Partial Chlorination of Organopolyhydrosilanes

Yoichiro NAGAI, Takeo YOSHIHARA and Setsuko NAKAIDO

Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma

(Received July 5, 1967)

Chlorination of an organosilicon hydride to the corresponding organosilicon chloride(s) can be effected by organic chlorides[1-5] by organosilicon chlorides[1] by molecular chlorine[5] and by other inorganic chlorides.[6-8] Among these reactions, the only method which has proved to be suitable for the synthesis of compounds containing both silicon-hydrogen and silicon-chlorine linkages is the use of chlorides of certain transitional elements.[7,8]

We have very currently found that the reaction between a triorganosilicon hydride and carbon tetrachloride in the presence of benzoyl peroxide gives the corresponding triorganosilyl chloride and chloroform in nearly quantitative yield.[9,10]

$$R_3SiH + CCl_4 \xrightarrow{\text{BPO}} R_3SiCl + CHCl_3$$

A rather obvious extrapolation of these results is to make a practical application of this radical reaction to the partial chlorination of polyhydrosilanes which is as yet uncommon.[11,12]

When an equimolar mixture of phenylsilane and carbon tetrachloride was heated at 80°C for 10 hr in the presence of benzoyl peroxide, phenylchlorosilane was obtained in a 71% yield. A similar reaction utilizing a 1 : 2 mixture resulted in the predominant formation of phenyldichlorosilane (51%). When the same silane was treated with three equivalents of carbon tetrachloride, a 80% yield of phenyltrichlorosilane was realized. Chloroform could also be used as monochlorination reagent. These results and some additional data are presented in Table 1. It is seen that the reaction is particularly useful for the stepwise chlorination of polyhydrosilanes. Phenylsilane is satisfactorily chlorinated to phenylchlorosilane, which can be chlorinated in turn to phenyldichlorosilane in high yield. Although the detailed mechanistic aspects have not been fully disclosed, the synthetic potential of such a partial chlorination is thus clear.

TABLE 1. CHLORINATION OF POLYHYDROSILANES WITH CARBON TETRACHLORIDE OR CHLOROFORM (80°C, 10 hr)[a]

Reactant, mmol	Conversion,[b] %	Product,[c] %
$PhSiH_3$ (10.0), CCl_4 (10.0), BPO (0.5)	58	$PhSiH_2Cl$ (71), $PhSiHCl_2$ (25), $PhSiCl_3$ (4)
$PhSiH_3$ (10.0), CCl_4 (20.0), BPO (0.5)	84	$PhSiH_2Cl$ (37), $PhSiHCl_2$ (51), $PhSiCl_3$ (12)
$PhSiH_3$ (10.0), CCl_4 (30.0), BPO (0.5)	98	$PhSiH_2Cl$ (trace), $PhSiHCl_2$ (20), $PhSiCl_3$ (80)
$PhSiH_3$ (5.0), $CHCl_3$ (5.0), BPO (1.5)	50	$PhSiH_2Cl$ (80), $PhSiHCl_2$ (20), $PhSiCl_3$ (—)[d]
$PhSiH_3$ (5.0), $CHCl_3$ (10.0), BPO (1.5)	76	$PhSiH_2Cl$ (60), $PhSiHCl_2$ (36), $PhSiCl_3$ (4)
$PhSiH_3$ (5.0), $CHCl_3$ (15.0), BPO (1.5)	93	$PhSiH_2Cl$ (49), $PhSiHCl_2$ (50), $PhSiCl_3$ (1)
Ph_2SiH_2 (3.0), CCl_4 (3.0), BPO (0.30)	59	Ph_2SiHCl (77), Ph_2SiCl_2 (23)
Ph_2SiH_2 (5.0), $CHCl_3$ (5.0), BPO (0.20)	45	Ph_2SiHCl (79), Ph_2SiCl_2 (21)
$PhSiH_2Cl$ (2.0), CCl_4 (2.0), BPO (0.3)	28	$PhSiHCl_2$ (85), $PhSiCl_3$ (15)
$PhSiHCl_2$ (2.0), CCl_4 (2.0), BPO (0.2)	44	$PhSiCl_3$ (100)

a) The reaction did not occur to any detectable extent in the absence of the peroxide.
b) No significance should be attached to the conversion with the exception that it is a rough measure of the extent of reaction.
c) Values cited in parentheses are yields based on the consumptions of phenylsilane which were estimated by the use of NMR spectroscopy and vapor phase chromatographic analysis.
d) Not detectable.

---

[1] F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, *J. Am. Chem. Soc.*, **69**, 2108 (1947).

[2] B. N. Dolgov, S. N. Borisov and M. G. Boronkov, *Zhur. Obshchei Khim.*, **27**, 716 (1957); *Chem. Abstr.*, **51**, 16282 (1957).

[3] J. W. Jenkins and W. Post, *J. Org. Chem.*, **15**, 556 (1950).

[4] H. Gilman, W. H. Atwell, P. K. Sen and C. L. Smith, *J. Organometal. Chem.*, **4**, 163 (1965).

[5] A. G. Taylor and G. B. V. de Walden, *J. Am. Chem. Soc.*, **66**, 842 (1944).

[6] N. S. Nametkin, A. V. Topchiev and L. S. Povarov, *Doklady Akad. Nauk, S. S. S. R.*, **103**, 435 (1955); *Chem. Abstr.*, **50**, 5515 (1956).

[7] H. H. Anderson and A. Hendifar, *J. Am. Chem. Soc.*, **81**, 1027 (1959).

[8] H. H. Anderson, *ibid.*, **82**, 1323 (1960).

[9] Y. Nagai, K. Yamazaki, N. Kobori and M. Kosugi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Soct.)*, **88**, 793 (1967).

[10] Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori and M. Hayashi, *J. Organometal. Chem.*, in press.

[11] V. Bazant, V. Chvalovsky and J. Rathousky, "Organosilicon Compounds," Vol. I, Academic Press, New York (1965), p. 131.

[12] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), p. 210.