Communications to the Editor

The Photochemistry of Silyl Ketones in Alcohol

Sir:

The n–π* absorption of silyl ketones occurs at abnormally long wavelength (380–420 mμ) with a relatively large extinction coefficient (100–300).[1,2] These facts suggested that silyl ketones might undergo interesting photochemical transformations, and indeed it was reported that the yellow solutions of benzoyltriphenylsilane and its *para*-substituted derivatives in alcohols rapidly faded on exposure to light, although they were stable indefinitely in the dark.[2] The only other reference to the photolysis of α-silyl ketones is by Kuivila, who indicated that the hydrolysis of benzoyltrimethylsilane in wet ether was accelerated by light from a mercury arc.[3] This communication describes results of the photolysis of silyl ketones in methanol and ethanol.

Table I. Silyl Ketone Photolyses in Alcohols[a]

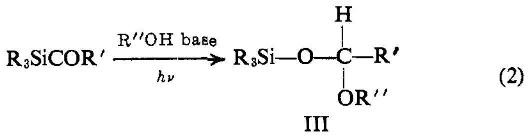
Additive	Time, min	Products (% yield)
		$Ph_3SiCOPh$ in MeOH
...	16	Ph_3SiOMe (75), Ph_3SiOH (25), $PhCH(OMe)_2$ (95), PhCHO (5)
30 μl of C_5H_5N	17	Ph_3SiOMe (5), $Ph_3SiOCHPhOMe$ (95)
30 μl of HOAc[b]	19	Ph_3SiOMe (67), Ph_3SiOH (27), $Ph_3SiOCHPhOMe$ (6), $PhCH(OMe)_2$ (94)
0.5 g of Na_2CO_3	15	Ph_3SiOMe (90), Ph_3SiOH (10), PhCHO (100)
30 μl of C_5H_5N + 30 μl of HOAc	16	Ph_3SiOMe (5), $Ph_3SiOCHPhOMe$ (95)
		$Ph_3SiCOPh$ in EtOH
...	19–24	Ph_3SiOEt (25–32), Ph_3SiOH(68–75), $PhCH(OEt)_2$ (100)[c]
50 μl of C_5H_5N	21	$Ph_3SiOCHPhOEt$ (100)
50 μl of HOAc	21	Ph_3SiOEt (55), Ph_3SiOH (45), $PhCH(OEt)_2$ (90+)
0.5 g of Na_2CO_3	21	$Ph_3SiOCHPhOEt$ (100)
		$Ph_3SiCOMe$ in MeOH[e]
...	40[d]	Ph_3SiOMe (79), Ph_3SiOH (21)
30 μl of C_5H_5N	45[d]	Ph_3SiOMe (7), $Ph_3SiOCHMeOMe$ (93)[f]
50 μl of HOAc	40[d]	Ph_3SiOMe (77), Ph_3SiOH (23)
		$Ph_3SiCOMe$ in EtOH[e]
...	30[d]	Ph_3SiOEt (75), Ph_3SiOH (25)
20 μl of C_5H_5N	30[d]	$Ph_3SiOCHCH_3OEt$ (90+)[f]
50 μl of HOAc	50[d]	Ph_3SiOEt (81), Ph_3SiOH (19)
0.5 g of Na_2CO_3	45[d]	$Ph_3SiOCHCH_3OEt$ (75+)
		α-NpMePhSiCOPh (racemic) in MeOH
...	23[g]	R_3Si^*OMe[h,i] (90+), $PhCH(OMe)_2$ (72), PhCHO (28)
50 μl of C_5H_5N	22[d]	R_3Si^*OMe (5), $R_3Si^*OCHPhOMe$ (95), $PhCH(OMe)_2$ (5)

[a] Unless otherwise specified 0.5 g of ketone in 10 ml of alcohol was used. Products present in only trace amount are not reported. Yields were estimated from nmr data determined in CCl_4 solution. [b] Proportions of methoxysilane and silanol varied from about 2:1 to 1:1 in different runs. [c] Results in neutral ethanol varied substantially from run to run. [d] 0.5 g of ketone in 15 ml of solvent. [e] Aldehyde or aldehyde acetal lost through evaporation and hence not detected in these runs. [f] Traces of unidentified by-products observed. [g] 0.75 g of ketone in 20 ml of alcohol. [h] R_3Si^* designates asymmetric silicon center bearing methyl, α-naphthyl, and phenyl groups. [i] Identified by mixture melting point with an authentic sample.

Two general types of reaction occur, depending on the conditions. In methanol or ethanol solutions, either neutral or with added traces of acetic acid, relatively rapid photolysis occurs and the major products were found to be the alkoxysilane I with variable amounts of the corresponding silanol, and the aldehyde dialkyl acetal II, sometimes accompanied by a little free aldehyde, as shown in eq 1.

$$R_3SiCOR' \xrightarrow[h\nu]{R''OH} \underset{\text{I}}{R_3SiOR''} + R_3SiOH + \underset{\text{II}}{R'CH(OR'')_2} \ (+\ R'CHO) \qquad (1)$$

In alcoholic solution to which a small amount of pyridine or other amine has been added, the reaction takes a different course, and the mixed acetal of the aldehyde with silanol and alcohol (III) is the major product, as shown in eq 2.



$$R_3SiCOR' \xrightarrow[h\nu]{R''OH\ \text{base}} R_3Si{-}O{-}\underset{\underset{\text{III}}{OR''}}{\overset{H}{C}}{-}R' \qquad (2)$$

a, R = R′ = Ph; R″ = Me
b, R_3Si = α-NpMePhSi; R′ = Ph; R″ = Me

Typical results are shown in Table I, where irradiation of the alcohol solutions in Pyrex glassware em-

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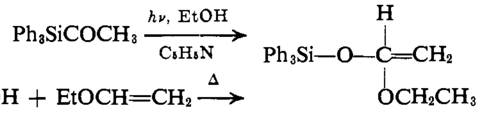
(1) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957); A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

(2) A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965).

(3) H. G. Kuivila and P. L. Maxfield, *Inorg. Nucl. Chem. Letters*, **1**, 29 (1965).

ployed a 100-w lamp.[4] Using 0.5-g quantities of ketone in 10–15 ml of solvent, complete reaction was accomplished within 15–45-min exposure, as evidenced with benzoylsilanes by the fading of the originally yellow solution to colorless. After removal of the solvent under reduced pressure, the resulting material was examined by nmr spectroscopy, which allowed determination of the compounds present and of their proportions. This was of considerable assistance since most of the products were liquids, and some were relatively unstable.

The compounds formed under slightly basic conditions are of particular interest. Thus photolysis of benzoyltriphenylsilane in methanol gave α-methoxy-α-triphenylsiloxytoluene (IIIa) (benzaldehyde methyl triphenylsilyl acetal), as an unstable oil, identified by analysis, by its infrared absorption at 3.52 (O–Me), 6.9 (C–Ph), 7.0 and 9.0 (Si–Ph), and 9.4 μ (Si–O–C), and by its nmr spectrum which consisted of a 1-proton singlet at δ 5.87 ppm, assigned to the alkyl proton deshielded by two adjacent oxygen atoms, a 3-proton singlet at 3.0 ppm for the methoxyl group, and a 20-proton aromatic multiplet from 7.1 to 7.9 ppm. Similarly the oil isolated from photolysis of acetyltriphenylsilane in ethanol was assigned the structure 1-ethoxy-1-triphenylsiloxyethane (IV), based on its spectral properties and its independent synthesis from triphenylsilanol and ethyl vinyl ether, based on the procedure of Shostakovskii, *et al.*[5]



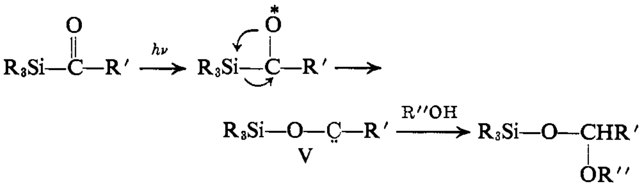
$$Ph_3SiCOCH_3 \xrightarrow[C_5H_5N]{h\nu,\ EtOH} Ph_3Si{-}O{-}\underset{OCH_2CH_3}{\overset{H}{C}}{=}CH_2 \xleftarrow{\Delta} Ph_3SiOH + EtOCH{=}CH_2 \qquad (3)$$

IV

Two other results are also of particular interest. When optically active (+)-benzoylmethyl-α-naphthylphenylsilane, $[\alpha]_D$ +6.05°, of known absolute configuration[6] was photolyzed in neutral methanol, the predominant product found was (−)-methyl-α-naphthylphenylmethoxysilane, $[\alpha]_D$ −8.0°, having a rotation corresponding to 78% net retention of configuration.[7]

On photolysis in methanol containing a trace of pyridine, (+)-benzoylsilane, $[\alpha]_D$ +6.18°, gave α-(methyl-α-naphthylphenylsiloxy)-α-methoxytoluene (IIIb) as the major product, as indicated by its nmr spectrum: δ 0.73 (s, 3 H, Si-*Me*), 3.05 (s, 3 H, O-Me), 5.75 (s, 1 H, C-*H*), and 7.1–8.2 (m, 17 H, ArH) ppm. The acetal was immediately reduced with lithium aluminum hydride in dibutyl ether, reaction conditions known to involve retention of configuration,[8] giving 77% of (−)-methyl-α-naphthylphenylsilane, (−)R_3Si^*H, with $[\alpha]_D$ −25.1°, corresponding to 90% over-all retention of configuration. Thus both photochemical pathways (eq 1 and 2) involve significantly stereoselective processes.

We consider it probable that the mixed acetals III arise from a photochemical isomerization of the silyl ketone to a siloxycarbene V, which then inserts into the OH bond of the alcohol.[9] Photochemical formation of oxacarbenes from ketones have been reported recently by several workers,[10] and Quinkert[11] has established that in such processes an adjacent asymmetric center retains its stereochemical configuration, as observed here. Retention of configuration at an asymmetric silicon center involved in silicon–oxygen bond formation and silicon–carbon bond rupture has been observed previously.[6,12]



$$R_3Si{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow{h\nu} R_3Si{-}\overset{\overset{*}{O}}{\overset{|}{C}}{-}R' \longrightarrow \underset{V}{R_3Si{-}O{-}\ddot{C}{-}R'} \xrightarrow{R''OH} R_3Si{-}O{-}\underset{OR''}{\underset{|}{C}}HR'$$

At present we do not understand the role of base in apparently changing the course of the photochemically catalyzed alcoholysis in neutral or acidic media to that described above. Preliminary rate studies suggest that the rate of conversion of mixed acetals of type III to alkoxysilanes I and aldehyde acetals II in alcohol medium having comparable acid concentrations is much slower than the direct rate of photolysis of ketone to I and II. In addition the displacement of alkoxide from asymmetric silyl ethers by alcohol, catalyzed either by base or acid, is known to involve inversion of configuration[13] at silicon.

Based on this evidence it is unlikely that the formation of I and II arises from an acid-catalyzed displacement on III by alcohol followed by acid-catalyzed acetal formation. Further studies are in progress.

Acknowledgment. This research was supported by the National Research Council of Canada.

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[4] General Electric "PAR-38" spot lamp, color temperature 2700°K.

[5] M. F. Shostakovskii, D. A. Kochkin, I. A. Shikhiev, and V. M. Vlasov, *J. Gen. Chem. USSR.*, **25**, 593 (1955); *Chem. Abstr.*, **50**, 3270 (1956).

[6] A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

[7] The relative and absolute configurations of a wide variety of methyl-α-naphthylphenylsilyl derivatives have been unambiguously established from stereochemical and X-ray studies.[6] See also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[8] L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964).

[9] Unpublished studies from this laboratory strongly indicate the intermediacy of a siloxycarbene in the photochemical reactions of diphenylsilacyclohexanone: A. G. Brook and J. B. Pierce, *J. Org. Chem.*, 30, 2566 (1965).

[10] P. Yates and L. Kilmurry, *Tetrahedron Letters*, 1739 (1964); *J. Am. Chem. Soc.*, **88**, 1563 (1966); H. V. Hosteller, *Tetrahedron Letters*, 687 (1965); R. F. C. Brown and R. K. Solly, *ibid.*, 169 (1966); H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966).

[11] G. Quinkert, G. Cimballek, and G. Burn, *ibid.*, 4573 (1966).

[12] A. G. Brook and C. M. Warner, *ibid.*, **18**, 815 (1962).

[13] R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometal. Chem.* (Amsterdam), **1**, 37 (1963).

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Direct Observation of Intermediates in the Chromic Acid Oxidation of Secondary Alcohols[1]

Sir:

Although the oxidation of secondary alcohols has been postulated to proceed *via* the series of steps[2]

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[1] This investigation was supported by the National Science Foundation.

[2] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); F. H. Westheimer and N. Nicolaides, *J. Am. Chem. Soc.*, **71**, 25 (1949); F. Holloway, M. Cohen, and F. H. Westheimer, *ibid.*, **73**, 65 (1951);