Journal of Organometallic Chemistry, **117 (1976) C58—C62**

Preliminary communication

PHOTOCHEMICALLY GENERATED SILICON-CARBON DOUBLE-BONDED INTERMEDIATES

IV. PHOTOLYSIS OF 1-ALKENYLDISILANES

MITSUO ISHIKAWA, TAKAMASA FUCHIKAMI and MAKOTO KUMADA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

(Received May 26th, 1976)

Summary

Photolysis of 1,2-divinyl- and 1-phenyl-2-vinyltetramethyldisilane and 1-phenylethenylpentamethyldisilane has been investigated. All three compounds afforded a new type of silicon-carbon double-bonded intermediate *via* photorearrangement of a silyl group to the terminal carbon of a vinyl group.

Recently, we have demonstrated that photolysis of aryl-substituted disilanes gives reactive silicon-carbon double-bonded intermediates which can be trapped by acceptors such as olefins [1], alcohols [2] and acetylenes [3]. In this communication we report the first examples of the photochemical formation of silicon-carbon double-bonded intermediates from 1-alkenyldisilanes.

The UV absorption of 1-alkenyldisilanes [4] suggests that these compounds would be interesting materials for photochemical studies.

Indeed, we have found that irradiation of 1,2-divinyltetramethyldisilane (Ia) (5.63 mmol) at 2537Å for 18 h in the presence of methanol (6 ml) in 80 ml of dry benzene afforded 1-methoxydimethylsilyl-2-vinyldimethylsilylethane (IIa) in 72% yield as the sole volatile product when 83% of the starting disilane was photolyzed. Compound IIa was isolated by preparative GLC and identified by ^{1}H NMR spectrum (δ) [0.04 (CH_3-Si, s, 12H), 0.47 (CH_2CH_2, s, 4H), 3.34 (CH_3-OSi, s, 3H), 5.5-6.3 (vinyl protons, ABX, 3H)] and mass spectroscopic studies. Similarly, photolysis of Ia in the presence of methanol-d_1 under similar conditions gave compound (IIb) which had high isotopic purity (90%) as determined by measuring the relative areas of the CH_3-OSi and ethylenic protons in the ^{1}H NMR spectrum and by mass spectrometric analysis. Because the resonance of ethylenic protons in compound IIb was a sharp singlet, making it impossible to locate the deuterium, we obtained evidence for it on the basis of the following experiment. 1-Phenylethenylpentamethyldisilane (Ib) was photolyzed in the presence of methanol or methanol-d_1. With unlabeled methanol, 1-methoxydimethylsilyl-2-trimethylsilyl-1-phenylethane (IIc) was obtained in 43% yield, along with 22% of unchanged Ib. With methanol-d_1, monodeuterated product, 1-deuterio-1-methoxydimethylsilyl-2-trimethylsilyl-1-phenylethane (IId), which had high isotopic purity (80%) was produced in 47% yield, in addition to 6% of unchanged Ib.

The elemental analyses and IR and mass spectra of the two compounds, IIc and IId, were completely consistent with the proposed structures. The NMR spectrum of IIc showed proton absorptions (δ) at -0.17 (CH_3-$SiMe_2$, s, 9H), 0.05 (CH_3-SiMe, s, 6H), 1.00 (CH_2, $\underline{AB}$X, 2H), 2.19 (CH, AB$\underline{X}$, 1H), 3.35 (CH_3-O, s, 3H) and 6.9-7.3 (ring protons, m, 5H), while the spectrum of IId showed absorptions at -0.17 (CH_3-$SiMe_2$, s, 9H), 0.05 (CH_3SiMe, s, 6H), 1.02 (CH_2, m, 2H), 3.36 (CH_3-O, s, 3H), 6.9-7.3 (ring protons, m, 5H). The NMR spectrum of IId clearly indicated that the deuterium is bonded to the benzylic carbon.

These results can best be understood in terms of the photoisomerization* of 1-alkenyldisilanes to silicon-carbon double-bonded intermediates (A), followed by reaction with methanol (see Scheme 1).

Next we turned our attention to investigation into the photolysis of 1-phenyl-2-vinyltetramethyldisilane (Ic), because, in this system, there are two possible routes to the photochemical formation of the silicon-carbon double-bonded intermediate. One involves photorearrangement of a silyl group to the phenyl ring to give intermediate (B) and the other to the vinyl substituent to give intermediate (A).

Interestingly, irradiation of Ic in the presence of methanol for 1.5 h at room temperature gave a single product in 82% yield, in addition to 18% of unchanged Ic. The mass [m/e 252(M^+)] and ^{1}H NMR spectrum (δ) [0.03 (CH_3-SiOMe, s, 6H), 0.25 (CH_3-SiPh, s, 6H), 0.55 (CH_2CH_2, m, 4H), 3.33 (CH_3-OSi, s, 3H) and 7.2-7.5 (ring protons, m, 5H)] of the product clearly indicates that it must have a 1,2-disilylethane structure (IIe).

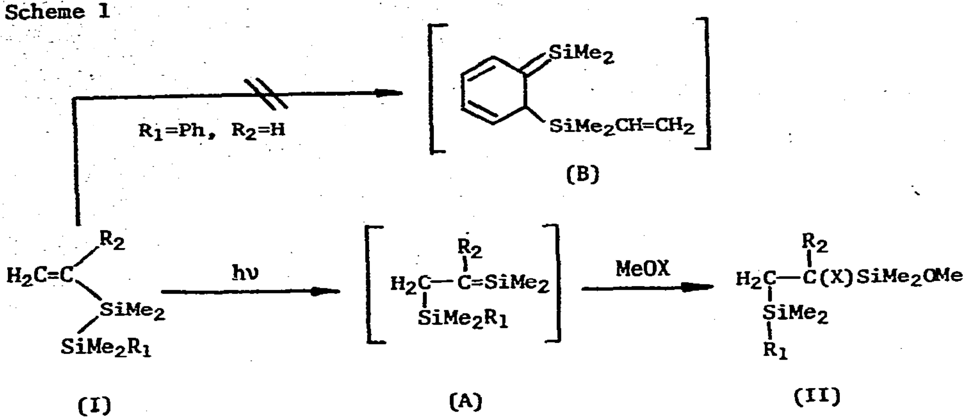
The silicon-carbon double-bonded intermediates thus formed react with ketones to give olefins *via* the well-known pseudo-Wittig reaction [6]. For example, returning to the photolysis of Ib (see above for structure of Ib), it was found that photolysis of Ib in the presence of one equivalent of acetone in benzene afforded 1-trimethylsilyl-2-phenyl-3-methylbut-2-ene (III) in 17% yield.

The photolysis of a variety of 1-alkenylpolysilanes in the presence of various types of quenching agents is currently being examined and will be reported elsewhere.

---

* 1,3-Thermal rearrangement of the silyl group in allylsilanes has been reported [7].

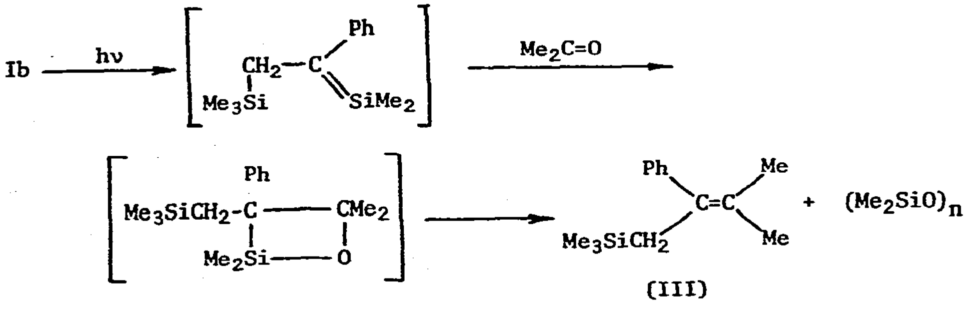
Scheme 1



Ia, $R_1=CH_2=CH-$, $R_2=H$
Ib, $R_1=Me$, $R_2=Ph$
Ic, $R_1=Ph$, $R_2=H$

IIa, $R_1=CH_2=CH-$, $R_2=H$
X=H (80%)
IIb, $R_1=CH_2=CH-$, $R_2=H$
X=D (87%)
IIc, $R_1=Me$, $R_2=Ph$
X=H (55%)
IId, $R_1=Me$, $R_2=Ph$
X=D (50%)
IIe, $R_1=Ph$, $R_2=H$
X=H (100%)

Scheme 2



Acknowledgments

The cost of this research was defrayed in part by a Grant-in-Aid for Scientific Research by the Ministry of Education to which the author's thanks are due. They also express their appreciation to Tochiba Silicon Co., Ltd. and Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes.

References

1 M. Ishikawa, T. Fuchikami, T. Sugaya and M. Kumada, J. Amer. Chem. Soc., 97 (1975) 5923.

2 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., in press.

3 M. Ishikawa, T. Fuchikami and M. Kumada, to be published.

4 M. Kumada and K. Tamao, Adv. Organometal. Chem., 6 (1968) 19.

5 H. Gilman, W.H. Atwell and G.L. Schwebke, J. Organometal. Chem., 2 (1964) 369.

6 C.M. Golino, R.D. Bush, P.N. Roark and L.H. Sommer, J. Organometal. Chem., 66 (1974) 29.

7 H. Kwart, J. Slutsky, J. Amer. Chem. Soc., 94 (1972) 2515.