Journal of Organometallic Chemistry, 85 (1975) 15–18
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIONS OF BIS(TRIPHENYLSILYL)MERCURY WITH HYDROXY COMPOUNDS

C. EABORN, R.A. JACKSON AND M.T. RAHMAN*
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
(Received August 15th, 1974)

Summary

Bis(triphenylsilyl)mercury reacts with hydroxy compounds to give hydrogen, triphenylsilyl ethers, and mercury as the major products, along with some triphenylsilane. A molecular mechanism is proposed, in contrast to the free radical reactions of the mercurial which occur at higher temperatures in hydrocarbon solvents.

Introduction

The reactions of bis(triphenylsilyl)mercury with hydrocarbons under both pyrolytic and photolytic conditions have been reported previously [1,2]. There is considerable evidence that under these conditions this mercurial decomposes to triphenylsilyl radicals, which react subsequently to give products typical of organosilyl radical reactions [3]. In this paper, we describe the reactions of bis(triphenylsilyl)mercury with some hydroxy compounds, and present evidence for molecular mechanisms for these reactions.

Experimental

Bis(triphenylsilyl)mercury was prepared as described previously [1]. Alcohols were purified by drying over anhydrous magnesium sulphate followed by fractional distillation. Triphenylsilane [4], m.p. 45-46°; phenoxytriphenylsilane [5], m.p. 103-104°; triphenylsilanol [6], m.p. 152-153°; and n-octyloxytriphenylsilane [7] (from n-octanol, chlorotriphenylsilane and diethylamine), m.p. 25°, b.p. 192°/0.3 mm were prepared by published procedures. Other compounds used for comparison were available in the laboratory.

---

* Present address: Department of Chemistry, University of Dacca, Ramna, Dacca 2, Bangladesh.

TABLE 1

DECOMPOSITION TIMES FOR SOLUTIONS OF BIS(TRIPHENYLSILYL)MERCURY IN VARIOUS HYDROXY COMPOUNDS

Hydroxy compound	Temperature (°C)	Time for complete decomposition[a]
H—OH[b]	Ambient	Very fast[c]
n-C_8H_{17}—OH	120	0.5 h
cy-C_6H_{11}—OH	140	0.5 h
C_6H_5—OH	220	2.0 h
cy-C_6H_{12}	220	21 days[c]

[a] As judged visually by following the disappearance of the yellow-green colour of the mercurial. [b] Saturated solution in benzene. [c] Reported in ref. 1.

Sample preparation and pyrolysis procedure

The reaction mixtures were made up in a glove-box which was filled with dry, oxygen-free nitrogen. Bis(triphenylsilyl)mercury (ca. 0.05 g) and the appropriate alcohol (ca. 1 ml), which had previously been degassed, were introduced into a Pyrex ampoule, which was then stoppered, removed from the glove-box, attached to a vacuum line, degassed further and sealed off under vacuum. The ampoules were heated in the dark in an oil bath, the temperature of which was maintained with ± 2°; the times required for complete decomposition (as judged by the disappearance of the yellow-green colour) are noted in Table 1.

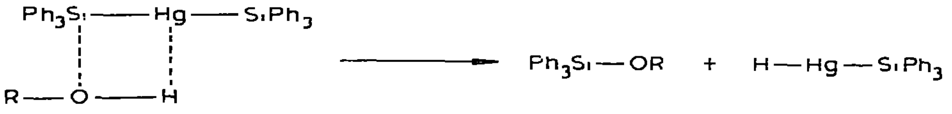
Product analysis

Mercury was estimated either complexometrically [8] or by direct weighing. For hydrogen determinations, special ampoules with long necks were used, which could be attached (unopened) to a vacuum line by pressure tubing and then opened to the vacuum line by breaking the narrow part of the ampoule which was inside the pressure tubing. Hydrogen was identified mass spectrometrically and determined quantitatively by noting the pressure when a known volume was occupied, after other components had been condensed by liquid nitrogen.

Other products were identified by comparison of GLC retention times with those of authentic compounds; the major components were estimated by GLC using octacosane as the internal standard.

Results and discussion

The products obtained from the reactions of bis(triphenylsilyl)mercury with various hydroxy compounds are shown in Table 2. The absence of tetraphenylsilane and hexaphenyldisilane among the products is an indication that triphenylsilyl radicals do not participate in the reactions, and it is suggested that molecular reactions, such as those shown in equations (1) to (4) are involved.



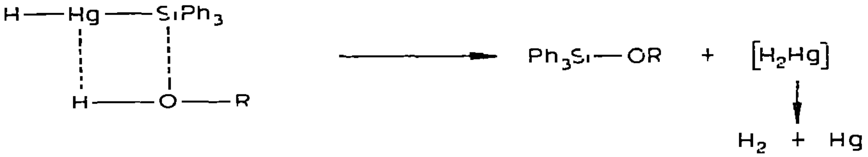
$$\begin{array}{ccccc} Ph_3Si & — & Hg & — & SiPh_3 \\ \vdots & & \vdots & & \\ R—O & — & H & & \end{array} \longrightarrow Ph_3Si—OR + H—Hg—SiPh_3 \qquad (1)$$

TABLE 2

REACTION OF BIS(TRIPHENYLSILYL)MERCURY WITH HYDROXY COMPOUNDS ROH

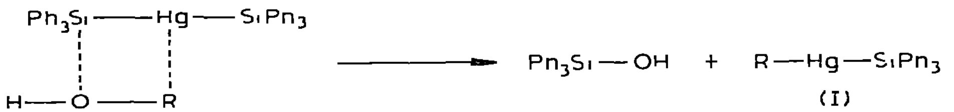
Products	Yields (%) R =			
	H[a]	Ph	cy-C_6H_{11}	n-C_8H_{17}
H_2	Present	Present	0.75 mole[b]	0.6 mole[b]
Ph_3SiH	Minor product	10-12	5-6	1
Ph_3SiOH	Major product	Trace	Trace	Trace
Ph_3SiOR	Major product	75-80	87	86
Ph_4Si	Nil	Nil	Nil	Nil
$Ph_3Si{-}SiPh_3$	Trace	Nil	Nil	Nil
R—R		Trace	Trace?	Trace
RH			Nil	Nil
RHgR		Nil	Nil	
Hg	100	96	96	97

[a] See ref. 1. [b] Per mole of mercurial.



(2)

$$H{-}Hg{-}SiPh_3 \longrightarrow HSiPh_3 + Hg \qquad (3)$$



(4)

The intermediate I may react further to give other minor products, but since the yields of triphenylsilanol are very small compared with those of the silyl ethers, reaction (4) appears to be relatively unimportant.

From Table 1, the rates of decomposition in various solvents are seen to fall along the series: H-OH > n-$C_8H_{17}OH$ > cy-$C_6H_{11}OH$ > C_6H_5OH > cy-C_6H_{12}. The much faster decomposition rates in the hydroxylic solvents compared with cyclohexane rule out simple homolysis of the mercurial as the mechanism for its disappearance in hydroxylic solvents. A radical chain mechanism could not be ruled out on this evidence alone, but is unlikely in view of the products (see above). Four-centre processes of type (1) have been postulated for other reactions of silyl mercurials [9]; the strength of the silicon—oxygen bond formed is doubtless important as a driving force [10]. The differences in reactivity of the various hydroxy compounds (H_2O > n-$C_8H_{17}OH$ > cy-$C_6H_{11}OH$) may be partly steric in origin, while the relative unreactivity of phenol may be due to the delocalizing effect of the phenyl ring on the lone pair oxygen electrons. The somewhat greater proportion of triphenylsilane formed from the reaction of bis(triphenylsilyl)mercury with phenol compared with the other alcohols may be explained in terms of the reaction sequence (1) to (4) and the observed reactivity order: if reaction (1) is slow, the removal of H—Hg—$SiPh_3$ by reaction (2) would also be expected to be slow, and hence removal of this intermediate by reaction (3) [either a unimolecular or a bimolecular reaction] to give triphenylsilane will be favoured.

Acknowledgement

We thank the Commonwealth Scholarship Commission for the award of a research studentship (to M.T.R.).

References

1 R.A. Jackson, Chem. Commun., (1966) 827; C. Eaborn, R.A. Jackson and M.T. Rahman, J. Chem. Soc. Perkin Trans. II, (1972) 55.
2 N.S. Vyazankin, O.A. Kruglaya, G.S. Kalinina and E.N. Gladyshev, J. Gen. Chem. USSR, 38 (1968) 1544.
3 R.A. Jackson, Advan. Free Radical Chem., 3 (1969) 231.
4 H.H. Reynolds, L.A. Bigelow and C.A. Kraus, J. Amer. Chem. Soc., 51 (1929) 3067.
5 H. Gilman and G.N.R. Smart, J. Org. Chem., 19 (1954) 441.
6 R. West, R.H. Baney and D.L. Powell, J. Amer. Chem. Soc., 82 (1960) 6269.
7 M.M. Sprung and F.O. Guenther, J. Org. Chem., 26 (1961) 552.
8 G. Schwarzenbach, Complexometric Titrations, Methuen, London, 1957, pp. 87-88.
9 C. Eaborn, R.A. Jackson and R.W. Walsingham, J. Chem. Soc. C, (1967) 2188, R. Fields, R.N. Haszeldine and R.E. Hutton, ibid., (1967) 2559; S.W. Bennett, H.J. Clase, C. Eaborn and R.A. Jackson, J. Organometal. Chem., 23 (1970) 403; C. Eaborn, R.A. Jackson and R.W. Walsingham, J. Chem. Soc. Perkin Trans. II, (1973) 366.
10 R.A. Jackson, J. Chem. Soc. B, (1970) 58.