

DECOMPOSITION OF SOME FREE RADICAL INITIATORS IN HEXAMETHYLDISILANE

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INTRODUCTION

It has previously been reported¹ that hexamethyldisilane undergoes rearrangement at 600° to give trimethyl[(dimethylsilyl)methyl]silane. This interesting rearrangement was further investigated and has been shown to involve (pentamethyldisilanyl)methyl as an intermediate radical². Since at present there is no positive evidence indicating the 1,2 shift of an alkyl group or a hydrogen atom during the life time of radicals at least in detectable amount³, this rearrangement which involves migration of the trimethylsilyl group seemed to be of particular interest. We have initiated the present work to investigate the behavior of the (pentamethyldisilanyl)-methyl radical in solution.

RESULTS AND DISCUSSION

The reaction of hexamethyldisilane with di-tert-butyl peroxide in carbon tetrachloride was carried out in a sealed tube at $129 \pm 0.5^\circ$. The reaction products were analyzed by vapor phase chromatography (VPC) using bis(trimethylsilyl)-methane as an internal standard. All compounds were identified with authentic samples by comparing VPC and IR spectra, in some cases being isolated by fractional distillation.

TABLE 1
THE REACTION OF HEXAMETHYLDISILANE WITH
DI-tert-BUTYL PEROXIDE IN CARBON
TETRACHLORIDE AT $129 \pm 0.5^\circ$

Compound	Amount (mmole)
Original hexamethyldisilane	77.3
Original carbon tetrachloride	119.2
Original di-tert-butyl peroxide	1.94
Recovered hexamethyldisilane	58.8
Recovered carbon tetrachloride	100
Chloroform	14.3
(Chloromethyl)pentamethyldisilane	10.0
tert-BuOH/acetone ratio	1.56 ^a

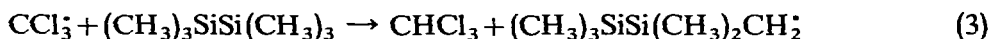
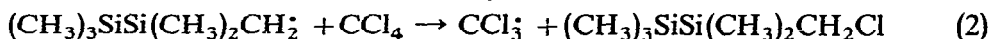
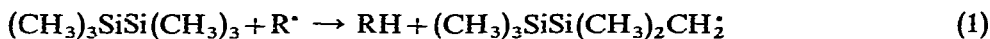
^a Only the ratio was determined.

TABLE 2
THE REACTION OF HEXAMETHYLDISILANE WITH
BENZOYL PEROXIDE IN CARBON
TETRACHLORIDE AT REFLUX TEMPERATURE

Compound	Amount (mmole)
Original hexamethyldisilane	190
Original carbon tetrachloride	962
Original benzoyl peroxide	15.9
Recovered hexamethyldisilane	148.7
Recovered carbon tetrachloride	775.0
Chloroform	12.0
(Chloromethyl)pentamethyldisilane	14.5
Benzene	2.6
Chlorobenzene	19.6

The results are listed in Table 1. The results of the reaction of hexamethyldisilane with benzoyl peroxide in carbon tetrachloride at the reflux temperature are also recorded in Table 2.

In both cases, the main product derived from hexamethyldisilane was (chloromethyl)pentamethyldisilane, no rearrangement product, trimethyl[(dimethylsilyl)methyl]silane, being obtained. These results are interpreted in terms of the intermediate (pentamethyldisilanyl)methyl radical which abstracts a chlorine atom from carbon tetrachloride.



The formation of acetone is the result of competitive decomposition of the tert-butoxy radical. Also the phenyl radical abstracts a chlorine atom competitively from carbon tetrachloride to give chlorobenzene.



The ratios of tert-butyl alcohol/acetone and benzene/chlorobenzene represent the relative reactivity of hydrogen abstraction for hexamethyldisilane toward the tert-butoxy radical and the phenyl radical, respectively. More detailed treatment of the relative reactivities toward free radicals for various organosilicon compounds will be the subject of the forthcoming papers.

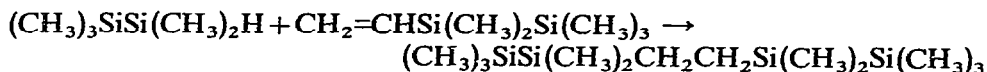
Absence of the rearrangement product indicates that the step (6) observed only at pyrolysis requires a high activation energy.



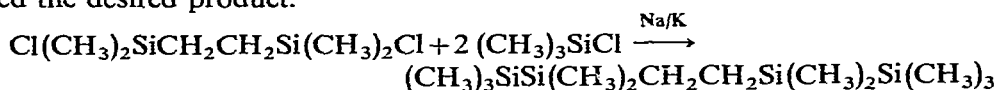
Since the (pentamethyldisilanyl)methyl radical has no or very little tendency to undergo the rearrangement at lower temperature, only dimerization may be the main fate of this radical in the absence of solvent.

In this connection, decomposition of benzoyl peroxide in pure hexamethyldisilane was investigated. The main products of the reaction between hexamethyldisilane and benzoyl peroxide at 80° were benzene, benzoic acid, 1,2-bis(pentamethyldisilanyl)ethane, benzylpentamethyldisilane and a small amount of an unidentified compound. Again no rearrangement product, trimethyl[(dimethylsilyl)methyl]silane, was formed².

The authentic 1,2-bis(pentamethyldisilanyl)ethane was prepared by (a) addition of pentamethyldisilane to vinylpentamethyldisilane catalyzed by di-tert-butyl peroxide and by (b) Wurtz type condensation of 1,2-bis(chlorodimethylsilyl)ethane with trimethylchlorosilane using sodium/potassium alloy. Peroxide-catalyzed addition of pentamethyldisilane to vinylpentamethyldisilane was carried out without any difficulties that were observed in chloroplatinic acid catalyzed hydrosilation with the same disilanyl hydride⁴.



The coupling of 1,2-bis(chlorodimethylsilyl)ethane with trimethylchlorosilane also afforded the desired product.



The yield was relatively low, but no effort to improve it was made.

The present reaction seems to be promising as a preparative method of (chloromethyl)pentamethyldisilane, an important intermediate of carbon-functional organodisilanes.

EXPERIMENTAL

Reaction of hexamethyldisilane with di-tert-butyl peroxide in carbon tetrachloride

In a two-necked reaction flask with a break-seal, 0.28 g of di-tert-butyl peroxide, 11.32 g of hexamethyldisilane and 18.34 g of carbon tetrachloride were placed. The solution was degassed several times by alternatively freezing and melting while under vacuum. The flask was then sealed under vacuum and immersed in a constant temperature bath kept at $129 \pm 0.5^\circ$ for 52 h. The flask containing products was cooled with a Dry Ice/methanol bath, attached onto a vacuum system and opened by means of the break-seal to a closed, evacuated system. The flask was allowed to warm to room temperature and the products were distilled into a trap cooled by a Dry Ice/methanol bath. No solid product was obtained. The products were analyzed with VPC using di(trimethylsilyl)methane as an internal standard.

Reaction of hexamethyldisilane with benzoyl peroxide in carbon tetrachloride

A mixture of 27.86 g of hexamethyldisilane and 3.83 g of benzoyl peroxide in 147.79 g of carbon tetrachloride was refluxed for 58 h. The products were distilled through a short column and analyzed with VPC.

Preparation of 1,2-bis(pentamethyldisilanyl)ethane by hydrosilation

In a 100-ml three-necked flask fitted with a reflux condenser, thermometer, mechanical stirrer and dropping funnel which was equipped with a nitrogen gas inlet, there was placed 4.75 g (0.030 mole) of vinylpentamethyldisilane and 15.5 g (0.117 mole) of pentamethyldisilane, after sweeping the system with nitrogen. To the mixture was added dropwise from the dropping funnel, a solution of 1.0 g (0.006 mole) of di-tert-butyl peroxide dissolved in 4.75 g (0.030 mole) of vinylpentamethyldisilane at the refluxing temperature (105°) of the mixture. After completion of the addition, the reaction mixture was refluxed for 30 h during which time the temperature of the reaction mixture rose to 135° , and then remained constant at this temperature. Fractionation of the mixture gave 15.1 g (0.048 mole) of 1,2-bis(pentamethyldisilanyl)ethane (80% yield based on vinylpentamethyldisilane), b.p. $121\text{--}123^\circ/20\text{ mm}$; n_D^{20} 1.4664; d_4^{20} 0.8054; MR_D 100.06 (calcd. 100.30). (Found: C, 50.07; H, 12.13. $\text{C}_{12}\text{H}_{34}\text{Si}_4$ calcd.: C, 49.57; H, 11.79%.)

Preparation of 1,2-bis(pentamethyldisilanyl)ethane by coupling of 1,2-bis(chlorodimethylsilyl)ethane

In a 2-l three-necked flask equipped with a stirrer, reflux condenser, thermo-

meter and dropping funnel, a dispersion of sodium/potassium alloy was prepared from 15 g (0.65 g-atom) of sodium and 100 g (2.56 g-atom) of potassium in 200 ml of dry xylene. To the stirred dispersion was added dropwise, over 2.5 h, a solution of 217 g (1.99 mole) of trimethylchlorosilane and 46.5 g (0.21 mole) of 1,2-bis(chlorodimethylsilyl)ethane in 500 ml of dry xylene at a temperature below 40° with external cooling. After complete addition, the mixture was stirred about 22 h and then heated at 50° for an additional 4 h. The reaction mixture was treated with 200 ml of ethanol and then with 800 ml of water. A considerable amount of polymeric products was separated by filtration. The organic liquid was separated and the water layer was extracted with ether. The extracts were combined, dried over calcium chloride, and distilled. Fractionation gave 110 g of hexamethyldisilane, b.p. 110–113° and 7 g (0.024 mole) of 1,2-bis(pentamethyldisilanyl)ethane, b.p. 116°/16 mm (11.5% yield).

ACKNOWLEDGEMENT

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SUMMARY

Free radical reactions with hexamethyldisilane were investigated. In carbon tetrachloride, di-tert-butyl peroxide- or benzoyl peroxide-catalyzed reactions of hexamethyldisilane give rise to the formation mainly of (chloromethyl)pentamethyldisilane. The results are interpreted in terms of an intermediate (pentamethyldisilanyl)methyl radical which abstracts a chlorine atom from the solvents. Without solvent, the (pentamethyldisilanyl)methyl radical affords the dimerized product, 1,2-bis(pentamethyldisilanyl)ethane. Alternative preparations for the latter compound are also recorded.

In these cases, no rearrangement product, trimethyl[(dimethylsilyl)methyl]silane, which was observed at pyrolysis of hexamethyldisilane, was obtained.

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