no silyl-enol ether was produced. The latter could be expected to form by OH addition of the enol

Scheme 1



(Ia) R^1=H

(Ib) R^1=CH$_3$

(Ic) R^1=t-Bu

(II)	R^1=H, R^2=R^3=Me	(VIII)	R^1=H, R^2,R^3=-(CH$_2$)$_6$-
(III)	R^1=H, R^2=Me, R^3=Ph	(IX)	R^1=R^2=R^3=Me
(IV)	R^1=R^2=H, R^3=Ph	(X)	R^1=Me, R^2,R^3=-(CH$_2$)$_5$-
(V)	R^1=H, R^2=t-Bu, R^3=Ph	(XI)	R^1=t-Bu, R^2,R^3=-(CH$_2$)$_5$-
(VI)	R^1=H, R^2,R^3=-(CH$_2$)$_4$-	(XII)	R^1=R^2=Me, R^3=CH=CH$_2$
(VII)	R^1=H, R^2,R^3=-(CH$_2$)$_5$-	(XIII)	R^1=R^2=H, R^3=CH=CH$_2$

form of acetone across the silicon—carbon double bond, as observed by Sommer and his co-workers [7]. Similarly, the intermediate A from Ia reacted with acetophenone to give 2-trimethylsilyl(α-methylbenzyloxydimethylsilyl)-benzene (III) in 87% yield, as a single product.

The photolysis of Ia in the presence of cyclic ketones such as cyclopentanone, cyclohexanone and cycloheptanone under the same conditions, gave results analogous to those observed with the acyclic ketones. Again, in no case were any silyl-enol ethers obtained.

Interestingly, the irradiation of Ia in the presence of non-enolizable carbonyl compounds gave similar results. Thus, with benzaldehyde and pivalophenone, 2-trimethylsilyl(benzyloxydimethylsilyl)benzene (IV) and 2-trimethylsilyl-(α-t-butylbenzyloxydimethylsilyl)benzene (V), respectively, were obtained in high yield. In the latter case, however, a small amount of compound IV (18% yield) was produced. Irradiation of V in benzene for 5 h did not afford compound IV. Therefore, the formation of IV could be attributed to the photochemical degradation of pivalophenone to benzaldehyde, followed by reaction with intermediate A. Indeed, this was confirmed by the observation that irradiation of pivalophenone alone under similar conditions gave significant amounts of benzaldehyde.

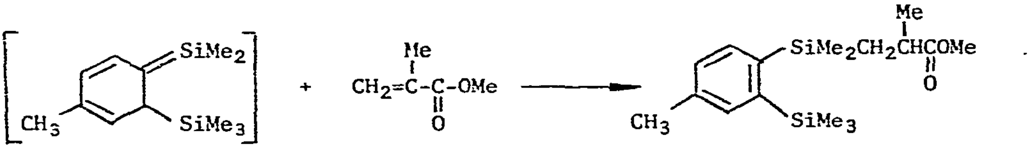
The present results obtained in our study of the reactions of intermediate A with non-enolizable ketones are in sharp contrast with those observed in the copyrolysis of silacyclobutanes with such ketones, where [2+2] cycloaddition took place to give unstable silaoxetane derivatives, followed by decomposition to afford the corresponding olefins and cyclic siloxanes. The absence of silaoxetane derivatives is consistent with the previously established fact that the reaction of the intermediate A with methyl alcohol afforded no 1,2-adduct [10].

We also carried out the photolysis of *p*-tolylpentamethyldisilane (Ib) in the presence of acetone under the same conditions. A high yield of the expected adduct IX was obtained. It was reported previously that the silicon—carbon double-bonded intermediate from Ib readily adds to olefins and dienes and always gives higher yields of the adducts than the analogous intermediate from Ia. With cyclohexanone, however, the yield of the adduct from Ib was found to be lower than that from Ia. A still lower yield of the adduct XI was obtained from photolysis of *p*-t-butylphenylpentamethyldisilane (Ic) in the presence of cyclohexanone. Some steric interaction between the methyl or t-butyl substituent on the cyclohexadienyl ring in the intermediate A and the ketone molecule may occur in the addition step.

Next, we examined the reaction of the silicon—carbon double-bonded intermediates with conjugated carbonyl compounds. Irradiation of Ib with methyl vinyl ketone under similar conditions produced 2-trimethylsilyl-4-methyl-(methylallyloxydimethylsilyl)benzene (XII) in 51% yield as the only volatile product. No product that might be expected from [2+4] cycloaddition could be observed. Acrolein also reacted with Ia to afford 2-trimethylsilyl(allyloxydimethylsilyl)benzene (XIII) in 40% yield.

Recently, Valkovich and Weber [11] have reported that copyrolysis of silacyclobutane with acrolein affords products which can be accounted for in terms of initial competing [2+2] and [2+4] cycloaddition reaction between the Si=C intermediate and acrolein. In our case, however, no [2+2] nor [2+4] cycloaddition product was found by spectroscopic analyses of the reaction mixture.

It should be noted that photolysis of Ib in the presence of a conjugated ester, methyl methacrylate, proceeds in a different manner to give a product that results from addition of the intermediate to the carbon—carbon double bond, but not to the carbon—oxygen double bond.



(XIV)

Yields of the adducts and reaction conditions are summarized in Table 1, and refractive indices and analytical data for isolated products are shown in Table 2.

The silicon—carbon double-bonded intermediates described here dit not add to the carbonyl group of methyl acetate or *N,N*-dimethylacetamide, but gave only non-volatile substances arising from the polymerization of the reactive intermediates. In contrast to the reaction of Ia with benzaldehyde, in which adduct IV was formed in high yield, irradiation of Ia with propionaldehyde did not afford an appreciable amount of adduct. Such a dramatic change in reactivity

TABLE 1

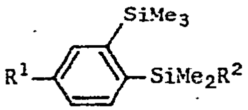
PHOTOLYSIS OF ARYLDISILANES IN THE PRESENCE OF CARBONYL COMPOUNDS (2537Å)

Aryldisilane g (mmol)	Carbonyl compound g (mmol)	Time (h)	Adduct[a] (yield %)	Recovered disilane (%)
$PhMe_2SiSiMe_3$ 0.990 (4.75)	acetone 0.319 (5.50)	10	II (59)	21
$PhMe_2SiSiMe_3$ 0.952 (4.57)	acetophenone 0.637 (5.30)	16	III (87)	8
$PhMe_2SiSiMe_3$ 0.991 (4.75)	benzaldehyde 0.740 (6.97)	7	IV (74)	54
$PhMe_2SiSiMe_3$ 0.993 (4.76)	pivalophenone 0.859 (5.30)	10	V (61) IV (18)	34
$PhMe_2SiSiMe_3$ 1.022 (4.91)	cyclopentanone 0.425 (5.06)	10	VI (31)	19
$PhMe_2SiSiMe_3$ 0.966 (4.64)	cyclohexanone 0.487 (4.96)	10	VII (52)	12
$PhMe_2SiSiMe_3$ 0.955 (4.58)	cycloheptanone 0.526 (4.69)	10	VIII (26)	11
p-$CH_3C_6H_4SiMe_2SiMe_3$ 0.972 (4.37)	acetone 0.320 (5.50)	14	IX (75)	17
p-$CH_3C_6H_4SiMe_2SiMe_3$ 0.772 (3.47)	cyclohexanone 0.429 (4.37)	10	X (46)	11
p-t-$BuC_6H_4SiMe_2SiMe_3$ 0.969 (3.66)	cyclohexanone 0.401 (4.09)	10	XI (36)	8
p-$CH_3C_6H_4SiMe_2SiMe_3$ 0.972 (4.37)	methyl vinyl ketone 0.345 (4.92)	10	XII (51)	20
$PhMe_2SiSiMe_3$ 0.998 (4.79)	acrolein 0.274 (4.89)	7	XIII (40)	12
$PhMe_2SiSiMe_3$ 0.985 (4.73)	methyl methacrylate 0.503 (5.02)	10	XIV (27)	15

[a] Based on unrecovered disilane.

TABLE 2

REFRACTIVE INDICES AND ANALYTICAL DATA FOR



Compound			n_D^{20}	Found (calcd.) (%)	
No.	R^1	R^2		C	H
II	H	$OCHMe_2$	1.4978	63.10 (63.09)	9.93 (9.83)
III	H	$OCH(Me)Ph$	1.5377	69.15 (69.45)	8.70 (8.59)
IV	H	OCH_2Ph	1.5323	68.85 (68.73)	8.45 (8.33)
V	H	OCH(Ph)(t-Bu)	m.p. 60°	71.00 (71.29)	9.48 (9.25)
VI	H	$O-CH(CH_2)_3CH_2$	1.5154	65.50 (65.69)	9.70 (9.65)
VII	H	$O-CH(CH_2)_4CH_2$	1.5160	66.47 (66.60)	9.95 (9.86)
VIII	H	$O-CH(CH_2)_5CH_2$	1.5190	67.16 (67.43)	9.81 (10.06)
IX	CH_3	$OCHMe_2$	1.4992	64.52 (64.22)	10.36 (10.06)
X	CH_3	$O-CH(CH_2)_4CH_2$	1.5169	67.26 (67.43)	10.04 (10.06)
XI	t-Bu	$O-CH(CH_2)_4CH_2$	1.5111	69.71 (69.54)	10.83 (10.56)
XII	CH_3	$OCH(Me)CH=CH_2$	1.5062	65.98 (65.69)	9.81 (9.65)
XIII	H	$OCH_2CH=CH_2$	1.5077	63.32 (63.57)	9.26 (9.15)
XIV	H	$CH_2CH(Me)COOMe$	1.5083	62.20 (62.28)	9.20 (9.15)

can be rationalized in terms of the formation of biradical intermediate B in the addition step as proposed previously [1]. Thus, only those carbonyl compounds which bear a substituent, such as a phenyl group, capable of stabilizing the neighbouring carbon radical can react readily with intermediate A to give adducts in high yields. This hypothesis is in good accord with the results shown in Table 1.

The structure of the adducts reported here was confirmed by IR, mass and ^1H NMR spectroscopic studies and elemental analyses. The spectral data for all adducts are listed in Tables 3 and 4.

TABLE 3

PROTON NMR CHEMICAL SHIFTS FOR ADDUCTS

Compound	Chemical shifts (δ)[a] in CCl_4
II	0.36(CH_3-$SiMe_2$, s, 9H), 0.40(CH_3-SiMe, s, 6H), 1.22(CH_3-CH, d, J=6.1 Hz, 6H), 4.14(HC-O, sept, J=6.1 Hz, 1H), 7.18-7.64(ring protons, m, 4H)
III	0.20(CH_3-Si, s, 3H), 0.35(CH_3-Si, s, 12H), 1.47(CH_3-CH, d, J=6.5 Hz, 3H), 4.88(HC-O, q, J=6.5 Hz, 1H), 7.08-7.65(ring protons, m, 9H)
IV	0.29(CH_3-$SiMe_2$, s, 9H), 0.37(CH_3-SiMe, s, 6H), 4.73(H_2C-O, s, 2H), 7.15-7.63(ring protons, m, 9H)
V	0.11(CH_3-Si, s, 3H), 0.36(CH_3-Si, s, 12H), 0.87(CH_3-CMe_2, s, 9H), 4.37(HC-O, s, 1H), 7.08-7.80(ring protons, m, 9H)
VI	0.35(CH_3-$SiMe_2$, s, 9H), 0.40(CH_3-SiMe, s, 6H), 1.46-1.87(-$(CH_2)_4$-, m, 8H), 4.33(HC-O, m, 1H), 7.19-7.62(ring protons, m, 4H)
VII	0.37(CH_3-$SiMe_2$, s, 9H), 0.40(CH_3-SiMe, s, 6H), 1.12-2.02(-$(CH_2)_5$-, m, 10H), 3.72(HC-O, m, 1H), 7.19-7.63(ring protons, m, 4H)
VIII	0.36(CH_3-$SiMe_2$, s, 9H), 0.39(CH_3-SiMe, s, 6H), 1.24-2.06(-$(CH_2)_6$-, m, 12H), 3.93(HC-O, m, 1H), 7.18-7.62(ring protons, m, 4H)
IX[b]	0.46(CH_3-SiMe, s, 6H), 0.57(CH_3-$SiMe_2$, s, 9H), 1.21(CH_3-CH, d, J=6.1Hz, 6H), 2.26(CH_3-C_6H_3, bs, 3H), 4.02(HC-O, sept, J=6.1 Hz, 1H), 7.05-7.70(ring protons, m, 3H)
X	0.35(CH_3-$SiMe_2$, s, 9H), 0.37(CH_3-SiMe, s, 6H), 1.13-1.99(-$(CH_2)_5$-, m, 10H), 2.35(CH_3-C_6H_3, s, 3H), 3.69(HC-O, m, 1H), 7.05(ring proton, bd, J=7.6 Hz, 1H), 7.37(ring proton, bs, 1H), 7.44(ring proton, d, J=7.6 Hz, 1H)
XI	0.36(CH_3-$SiMe_2$, s, 9H), 0.37(CH_3-SiMe, s, 6H), 1.11-1.98(-$(CH_2)_5$-, m, 10H), 1.32(CH_3-CMe_2, s, 9H), 3.69(HC-O, m, 1H), 7.23(ring proton, dd, J_{ortho}=8.0 Hz, J_{meta}=2.0 Hz, 1H), 7.46(ring proton, d, J=8.0 Hz, 1H), 7.60(ring proton, d, J=2.0 Hz, 1H)
XII	0.36(CH_3-$SiMe_2$, s, 9H), 0.38(CH_3-SiMe, s, 3H), 0.39(CH_3-SiMe, s, 3H), 1.28(CH_3-CH, d, J=6.1 Hz, 3H), 2.33(CH_3-C_6H_3, bs, 3H), 4.37(HC-O, m, 1H), 4.89-6.04(vinylic protons, ABMX, J_{trans}=17.3 Hz, J_{cis}=10.2 Hz, J_{vic}=6.3 Hz, 3H), 7.06(ring proton, bd, J=7.6 Hz, 1H), 7.38(ring proton, bs, 1H), 7.43(ring proton, d, J=7.6 Hz, 1H)
XIII	0.32(CH_3-$SiMe_2$, s, 9H), 0.38(CH_3-SiMe, s, 6H), 4.20(H_2C-O, m, 2H), 4.96-6.11(vinylic protons, ABMX, J_{trans}=17 Hz, J_{cis}=10 Hz, J_{vic}=5 Hz, 3H), 7.15-7.67(ring protons, m, 4H)
XIV	0.37(CH_3-$SiMe_2$, s, 9H), 0.38(CH_3-SiMe, s, 3H), 0.39(CH_3-SiMe, s, 3H), 0.90(CH_2-Si, dd, J_{gem}=14.7 Hz, J_{vic}=6.7 Hz, 1H), 1.36(CH_2-Si, dd, J_{gem}=14.7 Hz, J_{vic}=8.7 Hz, 1H), 1.13 (CH_3-CH, d, J=7.1 Hz, 3H), 2.46(HC-C, m, 1H), 3.48(CH_3-O, s, 3H), 7.18-7.63(ring protons, m, 4H)

[a] Chemical shifts are reported relative to CH_2Cl_2 at 100 MHz; s, singlet; d, doublet; dd, double doublet; m, multiplet. [b] In C_6D_6.

Experimental

Spectra

^1H NMR spectra were determined with a JEOL Model JNM-MH-100 and a Varian Model HA-100 spectrometer using carbon tetrachloride solution containing methylene chloride as a rock signal. Mass spectra were measured on a Hitachi Model RMU-6D fitted with an all-glass direct inlet accessory. Ionizing voltage was 70 eV for all compounds. Infrared spectra of thin liquid films were determined using a Hitachi Model EPI-G3 Grating infrared spectrophotometer.

Gas chromatography

An Aerograph Model 90 gas chromatograph with a thermal conductivity

TABLE 4

SIGNIFICANT IR BANDS (cm^{-1}) AND IMPORTANT MASS PEAKS FOR ADDUCTS

Compound	IR (neat)	Mass (relative intensity)
II	1385(m), 1370(m), 1255(s), 1120(s), 1020(s), 840(s), 745(s)	262(M^+), 209(57), 193(100), 116(61), 73(66), 43(73)
III	1255(s), 1120(s), 1080(s), 1030(s), 960(s), 840(s), 780(s), 745(s)	328(M^+), 193(10), 178(25), 105(100), 75(33), 73(8)
IV	1255(s), 1065(s), 850(s), 745(s), 695(s), 665(s)	314(M^+), 193(10), 147(16), 135(16), 105(8), 92(8), 91(100), 73(20)
V	1395(s), 1365(s), 1260(s), 1065(s), 840(s), 745(s), 700(s), 670(s)	370(M^+), 313(27), 207(60), 191(50), 147(100), 105(25), 91(62), 73(63)
VI	1255(s), 1040(s), 840(s), 745(s)	292(M^+), 219(35), 209(81), 193(100), 142(83), 135(28), 75(92), 73(55), 69(66), 41(58)
VII	1450(m), 1255(s), 1075(s), 840(s), 745(s)	306(M^+), 233(41), 209(71), 193(59), 156(80), 83(77), 75(100), 73(48), 55(89)
VIII	1255(s), 1030(s), 840(s), 750(s)	320(M^+), 209(38), 193(28), 170(28), 135(37), 75(90), 73(100), 57(28), 55(76)
IX	1385(m), 1370(m), 1255(s), 1175(m), 1150(m), 1115(s), 1020(s), 885(s), 840(s), 775(s)	280(M^+), 223(55), 207(100), 149(24), 147(37), 116(56), 75(43), 73(32), 43(49)
X	1450(m), 1255(s), 1075(s), 885(s), 840(s)	320(M^+), 223(52), 207(49), 156(86), 83(60), 75(76), 73(36), 55(100), 41(38)
XI	1450(m), 1380(m), 1255(s), 1075(s), 880(s), 840(s)	362(M^+), 265(29), 249(36), 156(100), 83(43), 75(80), 73(38), 57(50), 55(80), 41(32)
XII	1255(s), 1075(s), 990(s), 920(s), 885(s)	292(M^+), 223(13), 207(24), 149(26), 147(17), 128(24), 75(27),73(26) 55(100)
XIII	1255(s), 1120(s), 1080(s), 1040(s), 920(s), 840(s), 780(s), 745(s)	264(M^+), 249(10), 193(97), 159(23), 147(31), 135(57), 133(31), 105(15), 104(12), 75(10), 73(54), 59(16), 45(17), 43(10), 41(100)
XIV	1740(s), 1255(s), 1205(s), 1150(s), 1115(s), 840(s)	308(M^+), 191(16), 159(100), 89(46), 73(38), 59(15)

detector was used for separation of the products. All the products were easily separated by using a column containing 30% Silicone-DC (3/8 in × 20 ft).

Materials

Phenylpentamethyldisilane [12] and *p*-tolylpentamethyldisilane [1] were made as reported in the literature. Benzene was dried over lithium aluminum hydride and distilled before use. Carbonyl compounds were used as received.

p-t-Butylphenylpentamethyldisilane

To the Grignard reagent prepared from 1.6 g (0.067 g-atom) of magnesium and 14 g (0.066 mol) of *p*-t-butylbromobenzene in 50 ml of tetrahydrofuran (THF) was added 9.3 g (0.056 mol) of chloropentamethyldisilane in 20 ml of THF. The reaction mixture was heated at reflux for 3 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation gave 10 g (68% yield) of *p*-t-butylphenylpentamethyldisilane [13], b.p. 100°C/3 Torr, n_D^{20} 1.5048; NMR (δ, ppm) 0.06 (CH_3—$SiMe_2$, s, 9H), 0.29 (CH_3—SiMe, s, 6H), 1.31 (CH_3—CMe_2, s, 9H), 7.27 (ring protons, s, 4H).

Photolysis of aryldisilanes in the presence of carbonyl compounds

The following is typical of the procedure used. A solution of 0.990 g (4.75 mmol) of phenylpentamethyldisilane (Ia) and 0.319 g (5.50 mmol) of acetone in 100 ml of dry benzene was irradiated for 10 h with a low-pressure mercury lamp (10 Watt) having a Vycor filter under bubbling nitrogen gas at ca. 45°C. Most of the solvent benzene was evaporated and the residue was distilled under reduced pressure to give a volatile product boiling up to ca. 200°C/1 Torr. The yield of 2-trimethylsilyl(isopropoxydimethylsilyl)benzene (II) in the distillate was determined by GLC using n-octadecane as an internal standard. Compound II was then isolated by preparative GLC.

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