

SHORT COMMUNICATION

Preparation of 5,5-dimethyldibenzosilole

A considerable amount of interest in aryl- and mixed arylalkylsilanes has resulted because of the relatively high degree of thermal stability exhibited by these compounds. Much of this interest has been concerned with the phenylmethylsilanes, biphenylsilanes, and compounds containing the dibenzosilole nucleus. In general, these compounds have been prepared via a Wurtz-type reaction^{1,2,3}. In a previous communication, we have suggested a different approach to the synthesis of the biphenylsilanes whereby the biphenylsilanes are prepared by reacting phenyl radicals (from benzil) with tetraphenylsilane⁴.

During the course of our investigation of the kinetics and mechanisms of thermal decomposition of several phenylsilanes, we have found that there is a tendency towards intramolecular cyclization within certain of these compounds, with the resultant formation of compounds containing the dibenzosilole nucleus. In the pyrolysis of tetraphenylsilane, a minor amount of 5,5'-spirobi(dibenzosilole) is formed. In the pyrolysis of diphenyldimethylsilane, a major product is 5,5-dimethyldibenzosilole*.

In a typical experiment, 5.11×10^{-4} moles of diphenyldimethylsilane (purified by vapor phase chromatography) was heated to 534° for 200 minutes in an evacuated, sealed vial having a volume of 49.5 cc. Chromatographic analysis of the residues showed 1.48×10^{-4} moles of diphenyldimethylsilane and 1.30×10^{-4} moles of 5,5-dimethyldibenzosilole to be present.

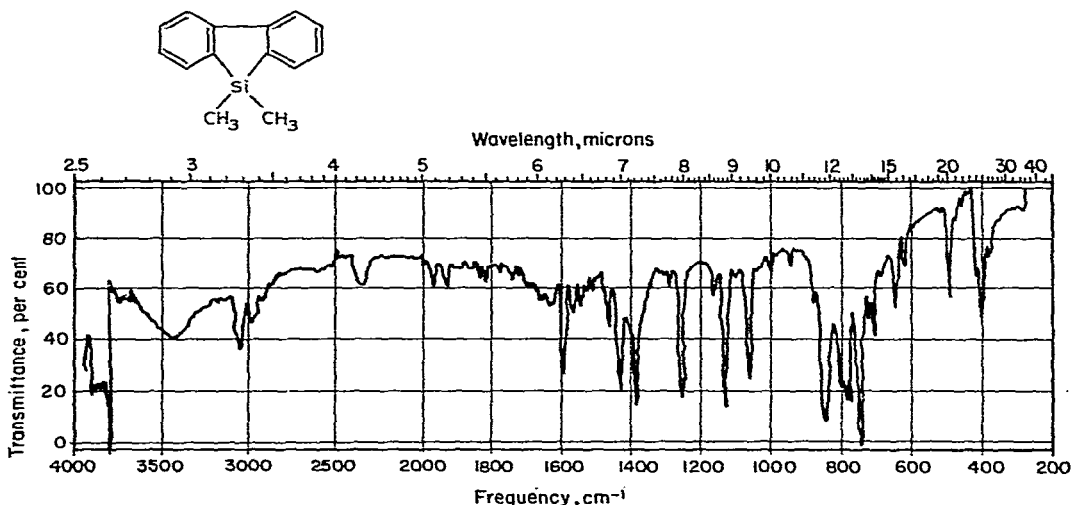


Fig. 1. Infrared spectrum of 5,5-dimethyldibenzosilole.

* Note added in proof. Recent evidence in our laboratory indicates similar thermal cyclisation occurs with methyltriphenylsilane, trimethylsilyldimethylphenylsilylbenzene, and bis(dimethylphenylsilyl)benzene to form corresponding compounds containing the dibenzosilole nucleus.

Since it is likely that some of the initial diphenyldimethylsilane was lost during initial evacuation of the vial, the indicated conversion of 36 percent should be considered as a minimum yield for these conditions. Other products of this reaction, such as, phenyltrimethylsilane and phenyldimethylsilane are present in only relatively minor amounts.

Chromatographic analyses were carried out using a 5-ft $\times$ $\frac{1}{4}$ -in. stainless steel column, packed with 10% General Electric Co. SE-30 on Chromosorb-W. Retention times at 155°, and a helium flow rate of 100 cc/min, were 9 and 13 min, respectively, for the diphenyldimethylsilane and 5,5-dimethyldibenzosilole.

Certification of the identity of the dibenzosilole compound was made by means of infrared spectroscopy and mass spectrometry. The infrared spectrum shown in Fig. 1 was obtained via a KBr-pellet technique, using a Perkin-Elmer Model 521 grating spectrometer. This spectrum indicates the presence of both Si-methyl and Si-phenyl bonding and no monosubstituted aromatic rings. The mass spectrum, obtained with Associated Electronics Industries MS-9 double-focusing instrument, showed a parent peak at $m/e = 210.0863$ (5,5-dimethyldibenzosilole = 210.0864) and fragmentation peaks indicating successive loss of methyl groups.

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