Tetrahedron Letters No.29, pp. 3295-3297, 1968. Pergamon Press. Printed in Great Britain.

THE REACTION OF BIS (TRIMETHYLSILYL) MERCURY WITH 9-FLUORENONE

Edwin J. Louis and Grant Urry

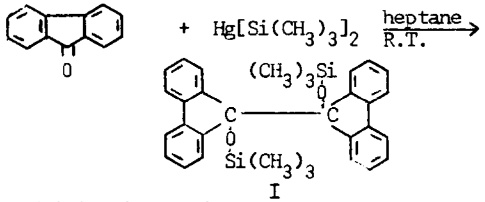
Richard Benbridge Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907

(Received in USA 28 February 1968; received in UK for publication 24 April 1968)

In 1963, E. Wiberg prepared bis (trimethylsilyl) mercury which he found would decompose to give mercury plus hexamethyldisilane by either heating it above 100°C or by allowing an ether solution of it to sit in light for several days.[1]

Later, Eaborn reported the decomposition of bis (trimethylsilyl) mercury at 190°C in various oxygen-, nitrogen-, and halogen-containing solvents.[2,3] Reaction with benzoquinone was reported to give p-bis (trimethylsilyl) benzene among other products. Other ketones gave hexamethyldisiloxane as the major product. On the basis of the products formed and the conditions of the reaction, Eaborn postulated the attack of trimethylsilyl radicals on the various solvents used.

In attempts to trap trimethyl silyl radicals in a stable radical, we added bis (trimethylsilyl) mercury to 9-fluorenone in heptane. A reaction took place at room temperature (well below the decomposition temperature of $Hg[Si(CH_3)_3]_2$). A white precipitate formed which, after recrystallization from ethanol, had a melting point of 240-241°C and proved to be 9,9' bis-(trimethylsiloxy)bifluorene I from elemental analysis, infrared spectrum, molecular weight, and N.M.R. spectrum. The reaction is represented in equation (1):



(1)

I

This compound (I) is similar in structure to the magnesium pinacolate formed as an intermediate in the pinacol reaction.[4] It is also analogous to the product obtained by Ramirez and Smith[5] in reactions of 9-fluorenone and phosphite esters.

The reaction was found to be independent of the stoichiometry of reactants.

EXPERIMENTAL

Preparation of 9,9' bis (trimethylsiloxy) bifluorene

In a 20 ml flask was placed 1.26 gm (0.007 moles) of 9-fluorenone. Attached to this flask was a tube containing 4.935 gm (0.014 moles) of bis (trimethylsilyl) mercury under vacuum with provisions for opening this tube to the flask. The flask was attached to a vacuum manifold and evacuated. Approximately 10 cc of dried heptane was distilled into the flask which then was sealed under vacuum. After opening the tube containing the silyl mercury compound, this reactant was washed into the reaction flask by means of the heptane. A white material precipitated and the undissolved 9-fluorenone apparently was consumed as the reaction proceeded.

Disappearance of the mercurial was accompanied by the deposition of mercury. The resulting solution was bright yellow at this point. This solution was separated from the white precipitate by vacuum filtration and extraction. After several extractions and filtrations of the reaction product with heptane only the mercury remained. Evaporation of the solvent from the extracted material left a mixture of yellow and white solids. The flask containing these solids was attached to a sublimation tube, evacuated and heated to 50-60°C. The excess yellow mercurial sublimed leaving a white solid slightly contaminated with mercurial. The white residue was sealed off from the sublimed mercurial and opened to the air. The yellow contamination changed to mercury droplets immediately after contacting the air. Subsequent recrystallization of the remaining white solid from ethanol gave beautiful white crystals with a melting point of 240-41°C (uncorrected). The following analysis was obtained on a portion of these crystals.

	C	H	Si
Calculated for $C_{32}H_{34}O_2Si_2$:	75.89	6.72	11.00
Found:	75.76	6.85	10.72

The molecular weight was found to be 487 in benzene by the osmometric method. This is in good agreement with the calculated molecular weight (506).

The infrared spectrum indicated a carbon-silicon symmetrical deformation at 8.00 μ, a silicon-carbon stretch at 11.90 μ, a silicon-methyl stretch at 13.25 μ, and a silicon-oxygen stretch at 9.3 μ.

N.M.R. showed aromatic proton peaks at 2.5-3.0 τ and a methyl silicon proton peak at 10.3T with respect to tetramethylsilane. These were in a ratio of $\frac{\text{Silicon methyl}}{\text{aromatic}} = \frac{1.1}{1}$

This is the spectrum expected for 9,9' bis (trimethylsiloxy)bifluorene.

The solvent was saved after work up of the reaction mixture. Upon gas chromatographic analysis it was determined that the liquid contained only one material with the exact retention time of heptane.

No hexamethyldisilane or hexamethyldisiloxane was produced in the reaction. The product of this reaction is most readily accounted for by assuming the intermediate formation of the trimethylsilyl radical followed by the addition of this radical to the oxygen of 9-fluorenone. The dimerization of the resulting radical would give the observed product.

Acknowledgement

The authors are grateful to the Atomic Energy Commission for partial support of this work under contract number AT (11-1)1388 (document number COO-1388-6).

References

1. E. Wiberg, O. Stecher, H. Andrascheck, L. Kreuzbickler, and E. Stande, Angrew. Chem. Intern. Ed., 2, 507 (1963).
2. A. Beaumont, C. Eaborn, R. Jackson, and R. Walsingham, J. Organomet. Chem., 5, 297 (1960).
3. C. Eaborn, R. Jackson, and R. Walsingham, Chem. Comm., 1965, 300.
4. L. Fieser and M. Fieser, Advanced Organic Chemistry, Reinhold Publishing Co., New York, 1961.
5. F. Ramirez and C. Smith, Chem. Comm., 1967, 662.