Journal of Organometallic Chemistry, 272 (1984) C10–C12
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOTOLYSIS OF DODECAMETHYLCYCLOHEXASILANE; FORMATION OF BOTH METHYLSILENE AND DIMETHYLSILYLENE

I.S. ALNAIMI, W.P. WEBER*,

Department of Chemistry and The Loker Hydrocarbon Research Institute, University of Southern California, University Park, Los Angeles, CA 90089-1661 (U.S.A.)

A.S. NAZRAN and D. GRILLER*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6 (Canada)

(Received April 24th, 1984)

Summary

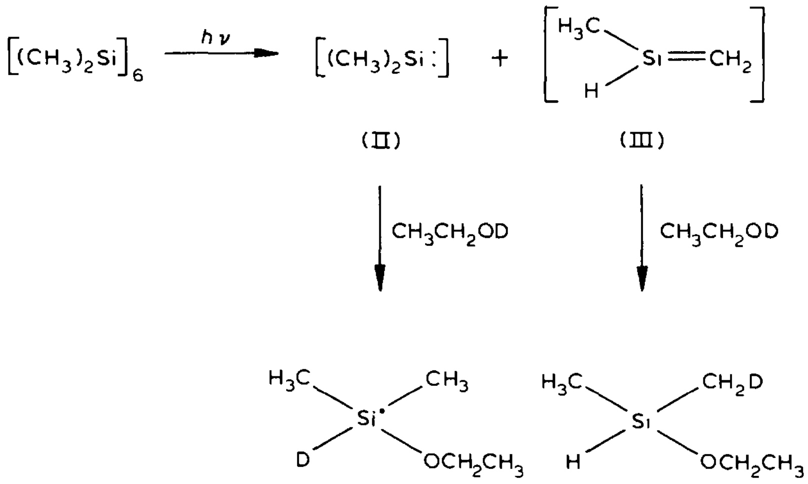
Experimental and spectroscopic investigations of the products of dodecamethylhexasilane photolysis on reaction with labeled organic reagents throw new light on the formation of methylsilene and dimethylsilylene and their interconversion reactions.

Photolysis of dodecamethylcyclohexasilane (I) with light of 254 nm has been reported to yield decamethylcyclopentasilane and dimethylsilylene (II) [1–3]. This procedure is in fact the standard method to generate II in solution. We would like to report experimental and spectroscopic observations which demonstrate that this system is more complicated than the current literature suggest. Specifically, that photolysis of I in the presence of ethanol-*O*-d_1 leads to both II and methylsilene (III). Dimethylsilylene (II) reacts with ethanol-*O*-d_1 to yield dimethylethoxysilane-*Si*-d_1 (IV-*Si*-d_1) [4,5] while III reacts with ethanol-*O*-d_1 to yield dimethylethoxysilane-*C*-d_1 (IV-*C*-d_1) [6–9].

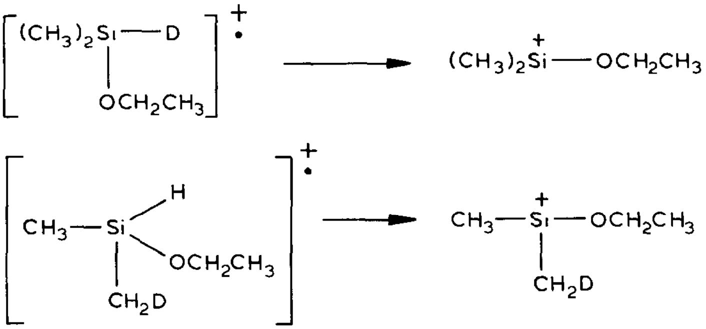
There has been considerable recent experimental [10–12] and theoretical [13–16] interest in the interconversion of II and III under pyrolysis conditions.

Photolysis of a deoxygenated THF (1.5 ml) solution of I (23 mmol) and ethanol-*O*-d_1 (44 mmol) [17] with a 450 W medium pressure Hanovia Hg lamp at 0°C gave IV-d_1 as expected. It was isolated by preparative GLPC [18] and had the following spectral properties: ^{1}H NMR δ 4.59 (sept. small J 2.8 Hz) [19], 3.68 (q, 2H, J 7 Hz), 1.19 (t, 3H, J 7 Hz) and 0.19 (s, 6H). IR-FT (gas phase) Si—H 2120 (w) cm^{-1} with a shoulder at 2128 cm^{-1} and Si—D 1542 (s) cm^{-1}.

0022-328X/84/$03.00



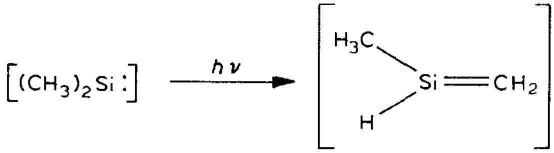
The most critical data comes from the deuterium NMR (^{2}H NMR) which was run on an IBM-WP-270-SY spectrometer operating at 41.467 MHz in the FT mode. Deuterium chemical shifts are reported relative to chloroform-d_1. With proton decoupling two singlets were observed: δ(Si—D) at 4.57 ppm and δ(C—D) at 0.118 ppm. In the undecoupled spectrum the Si—D was still a singlet but the C—D signal was now a triplet J 1.9 Hz. Under conditions where toluene-d_8 gave a correct 5/3 ratio integration, the ratio of the Si—D to C—D was 93/7. Analysis of the mass spectrum of this sample on the assumption that each molecule of IV-d_1 contains one deuterium and the known fragmentation patterns of dimethylsilyl ethers, which lose methyl groups or hydrogen from the silyl center to form siliconium ions [20,21], yields a ratio of Si—D to C—D 93/7 in remarkable agreement with that obtained by ^{2}H NMR. Mass spectrum: parent 105 (4.8%), $P - 1$ (11.6%), $P - 2$ (71%), $P - 15$ (100%) and $P - 16$ (14.1%) [22].



Similar results have been obtained from the photolysis of a diethyl ether solution of I and D_2O.

Additional evidence in support of the generation of II and III on photolysis of I is the observation of a transient absorption at 275 nm on laser flash photolysis (λ 249 nm) of a 3-methylpentane solution of I [23]. One of these is at 275 nm in close agreement with the UV absorption maximum of III in a matrix at low temperature which has been reported at 260 nm [24].

A more mundane interpretation of our data is that II undergoes photoisomerization to III by absorption of a second photon of light prior to reaction with ethanol-*O*-d_1.



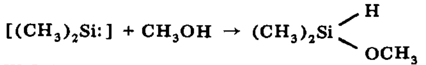
This process has in fact been observed in matrices at low temperature [25,26]. The fact that II is quenched by methanol in THF with a rate constant of greater than 10^6 M^{-1} sec^{-1} [27], strongly argues against this interpretation. At the very least, the possibility of simultaneous production of III or its secondary formation faster than reaction of II with various substrates must be considered in evaluation of all experiments in which II is generated by the photolysis of I.

Further experiments to clarify this situation are in progress.

Acknowledgement. I.S. Alnaimi and W.P. Weber thanks the Air Force Office of Scientific Research under grant number 80-0006 for its generous support.

References

1 M. Ishikawa and M. Kumada, J. Organomet. Chem., 42 (1972) 325.
2 M. Kumada, J. Organomet. Chem., 100 (1975) 127.
3 M. Ishikawa and M. Kumada, Advances in Organometallic Chemistry, Vol. 19, Academic Press, New York, 1981, p. 51—93.
4 T-Y.Y. Gu and W.P. Weber, J. Organomet. Chem., 184 (1980) 7.
5 K.P. Steele and W.P. Weber, J. Am. Chem. Soc., 102 (1980) 6095.
6 L.E. Gusel'nikov and M.C. Flowers, J. Chem. Soc. Chem. Commun., (1967) 64.
7 R.D. Bush, G.M. Golino, G.D. Homer, and L.H. Sommer, J. Organomet. Chem., 80 (1974) 37.
8 G. Bertrand, J. Dubac, P. Mazerolles, and J. Ancelle, J. Chem. Soc. Chem. Commun., (1980) 382.
9 M.C. Flowers and L.E. Gusel'nikov, J. Chem. Soc. B, (1968) 419 and 1396.
10 T.J. Barton, S.A. Burns, and G.T. Burns, Organometallics, 1 (1982) 210.
11 R.T. Conlin and D.L. Wood, J. Am. Chem. Soc., 103 (1981) 1843.
12 R.T Conlin and R.S. Gill, J. Am. Chem. Soc., 105 (1983) 618.
13 R. Walsh, J. Chem. Soc. Chem. Commun., (1982) 1415.
14 Y. Yoshioka and H.F. Schaefer, J. Am. Chem. Soc., 103 (1981) 1366.
15 H.F. Schaefer, Acct. Chem. Res., 15 (1982) 283.
16 C.F. Pau, W.J. Pietro, and W.J. Hehre, J. Am. Chem. Soc., 105 (1983) 16.
17 Merck Sharp of Canada.
18 GLPC was carried out at a 1/4" X 7' 20% Carbowax on 60/80 mesh Chromosorb P column.
19 We have previously assumed that this peak resulted from reaction of a small amount of unlabelled methanol with dimethylsilylene.



$$[(CH_3)_2Si:] + CH_3OH \rightarrow (CH_3)_2Si\begin{smallmatrix}H\\OCH_3\end{smallmatrix}$$

20 W.J. Richter and D.H. Hunnemann, Helv. Chim. Acta, 57 (1974) 1131.
21 K.P. Steele and W.P. Weber, Org. Mass Spectrom., 17 (1982) 222.
22 The observed intensity data for P(1) and P(2) must be corrected for ^{29}Si and ^{30}Si isotopes. K. Biemann, Mass Spectrometry Organic Chemical Applications, see Chapter 5. The Mass Spectra of Isotopically Labeled Molecules, McGraw Hill, 1962, p. 204—250.
23 Laser flash photolysis of a 4.4×10^{-4} M solution of I in 3-methylpentane was carried out with λ 249 nm excitation from a Krypton fluoride excimer, pulse width 12 nsec, power 250 mJ per pulse. It was not possible to measure the lifetime of the transient λ_{max} 275 nm due to competing absorption of I and decamethylcyclopentasilane.
24 H.P. Reisenauer, G. Mihm, and G. Maier, Angew. Chem. Int. Ed., 21 (1982) 1854.
25 T.J. Drahnak, J. Michl, and R. West, J. Am. Chem. Soc., 103 (1981) 1845.
26 C.A. Arrington, K.A. Klingensmith, R. West, and J. Michl, J. Am. Chem. Soc., 106 (1984) 525.
27 A.S. Nazran, J.A. Hawari, D. Griller, I.S. Alnaimi, and W.P. Weber, J. Am. Chem. Soc., submitted.