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Free-Radical Chlorination of Alkylsilanes. VII.* The Hydrogen Abstraction from 1-Silabicyclo[2.2.1]heptane by the Trichloromethyl Radical

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In general, carbon free radicals are assumed to have either the pyramidal configurations undergoing rapid inversion, or the planar structures, so that the bridgehead carbon radicals are formed only with difficulty.[1] For example, the homolytic chlorination of norbornane results in the formation of 2-chloronorbornane exclusively, the 1-chloro isomer being not formed in any appreciable amount.[2] In harmony with this fact, Applequist and Kaplan[3] reached a conclusion that the 1-bicyclo[2.2.1]heptyl radical is less stable than simple alkyl radicals from their results of the decarbonylation of aliphatic and bridgehead aldehydes. In constrast, simple silyl radicals tend to maintain the original tetrahedral geometry without turning itself inside out, and some spectroscopic evidence supporting this point has recently been obtained by several workers.[4–6] Also, two groups of workers[7,8] have reported that silyl radicals, consistent with their tetrahedral structures, abstract a chlorine atom from carbon tetrachloride with high retention of configuration. These preceding evidences might lead to an assumption that the 1-silabicyclo[2.2.1]hept-1-yl radical would readily be formed by the hydrogen abstraction from the corresponding bridgehead hydrosilane, but confirmation of this hypothesis must provide a desirable research objective. The present paper describes the homolytic hydrogen-chlorine exchange reaction between 1-silabicyclo[2.2.1]heptane and carbon tetrachloride which involves the hydrogen abstraction by the trichloromethyl radical from the bridgehead silicon hydride, the silicon analogue of norbornane.

Experimental

All the boiling and melting points are uncorrected. Spectral data of the bicyclic silicon hydride and chloride are presented in Table 1.

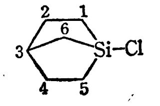
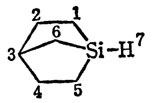
1-Silabicyclo[2.2.1]heptane. This compound was prepared by the method of Sommer and Bennett.[9] The pure product was a white crystalline solid which sublimed very readily and had mp 75°C in a sealed tube (lit.[9] mp 63°C)[10]

Chlorination of 1-Silabicyclo[2.2.1]heptane with Carbon Tetrachloride. Chlorination procedures were essentially the same as described previously.[11–13] Results obtained are summarized in Tables 2 and 3.

Results and Discussion

1-Silabicyclo[2.2.1]heptane was heated with carbon tetrachloride at 80°C in the presence or absence of benzoyl peroxide. As is seen from Table 2, the hydrogen-chlorine exchange reaction between the bridgehead hydrosilane and carbon tetrachloride readily occurs under homolytic conditions, giving a pair of the expected products, the corresponding chlorosilane and chloroform. The reaction can most pro-

Table 1. NMR, IR and MASS spectra of the bicyclic silicon compounds

Compound	NMR, δ, ppm	IR, cm^{-1} (intensity)	MS, *m/e* (rel. intensity)
	0.73 (H^1, H^5 and H^6; 6H), 1.87 (H^2 and H^4; 4H), 2.26 (H^3; 1H)	2955(s), 2920(s), 2150(s), 1445(w), 1406(w), 1250(w), 1154(m), 1142(w), 1134(w), 1100(w), 1055(m), 987(w), 928(w), 898(w), 882(w), 854(s)	114(8), 113(23), 112(54), 111(34), 85(40), 84(100), 83(77), 82(58), 56(92), 55(62), 43(60)
	0.50 (H^1, H^5 and H^6; 6H), 1.63 (H^2 and H^4; 4H), 2.33 (H^3; 1H), 4.51 (H^7; 1H), $J(^{29}Si\text{-}H) = -205.8$ Hz	2940(s), 2900(s), 1435(w), 1393(m), 1143(m), 1135(w), 1127(w), 1093(w), 1046(s), 972(w), 920(w), 888(w), 826(s), 813(s), 780(m), 743(w), 701(m)	148(19), 146(52), 120(36), 119(44), 118(100), 117(94), 92(15), 90(33), 82(28), 65(26), 63(45)

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* For Part VI, see Ref. 16.

1) W. A. Pryor, "Free Radicals," McGraw-Hill, New York (1966), p. 28.

2) J. D. Roberts, L. Urbanek, and R. Armstrong, *J. Amer. Chem. Soc.*, **71**, 3049 (1949).

3) D. P. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

4) P. J. Krusic and J. K. Kochi, *ibid.*, **91**, 3938 6161 (1969).

5) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969); Idem, *J. Chem. Soc.*, *B*, **1969**, 793.

6) S. W. Bennett, C, Eaborn, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc.*, *A*, **1970**, 348.

7) H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, **91**, 519 (1969).

8) A. G. Brook and J. M. Duff, *ibid.*, **91**, 2118 (1969).

9) L. H. Sommer and O. F. Bennett, *ibid.*, **79**, 1008 (1957).

10) Our value of mp is some 12°C higher than that of Sommer and Bennett, but the purity of our sample was confirmed by glpc to be not less than 99%.

11) Y. Nagai, K. Yamazaki, N. Kobori, and M. Kosugi, *Nippon Kagaku Zasshi*, **88**, 793 (1967).

12) Y. Nagai, K. Yamazaki, I. Shiojima, and M. Hayashi, *J. Organometal. Chem.*, **9**, p. 21 (1967).

13) Y. Nagai, K. Yamazaki, I. Shiojima, H. Matsumoto, and S. Nakaido, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 884 (1968).

Table 2. The reaction of 1-silabicyclo[2.2.1]heptane with carbon tetrachloride at 80°C for 10 hr

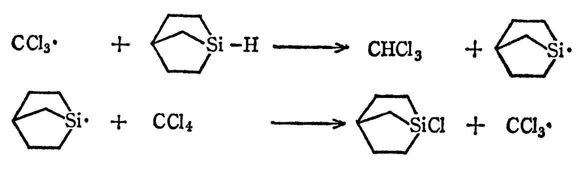
Without BPO		With BPO	
Reactants	(mmol)	Reactants	(mmol)
$C_6H_{12}Si$	(1.42)	$C_6H_{12}Si$	(1.51)
CCl_4	(2.73)	CCl_4	(3.33)
BPO	(none)	BPO	(0.02)
Products	(mmol)	Products	(mmol)
$C_6H_{12}Si$	(1.32)	$C_6H_{12}Si$	(0.44)
CCl_4	(2.54)	CCl_4	(2.04)
$C_6H_{11}SiCl$	(trace)	$C_6H_{11}SiCl$	(0.97)
$CHCl_3$	(trace)	$CHCl_3$	(1.09)

Table 3. Competitive chlorinations of 1-silabicyclo[2.2.1]heptane (A) and triethylsilane (B) with carbon tetrachloride (80°C)[a)]

$[A]_i$, mmol	$[A]_f$, mmol	$[B]_i$, mmol	$[B]_f$, mmol	$[CCl_4]_i$, mmol	k_A/k_B
1.13	0.681	1.20	0.382	12.19	0.442
1.12	0.665	1.23	0.353	12.43	0.452
				Av.	0.447

a) $[A]_i$, $[B]_i$, represent the initial concentrations of two hydrosilanes, $[A]_f$, $[B]_f$, the final concentrations and k_A/k_B the ratio of rate constants for the attack of the abstracting reagent on the two species.

bably be explained in terms of the following chain carrying processes and thus confirms an anticipation previously raised that the SiH hydrogen atom at the bridgehead position can be abstracted by carbon radicals with ease.



The reactivity of the bicyclic silicon hydride toward the trichloromethyl radical was next determined by competition experiments. A mixture of 1-silabicyclo-[2.2.1]heptane and triethylsilane was allowed to react with carbon tetrachloride at 80°C in the presence of benzoyl peroxide. The relative rate was calculated with the equation of Ingold and Shaw[14] from concentrations of the reactants or products as determined by glpc (Table 3). Results show that 1-silabicyclo-[2.2.1]heptane reacts with carbon tetrachloride 0.45 times as fast as triethylsilane. The hydrogen abstraction rate from the bridgehead silicon hydride was thus found to be comparable to that from its open chain analogue, triethylsilane.* However, it is noteworthy that the bridgehead hydride reacts distinctly slower than triethylsilane. This trend cannot be explained on the basis of electronic effects of substituents alone, since there is by no means expected any appreciable difference in the magnitude of the electronic effect between the bridgehead and open chain structures. An attractive explanation for the observed reactivity of the bicyclic system can be advanced, however, by taking into consideration the change in bond hybridization at the bridgehead silicon atom. The fraction of *s* character employed by the silicon in its bond to hydrogen[15] would be forced to increase by special geometrical situation which exists. This was found to be the case as indicated by the large value (in the absolute sence) of $J(^{29}Si\text{–}H)$ for 1-silabicyclo-[2.2.1]heptane, −205.8 Hz, compared to that for triethylsilane, −179.6 Hz. It should be noted at this point that the relative reactivities of a variety of Si–H bonds toward the trichloromethyl radical are linearly correlated with values of $J(^{29}Si\text{–}H)$ which reflect the magnitude of *s* character employed by silicon in the Si–H bonds.[16] In view of this relationship, data for the bridgehead silicon hydride were treated in a similar fashion (Fig. 1). Obviously, the point for 1-silabicyclo[2.2.1]heptane falls on the straight line with a reasonable precision and this fact again indicates that the trichloromethyl radical preferentially attacks a Si–H bond of smaller *s* character. More significant is that the special conformation modifies the electronic structure and hence the reactivity of the molecule to some appreciable extent.

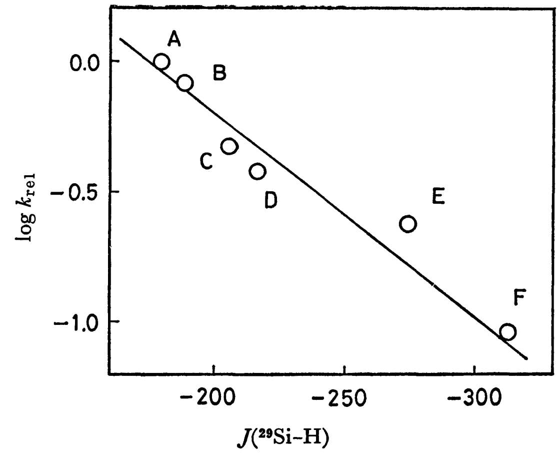


Fig. 1. A plot of relative rates for reactions of hydrosilanes toward the trichloromethyl radical (80°C) *versus* $J(^{29}Si\text{-}H)$. (A): Et_3SiH, (B): $PhMe_2SiH$, (C): 1-silabicyclo[2.2.1]-heptane, (D): Et_2ClSiH, (E): $EtCl_2SiH$, (F): Cl_3SiH.

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14) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, **1927**, 2918.

15) Y. Nagai, M. Ohtsuki, T. Nakano, and H. Watanabe, *J. Organometal. Chem.*, **35**, 81 (1972).

16) Y. Nagai, H. Matsumoto, M. Hayashi, E. Tajima, and H. Watanabe, This Bulletin, **44**, 3113 (1971).

* **Note added in proof.** After this paper was accepted for publication, we were informed that Sommer and Ulland reported similar kinetic measurements of the bicyclic silicon hydride under very nealy the same conditions: see *J. Amer. Chem. Soc.*, **94**, 3803 (1972). Their figures are in almost complete agreement with ours.