SHORT COMMUNICATIONS

Reductive Dehalogenation of Halobenzenes with Hydrosilanes in the Presence of Free-Radical Initiators[1]

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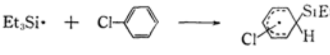
(Received January 28, 1969)

Reductive dehalogenation of unactivated aromatic halides is not easy, drastic reaction conditions being usually required.[2] In this communication, we present preliminary results of facile and mechanistically interesting reduction of halobenzenes with hydrosilanes involving free silyl radicals as intermediates.[3] To date, an example of the peroxide-catalyzed reaction of chlorobenzene with triphenylhydrosilane has been reported,[4] but no reduction product nor condensation product was detected.

In a typical experiment, 9.06 mmol of chlorobenzene, 8.94 mmol of triethylsilane, and 5.02 mmol of di-*t*-butyl peroxide were mixed and sealed in a small ampoule, and were allowed to react at 135 ± 1°C for 15 hr. Examination of the products by GLC revealed that benzene (3.16 mmol, 35.3%), phenyltriethylsilane (0.325 mmol, 3.6%), and hexaethyldisiloxane (2.57 mmol, 57.5%) were present along with a small amount of unchanged chlorobenzene, acetone, and *t*-butyl alcohol. Bromobenzene (5.15 mmol) was also reduced to benzene (3.08 mmol, 59%) with triethylsilane (5.13 mmol), and di-*t*-butyl peroxide (2.57 mmol). The product contains also unchanged bromobenzene (1.34 mmol, 26%), acetone, and *t*-butyl alcohol. In both cases, triethylsilane was consumed completely. It is also established that no reaction took place without an initiator in otherwise the same reaction conditions.

Only a trace amount of biphenyl was detected. Therefore, intermediacy of phenyl radicals may not be excluded completely, but in the present reaction, direct abstraction of a halogen atom by free silyl radicals seems less plausible as a main reaction since no chlorobiphenyl was detected in spite of careful examination. Furthermore, recent observation in this laboratory[5] has demonstrated that silyl radicals produced by the reaction of trialkylhydrosilane with peroxide undergo successful homolytic substitution with aromatic solvents such as benzene and toluene.

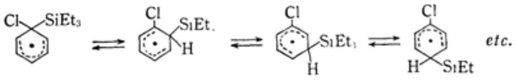
These facts suggest therefore that more plausible process of reduction involves addition-elimination reactions of free silyl radicals.



(I)

$$\text{I} \longrightarrow \text{Et}_3\text{SiPh} + \text{Cl}\cdot$$
$$\text{Cl}\cdot + \text{Et}_3\text{SiH} \longrightarrow \text{Et}_3\text{Si}\cdot + \text{HCl}$$
$$\text{Et}_3\text{SiPh} + \text{HCl} \longrightarrow \text{Et}_3\text{SiCl} + \text{PhH}$$
$$\text{I} + \text{Et}_3\text{Si}\cdot \longrightarrow \text{Et}_3\text{SiCl} + \text{Et}_3\text{SiPh}$$
$$\text{Et}_3\text{SiCl} + t\text{-BuOH} \rightarrow\rightarrow\rightarrow \text{Et}_3\text{SiOSiEt}_3$$

It should be noted, however, that no substitution product, (chlorophenyl)triethylsilane, was obtained contrary to the cases of other aromatic solvents. This may be rationalized by the explanation that intermediate free radicals, I, could be fluxional[6] at the reaction temperature, like (trimethylsilyl)-cyclopentadiene,[7] and, moreover, elimination or abstraction of the chlorine atom from the intermediate, Ia, would be faster than hydrogen abstraction to give substitution products.



(Ia) (Ib) (Ic) (Id)

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[1] Silyl Radicals III. Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968; Preprint, III, p. 1941.

[2] E. Ōsawa and Z. Yoshida, This Bulletin, **40**, 1996 (1967).

[3] For production of silyl radicals from hydrosilanes by hydrogen abstraction, see H. Sakurai, M. Murakami and M. Kumada, *J. Am. Chem. Soc.*, **91**, 519 (1969), and references cited therein.

[4] J. Curtice, H. Gilman and G. S. Hammond, *ibid.*, **79**, 4754 (1957); however, see Y. Nagai, K. Yamazaki, N. Kobori and. M Kosugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure. Chem. Sect*), **88**, 793 (1967).

[5] H. Sakurai, A. Hosomi and M. Kumada, *Tetrahedron Letters*, **1969**, No. 22 in press.

[6] F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[7] H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, 312 (1965); A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968).