

dimethyl sulfoxide, in the hope that a solvent of high polarity might affect the chemical shift of the two olefinic protons to different extents. However, only a single olefinic peak was obtained in this solvent.

Experimental

The preparation of these compounds has been described previously^{1,4}. We are grateful to Dr. REIICHI SUZUKI for samples of all three. The 100 Mc. NMR spectra were recorded on a Varian HA-100 spectrometer. Deuteriochloroform was used as solvent, and all chemical shifts are reported relative to tetramethylsilane. We are indebted to Mr. JERRY HOLCOMB of Varian Associates for obtaining these spectra.

The authors are grateful to the National Science Foundation for support of this work under Grant NSF-GP 2511.

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Received July 20th, 1965

* National Science Foundation Cooperative Graduate Fellow, 1961-1963; National Science Foundation Summer Graduate Fellow, 1963.

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J. Organometal. Chem., **5** (1966) 295-297

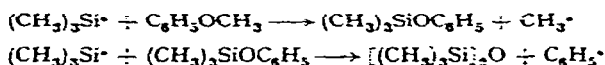
PRELIMINARY NOTES

Reactions of bis(trimethylsilyl)mercury with organic compounds containing oxygen, nitrogen, or halogen

In extension of our work on reactions of trimethylsilyl radicals¹, we have analysed the products of the thermal decomposition of bis(trimethylsilyl)mercury² in various oxygen-, nitrogen-, or halogen-containing organic solvents. We find that the dominant feature of the behaviour of trimethylsilyl radicals towards such compounds is the ease with which they abstract oxygen or halogen atoms.

When anisole is heated with bis(trimethylsilyl)mercury, the products (identified by gas chromatography) are trimethylsilane, tetramethylsilane, hexamethyldisilane, hexamethyldisiloxane, and phenoxytrimethylsilane, and it seems that silyl radicals can displace methyl or phenyl radicals from oxygen:

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Ethoxybenzene gives analogous products. Methoxycyclohexane gives trimethylsilane, methoxytrimethylsilane, cyclohexane, hexamethyldisiloxane, and hexamethyldisilane, along with higher boiling products which are probably cyclohexyltrimethylsilane, cyclohexoxytrimethylsilane, and bicyclohexyl.

With ketones, such as acetone or acetophenone, the major product is hexamethyldisiloxane, the formation of hexamethyldisilane being almost completely suppressed. Benzoquinone reacts very rapidly with bis(trimethylsilyl)mercury, giving a mixture of products which include *p*-bis(trimethylsilyl)benzene in low yield. The main product from nitrobenzene is azobenzene.

Bromobenzene gives hexamethyldisilane, trimethylsilane, bromotrimethylsilane, and phenyltrimethylsilane, along with fairly substantial quantities of biphenyl and mono- and di-bromobiphenyl, indicating that there is direct abstraction of a bromine atom from bromobenzene to give a phenyl radical (*cf.* ref. 3). Chlorobenzene gives the analogous products, but markedly less biphenyl, and it may be that in this case the predominant mechanism is of the type more commonly associated with homolytic aromatic substitution, and involves addition of the trimethylsilyl radical followed by loss of the chlorine atom. No detectable amount of biphenyl is obtained from fluorobenzene, which gives the expected phenyltrimethylsilane among other products.

Chlorine atoms are also readily abstracted from benzyl chloride, from which the main reaction product is bibenzyl, with a little benzyltrimethylsilane. In the reaction with toluene, trimethylsilyl radicals give mainly benzyltrimethylsilane with only a little bibenzyl¹, indicating that trimethylsilyl radicals abstract chlorine from benzyl chloride faster than they abstract hydrogen from toluene.

Phenyltrichlorosilane gives phenyltrimethylsilane, as would be expected from observation of a related reaction in the gas phase¹.

The bis(trimethylsilyl)mercury decomposes several times faster in some of these solvents, for example bromobenzene and benzoquinone, than it does in cyclohexane¹, and it is probable that in these cases intermediate radicals abstract trimethylsilyl groups from the mercury compound, increasing substantially its rate of decomposition and lowering the proportion of hexamethyldisilane formed.

We are grateful for the award of research studentships by Albright and Wilson Ltd., (to A.G.B.) and the Science Research Council (to R.W.W.), and to Courtauld's Educational Trust Fund for the provision of apparatus.

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Received January 3rd, 1966