Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

The reaction of silyl radicals with halobenzenes

It has been reported that substituted silyl radicals react with halobenzenes via an addition-displacement sequence rather than by a halogen abstraction mechanism[1,2]. Thus trimethylsilyl radicals produced by heating bistrimethylsilylmercury react with chlorobenzene to produce mainly phenyltrimethylsilane. The process does not involve the intermediacy of phenyl radicals[2] although traces of biphenyl were detected[3]. In the case of fluorobenzene no biphenyl was detected[3]. The analogous reaction of silyl radicals produced by photolysing substituted silicon hydrides is described here. The photochemical reactions appear to proceed substantially by both an addition-displacement mechanism and a halogen abstraction mechanism.

The irradiation of chlorobenzene and a four molar excess of trimethylsilane for 100 h gave phenyltrimethylsilane (11%) and benzene (13%) in addition to trimethylchlorosilane. Low percentages of biphenyl, chlorobiphenyl and a species (I) of mass number corresponding to either chlorotrimethylsilylcyclohexadiene or the corresponding aromatic compound were detected in the mass spectrum of the reaction products. Irradiation of trimethylsilane with a four molar excess of chlorobenzene led to suppression of benzene formation and an increase in the formation of the biphenyls. The reaction does not proceed in the dark and is inhibited by diphenylamine. Irradiation of chlorobenzene alone for the same periods of time as those of the reaction gave only very slight traces of biphenyl or substituted biphenyls. A mechanism which involves phenyl radicals produced by abstraction of the halogen atom is suggested for the formation of benzene and the biphenyls. The phenyltrimethylsilane may be formed by radical recombination of phenyl radicals with trimethylsilyl radicals, or by an addition-displacement mechanism which has been previously described[2]. The latter is more likely, particularly in view of the detection of compound (I). This allows an approximate estimation of the ratio of the addition-displacement reaction to the halogen abstraction reaction (addition/abstraction) of 0.83 : 1 by comparison of the yields of phenyltrimethylsilane and benzene. Analogous reactions occur between trimethylsilane and fluorobenzene (addition/abstraction = 17 : 1) and between trichlorosilane and chlorobenzene (addition/abstraction = 2.7 : 1). Benzene was not detected after photolysis of trichlorosilane and fluorobenzene.

The results suggest that the halogen abstraction reaction is facilitated by photolysis, and that chlorine is more readily abstracted than fluorine. It also appears that trimethylsilyl radicals are much more reactive towards halogen abstraction than are trichlorosilyl radicals. The reactions of arylsilicon hydrides with halobenzenes at 600° also gives products which can be accounted for by the operation of both an addition-displacement and an abstraction mechanism[4,5]. With trichlorosilane or methyldichlorosilane and dichlorobenzene at 600° however the products could be accounted for by the addition-displacement mechanism alone[5].

Chlorobenzene and fluorobenzene exhibit strong benzenoid absorption in the region 2450–2750 Å and as irradiation was with light mainly of wavelength 2537 Å electronic excitation of the aromatic molecules throughout the reaction is clearly possible. It has been shown that the triplet states of chlorobenzene and fluorobenzene can be appreciably populated during excitation by intersystem crossing from the shorter lived first excited singlet[6,7]*. The difference between the thermal and the photochemical reactions of silyl radicals with chlorobenzene and fluorobenzene may arise because of reaction with both ground state and excited molecules during the photochemical reaction.

The irradiations were carried out in quartz tubes using a Hannovia 250 watt mercury resonance lamp and with exposure of the liquid phase only. Percentages were estimated by means of gas–liquid chromatography for the benzene and by mass spectra for the phenyl silicon compounds. In each case the method was calibrated by comparison of the reaction products with solutions of known concentrations.

Acknowledgement

The author acknowledges support by the Science Research Council.

University Chemical Laboratory DEREK COOPER
Cambridge (Great Britain)

1 J. M. BIRCHALL, W. M. DANIEWSKI, R. N. HASZELDINE AND L. S. HOLDEN, *J. Chem. Soc.*, (1965) 6702.
2 C. EABORN, R. A. JACKSON AND R. W. WALSINGHAM, *Chem. Commun.*, (1965) 300.
3 A. G. BEAUMONT, C. EABORN, R. A. JACKSON AND R. W. WALSINGHAM, *J. Organometal. Chem.*, 5 (1966) 297.
4 A. D. PETROV AND E. FISHER, *Zh. Obshch. Khim.*, 32 (1962) 698; *Chem. Abstr.*, 58 (1963) 6853g.
5 A. D. PETROV, E. A. CHERNYSHEV AND GUAN-LIAN LI, *Doklady Akad. Nauk SSSR*, 132 (1960) 1099; *Chem. Abstr.*, 54 (1960) 20995i.
6 N. J. TURRO, *Molecular Spectroscopy*, Benjamin, New York, 1965, p. 75.
7 W. A. NOYES AND I. UNGER, *Advan. Photochem.*, 4 (1966) 49.
8 D. BRYCE SMITH AND H. C. LONGUET-HIGGINS, *Chem. Commun.*, (1966) 593.

Received December 7th, 1966

---

* The formation of various products during the irradiation of benzene has recently been ascribed to reaction of the excited states of the molecule[8].