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ORGANOMETALLIC PHOTOCHEMISTRY
PHOTOCHEMISTRY OF SOME ACYCLIC KETOSILANES

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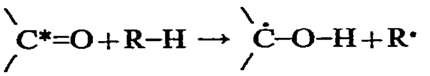
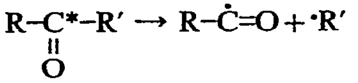
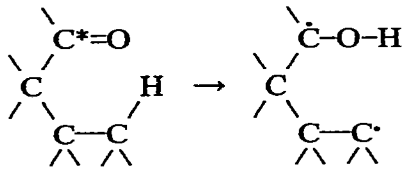
When saturated acyclic ketones are photolyzed in solution the products which are usually formed can be rationalized on the basis of one or more of three primary chemical reactions: abstraction of a hydrogen atom from the solvent by the carbonyl oxygen, cleavage of one of the acyl carbon–carbon bonds, or abstraction of a hydrogen atom from the γ-carbon by the carbonyl oxygen [eqns. (1)–(3)][2-6]. The reactions are generally considered to proceed from the lowest excited singlet or



$$\gt C^{*}{=}O + R{-}H \rightarrow \gt \dot{C}{-}O{-}H + R^{\bullet}$$ (1)



$$R{-}\underset{\underset{O}{\|}}{C^{*}}{-}R' \rightarrow R{-}\dot{C}{=}O + {}^{\bullet}R'$$ (2)



triplet states. We are interested in the question of whether the energy of such states can be transferred either radiatively or via vibration and rotation to another part or parts of the molecule at which a reaction might then occur. In the present investigation we have chosen the carbonyl group as the absorbing chromophore and the trimethylsilyl function as the potential seat of reaction. Since the carbon–silicon bond is weaker than the carbon–carbon bond by about 6 kcal per mole[7] one might expect any reaction resulting from conversion of the energy of the absorbed photon into vibrational energy to lead to rupture of a carbon–silicon bond. Other possible changes in the course of the "normal" reactions due to the presence of the silicon atom will be considered in the discussion of our results.

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*** At which address the experimental work was conducted. For a preliminary report on this work see ref. 1.

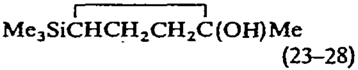
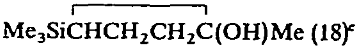
RESULTS AND DISCUSSION

The approach used in this investigation was to prepare a series of silyl ketones with the general structure, $(CH_3)_3Si(CH_2)_nCOR$, in which n was varied between zero and four and R was either methyl or phenyl. Methods used in the synthesis of the ketones are described in the *Experimental* section.

The photolyses were carried out with high pressure mercury lamps in quartz apparatus, although a Vycor sleeve was used in some experiments to filter out the shorter wavelength radiation. In some instances the substrate was irradiated neat, in others in solution. Some of the solutions were degassed, others were not. All liquid products except the most volatile, which were collected by distillation were separated by gas–liquid partition chromatography (GLPC) for characterization. Solid products were purified by column chromatography. Results are summarized in Table 1.

TABLE 1

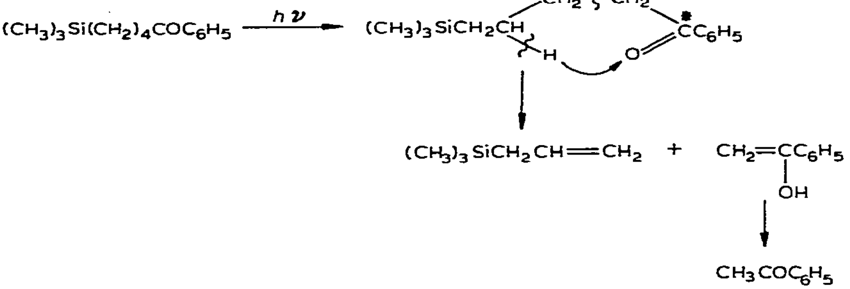
PHOTOLYSIS PRODUCTS OF KETOSILANES

No.	*Compound*	*Diluent (Wt. %)*	*Time (h)*	*Products (yields, %)*
1	$Me_3Si(CH_2)_4COC_6H_5$	cyclohexane (30–40) or neat	5–30	$Me_3SiCH_2CH{=}CH_2$(58–67) $C_6H_5COCH_3$ (52–61) unidentified alcohols (traces)
2	$Me_3Si(CH_2)_3COC_6H_5$[a]	cyclohexane (20) or neat	1–29	$Me_3SiCH{=}CH_2$ (66–69) $C_6H_5COCH_3$ (71–75) $(C_6H_5COCH_2)_2$ (10–13) unidentified alcohols (traces)
3	$Me_3Si(CH_2)_3COCH_3$[a]	pentane (87)	9	$Me_3SiCH{=}CH_2$ (39–42) $Me_3SiCHCH_2CH_2C(OH)Me$ (23–28) $Me_3Si(CH_2)_3COH(Me)R$[b] (13) CH_3COCH_3[e] (trace)[f]
		ethanol (23)	32	$Me_3SiCHCH_2CH_2C(OH)Me$ (18)[f]
4	$Me_3Si(CH_2)_2COC_6H_5$	cyclohexane (91)	8–80	$Me_3Si(CH_2)_2COH(R)C_6H_5$[b] (10) $Me_3SiCH_2CH_2R$[d] (6) unidentified alcohols (traces)
5	$Me_3Si(CH_2)_2COCH_3$	cyclohexane (30) or ethanol (30)	49–56	$Me_3SiCH{=}CH_2$ (33–39) $Me_3SiCH_2CH_3$ (14–17) $CH_3COCOCH_3$ (8–12) $(Me_3SiCH_2CH_2)_2$ (29–36)
6	$Me_3SiCH_2COC_6H_5$	wet ether[f]	7.5	Me_3SiOH (95–100) $C_6H_5COCH_3$ (10–15)[e]
7	$Me_3SiCH_2COCH_3$	wet ether[f]	21	Me_3SiOH (95–100) CH_3COCH_3 (trace)[f]
8	$Me_3SiCOC_6H_5$	wet ethanol[f]	23	$(Me_3Si)_2O$ (90–95) Me_3SiOEt (5) C_6H_5CHO (0–20)[c]

[a] Vycor filter. [b] R = 1-, 2-, or 3-pentyl. [c] Yields of other products not determined. [d] R = cyclohexyl. [e] Most of this product photolyzed. [f] See text.

(5-Oxo-5-phenylpentyl)trimethylsilane (I)

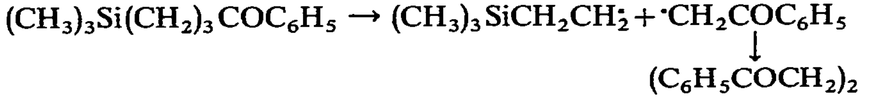
This ketone was photolyzed in the absence of solvent and in solutions containing up to 40% of cyclohexane. Results were virtually identical under all conditions. Allyltrimethylsilane and acetophenone were the only products characterized, the remainder being polymeric. Thus the reaction proceeds primarily by way of the Type II process[6] shown in eqn. (4).



(4)

(4-Oxo-4-phenylbutyl)trimethylsilane (II)

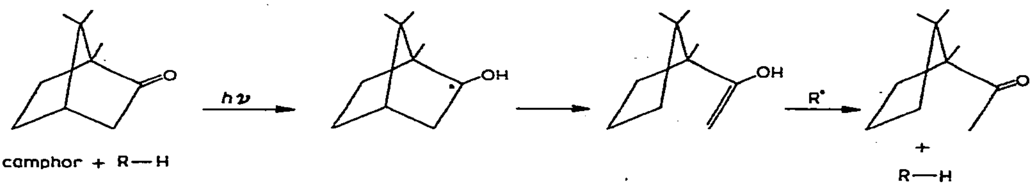
Photolysis of this ketone neat or in solution containing 20% cyclohexane or 96% heptane gave the same results if one takes into account the fact that vinyltrimethylsilane is quite volatile and that not all of it may have been collected in some experiments. The major course of the reaction is again the Type II reaction. However, significant amounts of 1,2-dibenzoylethane were also formed. This is indicative of cleavage of the bond between the carbons α and β to the carbonyl group, eqn. (5).



$$(CH_3)_3Si(CH_2)_3COC_6H_5 \rightarrow (CH_3)_3SiCH_2\dot{C}H_2 + {}^{\bullet}\underset{\displaystyle \downarrow \atop \displaystyle (C_6H_5COCH_2)_2}{CH_2COC_6H_5} \qquad (5)$$

No 1,4-bis(trimethylsilyl)butane, which would result from coupling of the 2-(trimethylsilyl)ethyl radicals, was detected. Neither was ethyltrimethylsilane, which could have been detected by GLPC, found. Thus, these radicals must either lose hydrogen atoms to form vinyltrimethylsilane or suffer some other fate. The high boiling residue which formed was shown by its infrared spectrum to contain hydroxyl groups but it was not characterized further.

Cleavage between the α- and β-carbons has been reported in the photolysis of camphor[8]. This was rationalized on the basis of an initial abstraction of a hydrogen from solvent in the resultant radical, eqn. (6). Formation of dibenzoylethane reveals



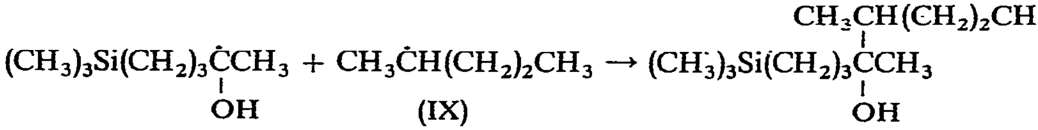
(6)

that phenacyl radicals must be formed in the reaction and lead to the conclusion that simple α–β cleavage is adequate to account for the results.

(4-Oxopentyl)trimethylsilane (III)[9]

The methyl analog of the ketone just discussed underwent the Type II reaction to the extent of about 40% as measured by the yield of vinyltrimethylsilane obtained. Acetone, the expected accompanying product, was not found because it is rapidly photolyzed under the conditions of the experiments. Two alcohols were isolated. One of these, obtained in 13% yield, was shown by comparison of its 3,5-dinitrobenzoate ester with an authentic sample to be (4-hydroxy-4,5-dimethyloctyl)-trimethylsilane (IX). The overall reaction for its formation is a reductive alkylation of the carbonyl group by the solvent pentane, eqn. (7).

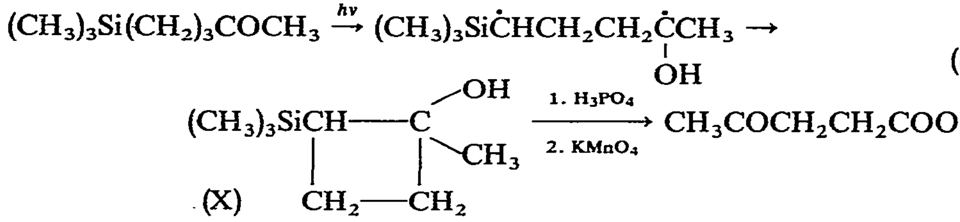
$$(CH_3)_3Si(CH_2)_3COCH_3^* + CH_3CH_2(CH_2)_2CH_3 \rightarrow$$



$$(CH_3)_3Si(CH_2)_3\underset{\substack{|\\ OH}}{\dot{C}}CH_3 + CH_3\dot{C}H(CH_2)_2CH_3 \rightarrow (CH_3)_3Si(CH_2)_3\underset{\substack{|\\ OH}}{\overset{\substack{CH_3CH(CH_2)_2CH_3\\ |}}{C}}CH_3 \qquad (7)$$

(IX)

The second alcohol had the same empirical formula as the starting ketone and is assigned the cyclobutanol structure (X) shown in eqn. (8). Bases for the assignment are analogy with observations on simple acyclic ketones by other investigators[10,11], the proton magnetic resonance spectrum and its degradation by dehydration followed by oxidation to levulinic acid.

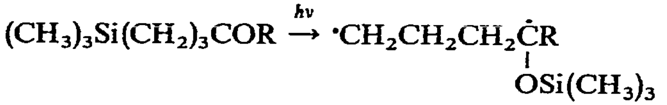


$$(CH_3)_3Si(CH_2)_3COCH_3 \xrightarrow{h\nu} (CH_3)_3Si\dot{C}HCH_2CH_2\underset{\substack{|\\ OH}}{\dot{C}}CH_3 \rightarrow \qquad (8)$$

(X)

$$\xrightarrow[\text{2. KMnO}_4]{\text{1. H}_3\text{PO}_4} CH_3COCH_2CH_2COOH$$

An alternate reaction path with these two ketones containing three methylene groups between the carbonyl and the trimethylsilyl groups was considered to be possible. This would involve abstraction by the carbonyl oxygen, not of the hydrogen on the γ-carbon, but of the trimethylsilyl group on this carbon, eqn. (9). Such a reaction would be less endothermic than the reaction actually observed by some 20 kcal per mole[7]: cleavage of the Si–C and C=O bonds would require about 76 and 90 kcal per mole, respectively and formation of the Si–O bond would produce about 108 kcal per mole making the reaction endothermic by some 58 kcal per mole; corresponding figures for the H–C and H–O bonds are about 99 and 111 kcal per mole, respectively making the reaction endothermic by about 78 kcal per mole. A rationale for the observed results is that the ketone spends very little of its time in conformations favorable for interaction between the carbonyl oxygen and the trimethylsilyl group and much more in conformations favorable for interaction between the carbonyl group and the γ-hydrogens. The energy of the molecule in the excited states exceeds



$$(CH_3)_3Si(CH_2)_3COR \xrightarrow{h\nu} \cdot CH_2CH_2CH_2\underset{\substack{|\\ OSi(CH_3)_3}}{\dot{C}}R \qquad (9)$$

the activation energy required for either abstraction and the course of the reaction is determined by the distribution of the population among the various conformers.

(3-Oxo-3-phenylpropyl)trimethylsilane (IV)

Photolysis of this ketone in cyclohexane through quartz or Vycor provided only small yields of low molecular weight products. The only ones isolated and characterized were (2-cyclohexylethyl)trimethylsilane (6%) and (3-hydroxy-3-cyclohexyl-3-phenylpropyl)trimethylsilane (10%). Formation of the latter product is most easily explained by a reaction sequence similar to eqn. (6). The former product would appear to arise from coupling between 2-(trimethylsilyl)ethyl radicals and cyclohexyl radicals. If this is correct, then the only carbon–carbon bond whose cleavage is established by the experiments is that between the carbonyl group and the 2-(trimethylsilyl)ethyl chain. Other products which were detected were 1,4-bis(trimethylsilyl)butane and vinyltrimethylsilane (1–2% yields) and traces of biphenyl.

(3-Oxobutyl)trimethylsilane (V)

In the photolysis of this compound considerably more than 85% of the trimethylsilyl groups were found in the products ethyltrimethylsilane, vinyltrimethylsilane and 1,4-bis(trimethylsilyl)butane indicating cleavage between the carbonyl carbon and the attached methylene group. Biacetyl was isolated in modest yields. The formation of the products found (no gas evolution occurred) can be rationalized in terms of eqns. (10)–(14). Perhaps the most curious fact is that vinyltrimethylsilane was formed in such high yields. No more than half of it could arise by disproportionation, eqn. (14) with $R^\cdot = (CH_3)_3SiCH_2CH_2^\cdot$. The remainder might form via disproportionation with acetyl radicals, or, less probably, a β-elimination of the elements of acetaldehyde directly from the excited molecule. Finally, if any of the Type II modification depicted in eqn. (10) occurred it amounted to less than 20%.

$$(CH_3)_3SiCH_2CH_2COCH_3 \xrightarrow{h\nu} (CH_3)_3SiCH_2CH_2^\cdot + CH_3\dot{C}O \quad (10)$$

$$2\,CH_3\dot{C}O \rightarrow CH_3COCOCH_3 \quad (11)$$

$$2\,(CH_3)_3SiCH_2CH_2^\cdot \rightarrow (CH_3)_3SiCH_2CH_2CH_2CH_2Si(CH_3)_3 \quad (12)$$

$$(CH_3)_3SiCH_2CH_2^\cdot + R^\cdot \rightarrow (CH_3)_3SiCH{=}CH_2 + RH \quad (13)$$

$$(CH_3)_3SiCH_2CH_2^\cdot + RH \rightarrow (CH_3)_3SiCH_2CH_3 + R^\cdot \quad (14)$$

Phenacyltrimethylsilane (VI)

Photolysis of this ketone in an inert solvent was exceedingly slow and produced traces of hexamethyldisiloxane. Since the utmost precautions were not taken to maintain anhydrous conditions, it was though that this product was that of simple hydrolysis, eqn. (15). It was shown that acetophenone is rapidly photolyzed under the reaction conditions. The following experiment shows that the hydrolysis is subject to photocatalysis. A solution containing 2 mmoles each of ketone and of water per ml of ether was irradiated for 7.5 h. Photolysis was virtually complete and

$$2\,(CH_3)_3SiCH_2COC_6H_5 + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_3 + 2\,C_6H_5COCH_3 \quad (15)$$

a quantitative yield of trimethylsilanol, as estimated by GLPC, was formed, and about 5% of acetophenone was detected. In the absence of irradiation the ketone underwent solvolysis to the extent of about 20% in the same time.

Acetonyltrimethylsilane (VII)

A sample of this ketone, carefully purified by GLPC underwent virtually no reaction upon irradiation for 70 h in methylcyclohexane. When a solution containing 4 mmoles of the ketone and 3 mmoles of water per ml of ether was irradiated for 21 h, 60–70% of the ketone reacted giving a quantitative yield of trimethylsilanol and a trace of acetone. The latter compound is photolyzed to the extent of 90–95% under the same conditions. A sample of acetonyltrimethylsilane in the dark was substantially unchanged under the conditions of the photolysis.

Benzoyltrimethylsilane (VIII)

The behavior of this ketone was similar to that of the preceding two. In methylcyclohexane about 30% of the ketone disappeared upon irradiation for 68 h resulting in the formation of 6% hexamethyldisiloxane and 4.5% of benzaldehyde. When a solution containing 1.15 mmoles of water and 2.8 mmoles of the ketone per ml of ethanol was irradiated for 23 h complete disappearance of the ketone and formation of 85–95% of hexamethyldisiloxane and a trace of benzaldehyde resulted, eqn. (16). A control sample showed no solvolysis in the dark. In another control experiment

$$(CH_3)_3SiCOC_6H_5 + H_2O \xrightarrow{h\nu} (CH_3)_3SiOSi(CH_3)_3 + C_6H_5CHO \qquad (16)$$

benzaldehyde was completely photolyzed in the same time interval. Thus we have in hand another example of a photocatalyzed solvolysis reaction.

An explanation for the photocatalysis lies in the electron distribution in the excited states resulting from $n \rightarrow \pi^*$ transitions of aldehydes and ketones. The oxygen is electron-deficient because one of its non-bonded p electrons has been promoted into an antibonding π orbital. Hence the carbonyl carbon should be relatively electron-rich. This would facilitate the electrophilic phase of the reaction (attack by the proton at the carbonyl carbon) in the excited state, which could be preceded, accompanied or followed by nucleophilic attack at the silicon atom of benzoyltrimethylsilane. A similar argument would hold for electrophilic attack at the methylene carbons of acetonyltrimethylsilane and phenacyltrimethylsilane whose electron density would be enhanced by inductive release from the carbonyl carbon.

EXPERIMENTAL

General

The infrared absorption spectra were determined using a Perkin–Elmer Model 21 infrared spectrophotometer with sodium chloride optics.

The ultraviolet absorption spectra were obtained using a Perkin–Elmer Model 4000 recording spectrophotometer. Unless otherwise stated, the solvent was Fisher reagent-grade methanol.

Microanalyses were determined by Galbraith Microanalytical Laboratory, Knoxville, Tennessee.

The nuclear magnetic resonance spectra were determined using a Varian A 60 instrument*. Unless otherwise stated, the chemical shifts are in ppm from tetramethylsilane used as an internal standard.

Product isolation. The more volatile products, vinyltrimethylsilane, hexamethyldisiloxane and biacetyl, were isolated by distillation; other liquid products were separated by GLPC; solids were separated by column chromatography. The columns used for GLPC separations and analyses were usually 20% Apiezon L on Chromosorb P or 5% silicone oil 200 on Haloport F.

Photolyses. When sufficient substrate was available the photolyses were carried out in an apparatus comprising a Hanovia 450 watt high pressure mercury lamp (679 A), placed within a double-walled cylindrical quartz vessel with inlet and outlet tubes so that water could be circulated between the walls. This was placed in a glass vessel which contained the solution to be photolyzed. If shorter wavelengths were to be filtered a Vycor sleeve was interposed between the lamp and the quartz vessel. Nitrogen was passed into the substrate solution through a fritted glass disc in the bottom of the glass vessel.

When smaller amounts of substrate were available the mercury vapor lamp, removed from a 400 watt lamp H400 A-33-1 (General Electric), was placed into the cylindrical quartz vessel. External to the vessel, 1–2 cm distant, were placed tubes 6 mm in diameter made of quartz or Vycor containing the solution to be photolyzed. Because this method of irradiation is much less efficient than that described above much longer irradiation times were required for given extents of reaction. The tubes were usually flushed with argon before photolysis.

(5-Oxo-5-phenylpentyl)trimethylsilane (I)

A solution of sodium ethoxide was made from 3.75 g (0.163 g-atom) of sodium in 1000 ml of absolute ethanol. To this was added 31.3 g (0.163 mole) of ethyl benzoylacetate (Matheson, Coleman and Bell). The solution was then added to 39.0 g (0.161 mole) of (3-iodopropyl)trimethylsilane[12] in 300 ml of absolute ethanol during a period of 50 min. A solution of 37% hydrochloric acid was added until slightly acidic (10 ml was required). The ethanol was distilled. The product was extracted with 100 ml of ether. After removal of the ether at reduced pressure, decarboxylation was attempted by heating with concentrated hydrochloric acid without success. Decarboxylation was achieved by heating the ester with 10 ml of water, 10 ml of 95% ethanol and 7 g of potassium hydroxide for 3 h. Distillation gave 8 g (40% yield based on iodo compound consumed; 18% was recovered) of the ketone; b.p. 148–152°/1 mm. The infrared spectrum of the compound (pure liquid) had bands at 3060 (w), 2940 (s), 1683 (s), 1592 (m), 1580 (m), 1449 (s), 1410 (m), 1245 (s), 1210 (s), 860 (s), 830 (s), 745 (m), 685 (m) cm^{-1}. The ultraviolet spectrum (in n-hexane) had a λ_{max} at 237.5 $m\mu$ ($\varepsilon = 15{,}000$). The NMR spectrum had peaks at 7.99 (multiplicity of 5), 7.35 (4), 2.85 (3), 1.16 (10), 0.46 (3), 0.00 (1) ppm from the peak of the Me_3Si protons. (Found: C, 71.63; H, 9.57; Si, 11.87. $C_{14}H_{22}OSi$ calcd.: C, 71.72; H, 9.47; Si, 11.99%.)

(4-Oxopentyl)trimethylsilane (II). This ketone was prepared by the method of Sommer and coworkers[12].

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* Purchase of this instrument was made possible by a grant from the National Science Foundation.

(4-Oxo-4-phenylbutyl)trimethylsilane (III)

To (3-cyanopropyl)methyldichlorosilane[12] (0.83 mole) in 300 ml of ether was added dropwise a Grignard reagent prepared from 47 g (1.9 moles) of magnesium and methyl bromide in 500 ml of dry ether. The mixture was poured on 10 g of ammonium chloride with sufficient ice to cool the reaction. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether distillation gave 87 g (75%) of (3-cyanopropyl)trimethylsilane; b.p. 90–95°/11 mm.

The (3-cyanopropyl)trimethylsilane was added dropwise to phenylmagnesium bromide prepared from 20 g (0.82 mole) of magnesium and 126 g (0.80 mole) of bromobenzene (Fisher reagent). After refluxing for 2 h, the mixture was poured into 15 g of ammonium chloride with sufficient ice to cool the reaction. The ethereal layer was washed successively with 10% sodium carbonate and saturated sodium chloride solution. Distillation gave 103 g (52%) of the crude ketone. The ketone was redistilled for further purification; the fraction boiling at 155°/21 mm was collected. The infrared spectrum of this compound (neat) had bands at 3030 (w), 2930 (s), 2880 (m), 1680 (s), 1598 (m), 1580 (w), 1247 (s), 1220 (m), 970 (m), 855 (s), 735 (m), 690 (m) cm^{-1}. The ultraviolet spectrum (n-hexane) had λ_{max} 237.5 mμ ($\varepsilon = 15{,}000$). The NMR spectrum of this compound had peaks at 8.00 (multiplicity of 4, area 2), 7.42 (4, 3); 2.87 (3, 2); 1.70 (8, 2); 0.54 (6, 2); 0.00 (1, 9) ppm from the Me_3Si group proton peak. (Found: C, 70.86; H, 9.15; Si, 12.90. $C_8H_{16}OSi$ calcd.: C, 70.80; H, 9.15; Si, 12.75%.)

(3-Oxo-3-phenylpropyl)trimethylsilane (IV)

(*a*) A mixture of 21.0 g (0.21 mole) vinyltrimethylsilane and 3.62 g benzoyl peroxide with 20 ml toluene to help dissolve the peroxide was added dropwise to 63.0 g (0.59 mole) freshly distilled benzaldehyde (Fisher)[13,14]. The mixture was refluxed 15 h. Flash distillation gave 9 ml over a boiling range of 120–140°/20 mm. The benzaldehyde impurity was air oxidized over a period of 2 months. Further distillation through a 15 cm Vigreux column gave 5.3 g (12%); b.p. 130°/15 mm.

(*b*) To a Grignard reagent made from 13.0 g (0.54 mole) of magnesium, 85.0 g (0.54 mole) of bromobenzene (Fisher) and 150 ml of dry ether was added 52.3 g (0.40 mole) (2-cyanoethyl)trimethylsilane within one-half h with stirring[15]. The mixture was refluxed for 1 h. The complex was hydrolyzed by pouring into 80 ml of a saturated solution of ammonium chloride with sufficient ice to moderate the reaction and then acidified with 18% hydrochloric acid. The ethereal layer was washed with water and saturated sodium bicarbonate solution before drying over anhydrous magnesium sulfate. Distillation gave 56 g (68%) of the ketone; b.p. 134–135°/15 mm. The infrared spectra of the ketones obtained in (*a*) and (*b*) were identical.

(3-Oxobutyl)trimethylsilane (V)

This compound was prepared by the method of Petrov *et al.*[16].

Phenacyltrimethylsilane (VI)

A Grignard reagent made from 12.27 g (0.10 mole) of (chloromethyl)trimethylsilane and 21.43 g (0.10 mole) of magnesium in 100 ml of dry ether was added dropwise to a stirred mixture containing 20.4 g (0.09 mole) of benzoic anhydride in 100 ml of dry ether in a carbon dioxide/acetone bath over a period of 45 min. The mixture was stirred another 45 min and allowed to warm up. When the temperature of the reaction mixture had reached −15°, 100 ml of 10% ammonium chloride solution was added dropwise. After washing the ether layer with saturated sodium bicarbonate and sodium chloride solution the ether was removed at reduced pressure. Distillation gave 12 g (73% yield) of the ketone; b.p. 130–134°/20 mm. The infrared spectrum of the compound (pure liquid) had bands at 3070 (w), 2970 (s), 2910 (m), 1668 (s), 1600 (m), 1580 (w), 1450 (m), 1415 (m), 1248 (s), 1260 (s), 1105 (m), 1010 (w), 850 (s), 753 (m), 705 (m) cm^{-1}. The ultraviolet spectrum (in sodium dried n-hexane had a λ_{max} of 235.5 mμ ($\varepsilon = 15{,}000$). The NMR spectrum had peaks at 8.05 (multiplicity of 4), 7.41 (4), 2.72 (1), 0.07 (1) ppm from tetramethylsilane. (Found: C, 68.44; H, 8.14; Si, 14.89. $C_9H_{16}OSi$ calcd.: C, 68.67; H, 8.39; Si, 14.62%.)

Acetonyltrimethylsilane (VII)

This compound was prepared by the method of Hauser and Hance[17].

Benzoyltrimethylsilane (VIII)

This compound was prepared according to the procedure developed by Brook and co-workers[18].

(4-Hydroxy-4,5-dimethyloctyl)trimethylsilane (IX)

To a Grignard reagent prepared from 0.73 g (0.03 mole) of magnesium and 4.6 g (0.03 mole) 2-bromopentane (Matheson, Coleman and Bell) in 50 ml of dry ether was added dropwise with stirring 2.25 g (0.0123 mole) of (4-oxopentyl)trimethylsilane. The mixture was refluxed for 30 min. The complex was hydrolyzed by pouring into 20 ml of saturated ammonium chloride solution. The ether layer was washed and dried over anhydrous magnesium sulfate. After removal of the ether under reduced pressure, the crude alcohol was purified by eluting with a pentane/ether mixture (4:1) through a dry packed column of silicic acid and infusorial earth (2:1). The infrared spectrum of this compound (pure liquid) had bands at 3450 (s), 2950 (s), 2860 (m), 1455 (m), 1375 (m), 1244 (s), 1180 (m), 1080 (w), 1040 (w), 990 (w), 925 (m), 860 (s), 835 (s), 740 (m) and 690 (m) cm^{-1}. The NMR spectrum contained peaks at 1.97 (multiplicity of 1), 1.40 (3), 0.97 (multiplet), 0.48 (8), 0.00 (1) ppm from the peak of the Me_3Si^- group protons. (Found: C, 67.55; H, 13.21; Si, 12.40. $C_{13}H_{30}OSi$ calcd.: C, 67.75; H, 13.12; Si, 12.19%.)

(2-Hydroxy-2-methylcyclobutyl)trimethylsilane (X)

The alcohol was obtained in 85–90% purity by microdistillation of the photolyzed (4-oxopentyl)trimethylsilane at 20 mm. The purer material was obtained as the 3,5-dinitrobenzoate ester by warming the crude alcohol with 3,5-dinitrobenzoyl chloride on the steam bath for 20 min. The solid formed was extracted first with ether and water to decompose the excess chloride. The ester was recrystallized from an ethanol/water mixture (80:20, volumes) for analysis, m.p. 99–101°. The infrared spectrum (of alcohol) contained bands at 3400 (s), 2960 (s), 1600 (w), 1379 (m), 1245 (s), 1165 (m), 860 (s), 750 (m) and 690 (m) cm^{-1}. The NMR spectrum (of alcohol) contained peaks at 3.70 (multiplicity of 1, area of 1), 1.12 (m, 4), 1.01 (m, 3), 0.09 (1, 5), 0.00 (1, 5) ppm from tetramethylsilane. (Found for ester: C, 51.28; H, 5.58; Si, 7.83. $C_{15}H_{20}N_2O_6Si$, calcd.: C, 51.11; H, 5.72; Si, 7.98%.)

In other experiments the entire photolyzed mixture was treated similarly with 3,5-dinitrobenzoyl chloride. The esters were separated by eluting through a silica column with pentane.

Degradation of (2-hydroxy-2-methylcyclobutyl)trimethylsilane

(*a*) *Dehydration of the alcohol.* A mixture of 1.27 g of the alcohol formed in the photolysis of (4-oxopentyl)trimethylsilane and 7 drops of 85% phosphoric acid was heated in a tube connected to a collection vessel in a carbon dioxide/acetone bath. Distillation from the heated tube gave 0.8 g of a liquid which contained no alcohol as shown by the infrared spectrum, 3080 (w), 2850 (s), 1575 (m), 1455 (m), 1375 (m), 1246 (s), 1050 (m), 985 (w), 860 (s), 835 (s), 760 (m), 670 (m) cm^{-1}.

(*b*) *Oxidation of the olefin.* A mixture of 0.8 g of the olefin obtained in the above dehydration and 1.5 g of potassium permanganate in 20 ml of water was cooled in an ice bath with stirring for 7 min. The mixture was allowed to come to room temperature. Enough 20% sodium hydrogen sulfite solution was added to reduce all of the manganese to the manganous ion. The water layer was extracted with ether by continuous extraction for 24 h. After evaporation of the ether 0.2 g of a liquid was obtained which had an infrared spectrum identical with that of levulinic acid.

(2-Cyclohexylethyl)trimethylsilane

A mixture of 7.25 g (0.055 mole) of cyclohexylchloromethane and 15.15 g (0.12 mole) of (chloromethyl)trimethylsilane were mixed and added to 4.14 g (0.18 g-atom) of thinly sliced sodium in 75 ml of anhydrous ether. After 14 h methanol was added to decompose the excess sodium. The mixture was distilled giving 3.5 g boiling at 84–117°/21 mm. The compound was purified by gas–liquid chromatography. The chromatogram indicated that the mixture contained 60% of the product, corresponding to a yield of 21% (2.1 g). The infrared spectrum of the compound (pure liquid) had bands at 2920 (s), 2860 (m), 1450 (s), 1246 (s), 860 (s), 833 (s), 745 (m) and 685 (m) cm^{-1}. The NMR spectrum had peaks at 1.75 (m), 1.14 (m), 0.68 (8) and 0.00 (1) ppm downfield from the peak for the Me_3Si protons. (Found: C, 71.63; H, 13.39; Si, 15.47. $C_{11}H_{24}Si$ calcd.: C, 71.62; H, 13.14; Si, 15.24%.)

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SUMMARY

Photolysis of a series of silyl ketones with the general structure $(CH_3)_3Si(CH_2)_nCOR$ with $n = 0$–4, $R = C_6H_5$ and with $n = 0$–3, $R = CH_3$ has been investigated. When $n = 3$ or 4 a major course of reaction is the Type II cleavage. When $R = CH_3$ and $n = 3$ a substantial amount of cyclobutanol formation occurs; none is detected when $R = C_6H_5$. If $n = 2$ and $R = C_6H_5$ the only photoreactions established are reductive alkylation (by solvent cyclohexane) and cleavage of the carbonyl–methylene bond. If $R = CH_3$ all of the products isolated can be rationalized on the basis of initial cleavage of the carbonyl–methylene bond. Little photochemical

decomposition occurred in an inert solvent with those compounds in which $n = 1$ or 0. However, each underwent facile photocatalyzed hydrolysis to form trimethylsilanol and the aldehyde or ketone.

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