Tetrahedron Letters No. 16, pp 1299 - 1302, 1976. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS OF ORGANOPOLYSILANES. PHOTOCHEMICAL ONE-STEP SYNTHESIS OF MONO- AND DISUBSTITUTED SILEPINS

Mitsuo Ishikawa, Takamasa Fuchikami, and Makoto Kumada

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

(Received in Japan 19 February 1976; received in UK for publication 11 March 1976)

Despite considerable activity in the area of heterocycloheptatrienes, there have been no reports of nonannulated silacycloheptatrienes except for 2,7-diphenylsilepin.[1] Moreover, a convenient, general procedure for the synthesis of the annulated[2] and nonannulated silepins is presently not available. We now wish to report photochemical one-step synthesis of certain mono- and dialkyl substituted silepins and their thermal behavior.

We recently reported that the photochemical formation of silicon-carbon doubly bonded intermediates and their reactions with some olefins.[3] In extension of these reactions to other systems, we have found that when vinylsilanes such as dimethylvinyl, trimethylvinyl- and ethyldimethylvinylsilane are used as quenching agents in the photolysis of aryldisilanes, silepin derivatives are always formed in 5-9% yield, in addition to the normal adducts (32-49%). Likewise, the photochemical reaction of aryldisilanes with 1-hexyne also gave silepin derivatives in 9-12% yield. Consequently, this novel development provides a facile and highly convenient synthesis of certain mono- and dialkyl substituted silepins.

The following procedure for the synthesis of 3-[1',2'-bis(trimethylsilyl)ethyl]silepin (3a) is representative. When a solution of phenylpentamethyldisilane (1a) (4.80 mmol) and trimethylvinylsilane (2a) (0.10 mol) in 110 ml of dry benzene was irradiated at 2537Å for 8 hr under a purified nitrogen atmosphere, 3a was obtained in 7% yield, in addition to *o*-(trimethylsilyl)-(β-trimethylsilylethyl)dimethylsilylbenzene (4)[3] at a stage where 80% of 1a was photolyzed. Similarly, silepin (3b) was obtained in 8% yield from 1b and 2a, while 3c in 5% yield from 1a and 2b.

The NMR spectral data shown in Table 1 for silepin derivatives thus obtained are quite consistent with the proposed structure.

In order to obtain further information concerning the production of silepin, *p*-tolylpentamethyldisilane (1c) was photolyzed in the presence of 2a in benzene solution. Surprisingly enough, only a 3,6-di-substituted silepin (3d) was obtained in 7% yield. No other isomers of silepin were detected by GLC analysis of the reaction mixture. The NMR spectrum of 3e prepared from the photolysis of 1c in the presence of 2c afforded crucial evidence for the presence of the trimethylsilyl moiety bonded to the terminal ethyl carbon atom. Thus, the proton resonances of the disilylethyl group [$-H^aC(SiMe_2H)C(H^b)(H^c)SiMe_3$] showed at δ 2.45 (double triplets), 0.70 (double doublets) and 1.19 (double doublets) corresponding to H^a, H^b and H^c protons, respectively.

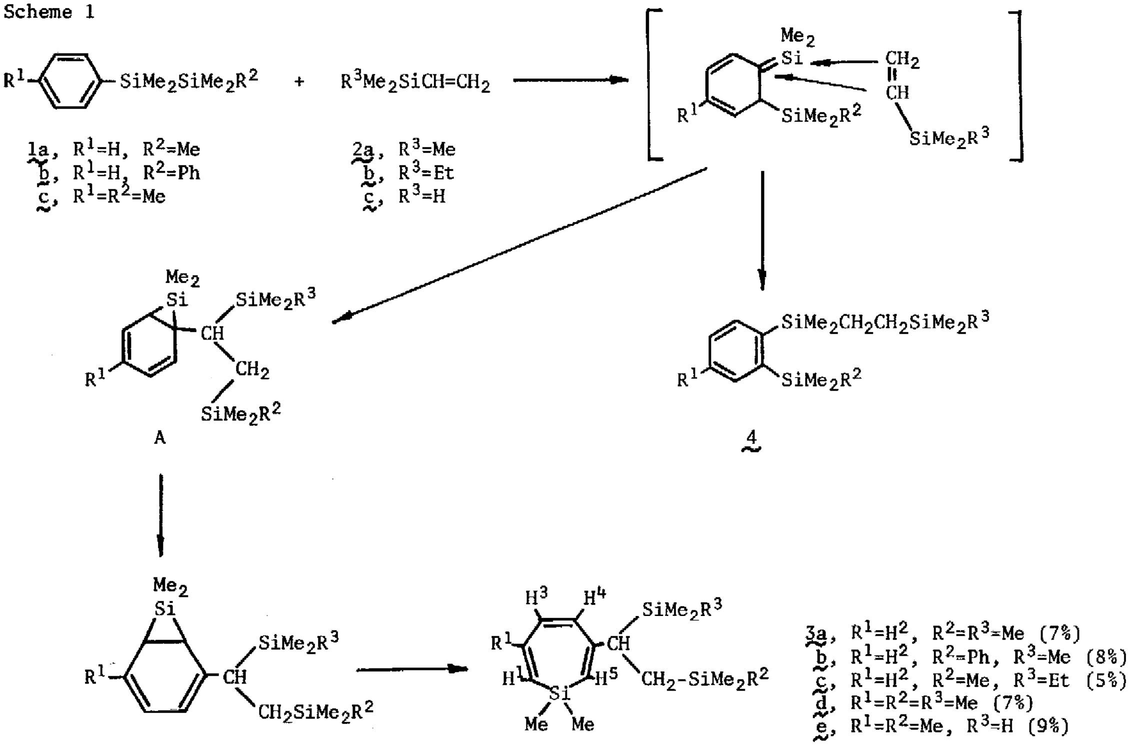
Table 1. NMR, UV and Mass Spectral Data for Compounds 3a-e and 5a-d

Compound	H^1	$H^2(R^1)$	H^3	H^4	H^5	H^6	$J_{H^1H^2}$	$J_{H^2H^3}$	$J_{H^3H^4}$	M^+	λ_{max}(in C_6H_{12}) (ε)
3a	5.42	6.37	5.84	5.84	4.93		15.1	2.6		308	223
3b	5.48	6.42	5.89	5.89	5.17		14.9	2.6		370	
3c	5.42	6.35	5.85	5.85	4.92		15.1	2.8		322	
3d	5.13		5.74	5.82	4.89				11.9	322	224
3e	5.28		5.78	6.03	5.22				11.7	308	
5a	5.38	6.58	5.93	6.07	5.19	5.47	13.9	2.7	11.3	290	250 (4,230)
5b	5.40	6.61	6.06	5.86	5.34	5.34	14.1	2.8	11.5	290	251 (6,100)
5c	5.05		5.89	6.00	5.21	5.44			11.1	304	251 (5,200)
5d	5.10		5.96	5.78	5.38	5.38			11.4	304	251 (6,440)
7[a]	4.8-5.2	5.8-6.2	6.2-6.4	6.2-6.4	4.8-5.2						
8[b]	5.97	7.34					15.2				

[a] Ref. 4. [b] Ref. 2a and 2b.

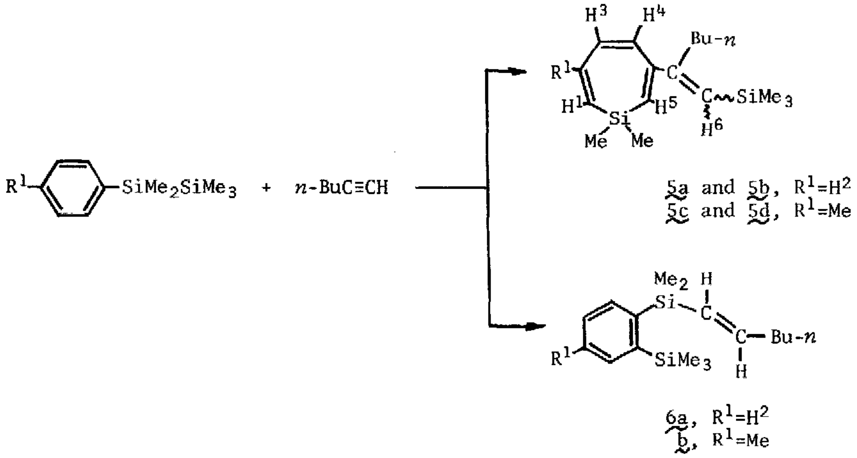
Irradiation of the hydrogen on the silicon atom changed the signal at H^a to double doublets and irradiation of the H^a resonance changed the signal at H^b and H^c to an AB quartet, in accordance with the proposed structure.

Scheme 1



The production of the silepins in the present reaction can be best explained in terms of initial formation of a 7-silabicyclo[4.1.0]heptadiene intermediate (A), which then undergoes walk rearrangement[4] to the sterically favored isomer, followed by ring expansion to the silepin, as shown in Scheme 1.

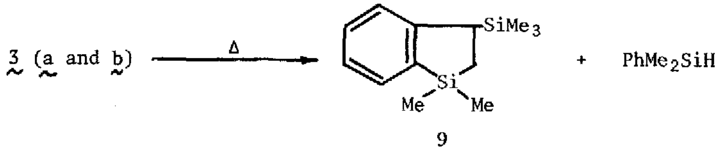
When **1a** was photolyzed in the presence of 1-hexyne under the same conditions as above, two isomers of silepin **5a** and **5b**, easily separable by preparative GLC, were obtained in 4 and 5% yield, respectively, together with 22% yield of *trans*-1-(*o*-trimethylsilylphenyl)dimethylsilyl-1-hexene (**6a**).[5] The photolysis of **1c** in the presence of the same quencher gave also two isomers of silepin, **5c** (6%) and **5d** (6%), in addition to a similar *trans* adduct (**6b**)[6] (26%). The chemical shifts of the silepin ring protons and vinyl protons are consistent with the proposed structure and given in Table 1 in comparison with those of 2,7,7-trimethyltropilidene (**7**)[4] and benzo[d]-silepin (**8**).[2a,b]



5a and **5b**, $R^1=H^2$
5c and **5d**, $R^1=Me$

6a, $R^1=H^2$
b, $R^1=Me$

The thermolysis of silepins reported to date is, to our knowledge, confined to the formation of benzene derivatives with simultaneous extrusion of silylene species.[1,2a] In contrast, the thermolysis of the silepins reported here proceeded to give the silaindane derivatives in 40-50% yield, with loss of hydrosilanes as volatile products. No dimethylsilylene was observed under the used conditions. For instance, both silepins **3a** and **3b** underwent thermolysis at 320° in a sealed tube for 0.5 hr to give 3-trimethyl-1-silaindane (**9**)[7] in 34 and 42% yield, respectively. In the case of **3b**, phenyldimethylsilane was also isolated in 38% yield.



9

Compound **9** can be shown unambiguously to have the proposed structure by comparison of its NMR data with those of the nonsubstituted silaindane.[8]

All of the products reported here could easily be separated by preparative GLC as colorless liquid.

The scope and generality of the photochemical formation of the silepins and thermal behavior are being examined and will be reported elsewhere.

Acknowledgment 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 authors' thanks are due. They also express their appreciation to Toshiba Silicone Co., Ltd. and Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes.

References and Notes

1. T. J. Barton, R. C. Kippenhan Jr., and A. J. Nelson, *J. Amer. Chem. Soc.*, **96**, 2272 (1974).
2. (a) L. Birkofer and H. Haddad, *Chem. Ber.*, **102**, 432 (1969); (b) *ibid.*, **105**, 2101 (1972); (c) L. Birkofer, H. Haddad, and H. Zamarlik, *J. Organometal. Chem.*, **25**, C57 (1970); (d) J. Y. Corey, M. Deuber, and B. Bichlmeir, *ibid.*, **26**, 167 (1971); (e) F. K. Cartledge and P. D. Mollere, *ibid.*, **26**, 175 (1971); (f) T. J. Barton, W. E. Volz, and J. L. Johnson, *J. Org. Chem.*, **36**, 3365 (1971); (g) K. A. Andrianov, L. M. Volkova, N. V. Delazari, and N. A. Chumachskii, *Khim. Geterotskil. Soedin.*, 435 (1967); (h) J. Y. Corey and E. R. Corey, *Tetrahedron Lett.*, 4669 (1972).
3. M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada, *J. Amer. Chem. Soc.*, **97**, 5923 (1975).
4. J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).
5. Compound **6a**: M^+ 290; IR (cm^{-1}) 1620, 995; NMR δ (CCl_4) 0.30 (CH_3-$SiMe_2$, s, 9H), 0.37 (CH_3-SiMe, s, 6H), 0.90 (CH_3-C, m, 3H), 1.38 (-CH_2CH_2-, m, 4H), 2.14 (CH_2-C=C, m, 2H), 5.81 (C=CH-Si, d, 1H, J=18.7 Hz), 5.99 (C=CH-Bu-*n*, dt, 1H, J=18.7 Hz, J=5.0 Hz), 7.10-7.64 (ring protons, m, 4H).
6. Compound **6b**: M^+ 304; IR (cm^{-1}) 1620, 995; NMR δ (CCl_4) 0.28 (CH_3-$SiMe_2$, s, 9H), 0.33 (CH_3-SiMe, s, 6H), 0.91 (CH_3-C, m, 3H), 1.36 (-CH_2CH_2-, m, 4H), 2.13 (CH_2-C=C, m, 2H), 2.31 (CH_3-C_6H_3, s, 3H), 5.79 (C=CH-Si, d, 1H, J=18.5 Hz), 5.96 (C=CH-Bu-*n*, dt, J=18.5 Hz, J=5.0 Hz), 7.01 (ring proton, bd, 1H, J=7.8 Hz), 7.35 (ring proton, bs, 1H), 7.43 (ring proton, d, 1H, J=7.8 Hz).
7. Compound **9**: M^+ 234; NMR δ (CCl_4) 0.00 (CH_3-$SiMe_2$, s, 9H), 0.23 (CH_3-SiMe, s, 3H), 0.33 (CH_3-SiMe, s, 3H), 0.89 (H-CH, dd, 1H, J_{gem}=15.6 Hz, J_{vic}=4.1 Hz), 1.15 (H-CH, dd, 1H, J_{gem}=15.6 Hz, J_{vic}=10.5 Hz), 2.73 (H-$CSiMe_3$, dd, 1H, J=10.5 Hz, J=4.1 Hz), 6.76-7.39 (ring protons, m, 4H).
8. W. Ando, A. Sekiguchi, T. Hagiwara, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 372 (1974).