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Preliminary communication

PHOTOLYSIS OF ORGANOPOLYSILANES. THE REACTION OF PHOTOCHEMICALLY GENERATED TRIMETHYLSILYLPHENYLSILYLENE WITH ALKYL CHLORIDES

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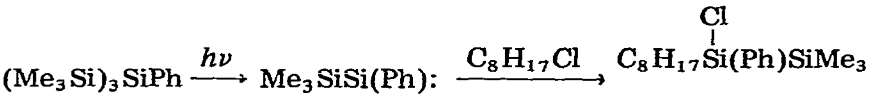
Summary

Photochemically generated trimethylsilylphenylsilylene reacted with octyl chloride and cyclopropylcarbinyl chloride to give the respective formal carbon—chlorine insertion products. With sec-butyl chloride, trimethylsilylphenylsilylene afforded both the carbon—chlorine insertion product and 1-chloro-1-phenyl-2,2,2-trimethyldisilane (IV), while with tert-butyl chloride, IV was obtained as the sole volatile product.

There has been a considerable interest recently concerning the reactions of silylene species with compounds bearing a functional group [1—10]. This paper is concerned with a novel reaction of trimethylsilylphenylsilylene with alkyl chlorides. When a mixture of 2.81 mmol of tris(trimethylsilyl)phenylsilane (I) [11], 14.10 mmol of octyl chloride and 0.29 mmol of pentadecane as an internal standard in 100 ml of dry hexane was irradiated at 0°C with a 10 W low-pressure immersion mercury lamp having a Vycor filter for 1.5 h under a nitrogen atmosphere, 62% of I reacted to give 1-chloro-1-octyl-1-phenyltrimethyldisilane (II) [^{1}H NMR δ (ppm) 0.16 (Me_3Si, s, 9H), 0.8—1.6 ($n\text{-}C_8H_{17}$, m, 17H), 7.3—7.6 (C_6H_5, m, 5H); M^+ 326; Found: C, 62.30; H, 9.50. $C_{17}H_{31}ClSi_2$ calcd.: C, 62.43; H, 9.55%] in 9% yield. No other volatile products arising from the silylene and the substrate were observed. Under identical



$$(Me_3Si)_3SiPh \xrightarrow{h\nu} Me_3SiSi(Ph){:} \xrightarrow{C_8H_{17}Cl} C_8H_{17}\overset{Cl}{\overset{|}{Si}}(Ph)SiMe_3$$

(I) (II)

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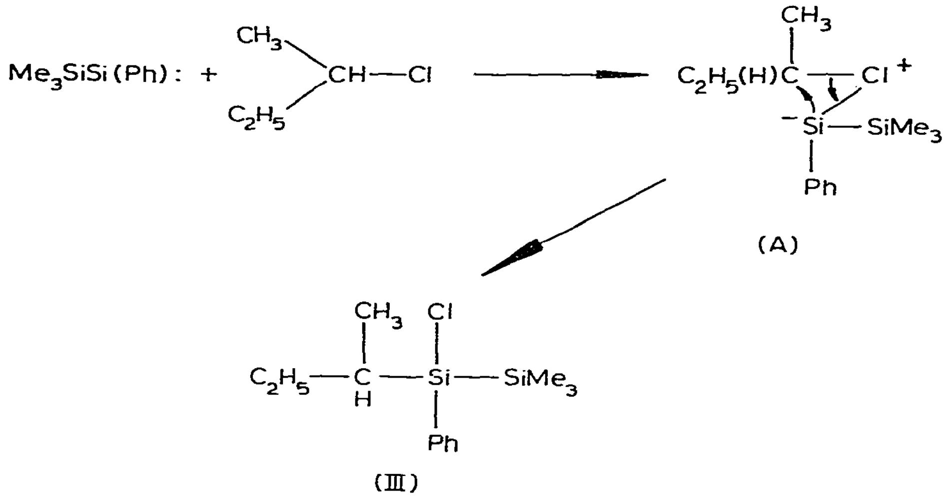
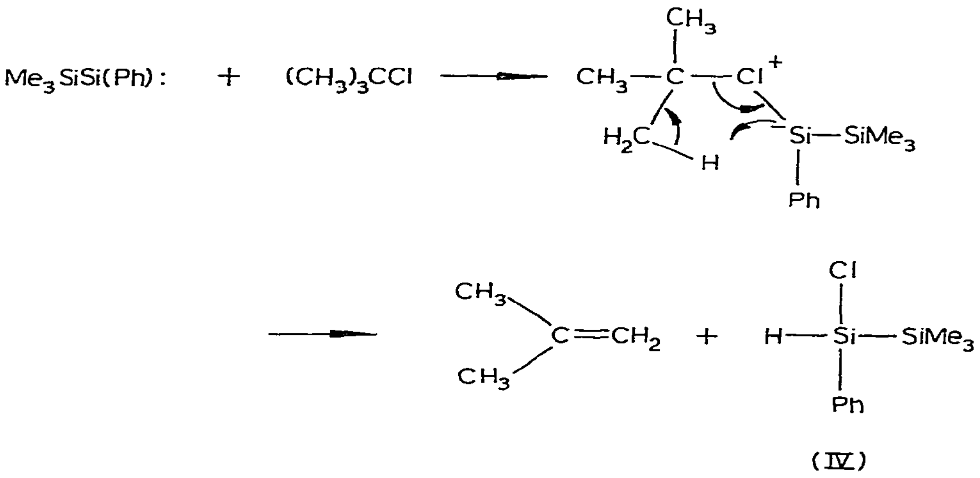
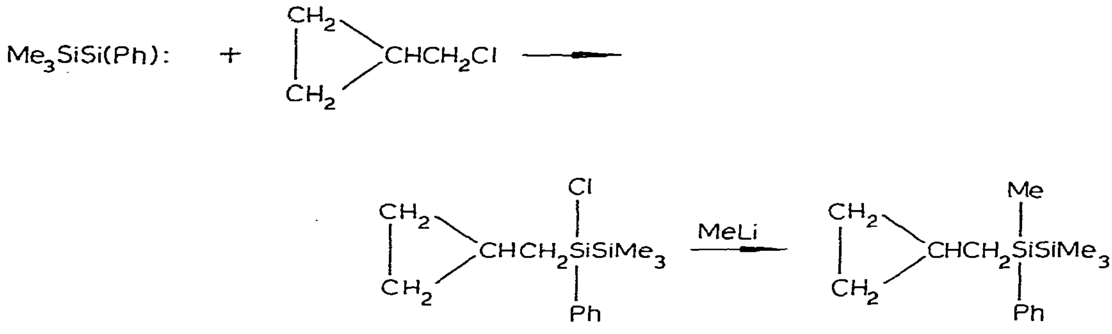


SCHEME 1

conditions, trimethylsilylphenylsilylene reacted with sec-butyl chloride to give 1-(sec-butyl)-1-chloro-1-phenyltrimethyldisilane (III) in 7% yield. All spectral data for III were identical with those of the authentic sample prepared by the reaction of sec-butyllithium with 1,1-dichloro-1-phenyltrimethyldisilane in 88% yield [^{1}H NMR δ (ppm) 0.19 (Me_3Si, s, 9H), 0.8—1.8 ($CH_3CH_2CHCH_3$, m, 9H), 7.3—7.6 (C_6H_5, m, 5H); M^+ 270; Found: C, 57.50; H, 8.45. $C_{13}H_{23}ClSi_2$ calcd.: C, 57.63; H, 8.56]. In this photolysis, 1-chloro-1-phenyl-2,2,2-trimethyldisilane (IV) [^{1}H NMR δ (ppm) 0.23 (Me_3Si, s, 9H), 5.20 (HSi, s, 1H), 7.3—7.6 (C_6H_5, m, 5H); IR (cm^{-1}) 2125; M^+ 214; Found: C, 50.70; H, 7.16. $C_9H_{15}ClSi_2$ calcd.: C, 50.32; H, 7.04] was also obtained in 10% yield, in addition to 1-butene (7% yield) and *trans*-2-butene (5% yield). Interestingly, the photolysis of I in the presence of tert-butyl chloride afforded compound IV in 27% yield, along with isobutene (28% yield). In this case, no formal carbon—chlorine insertion product was detected.





(V)

Although the nature of these reactions is uncertain, initial formation of a zwitterion such as A, followed by migration of the alkyl group to the silicon atom to give compound II or III seems reasonable (Scheme1). Compound IV may also be understood as a product of hydrogen transfer from the β-carbon atom to the silicon in the zwitterion intermediate. Intermediacy of the zwitterion has recently been proposed in the reaction of photochemically generated dimethylsilylene with 3,4-epoxybutadiene [7].

The photolysis of I in the presence of cyclopropylcarbinyl chloride, followed by methylation of the resulting product afforded 1-phenyl-1-cyclopropylcarbinyltetramethyldisilane (V) [^{1}H NMR δ (ppm) 0.05 (Me$_3$Si, s, 9H), 0.38 (MeSi, s, 3H), 0.5 to −0.1 (CH$_2$CH$_2$, m, 4H), 0.69 (HC, m, 1H), 0.88 (CH$_2$Si, m, 2H), 7.3—7.6 (C$_6$H$_5$, m, 5H); IR (cm^{-1}) 3000, 1015; Exact mass 248.1403 (calcd.: 248.1417)] in 14% yield. No ring-opened product was detected by either spectroscopic analysis or GLC analysis.

In the present photolysis, product yields are rather low, but by-products in the distillates are in trace amounts. Non-volatile substances presumably produced from polymerization of the silylene itself were always obtained, after distillation of the photolysis mixture.

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References

1 M.E. Childs and W.P. Weber, J. Org. Chem., 41 (1976) 1799.
2 W. Ando, M. Ikeno and A. Sekiguchi, J. Amer. Chem. Soc., 100 (1978) 3613.
3 W. Ando and M. Ikeno, Chem. Lett., (1978) 609.
4 D. Seyferth and T.F.O. Lim, J. Amer. Chem. Soc., 100 (1978) 7074.
5 C. Liu and T. Hwang, J. Amer. Chem. Soc., 101 (1979) 2996.
6 T.Y. Gu and W.P. Weber, J. Organometal. Chem., 184 (1980) 7.
7 D. Tzeng and W.P. Weber, J. Amer. Chem. Soc., 102 (1980) 1451.
8 V.J. Tortorelli and M. Jones, Jr., J. Chem. Soc. Chem. Commun., (1980) 785.
9 M. Ishikawa, K. Nakagawa, S. Katayama and M. Kumada, J. Amer. Chem. Soc., in press.
10 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 214 (1981) 277.
11 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 190 (1980) 117.