Preparation of triphenylbiphenylylsilanes

A considerable amount of interest in the arylated silanes has been generated because of their relatively high thermal stability. Much of this interest has centered around tetraphenylsilane the phenylmethylsilanes and the triphenylbiphenylylsilanes. The latter compounds have generally been synthesized via a Wurtz-type reaction[1,2,3].

During the course of our investigation of the kinetics and mechanisms of thermal decomposition of some arylsilanes, we have found the triphenylbiphenylylsilanes to comprise a major group of products from the pyrolysis of tetraphenylsilane. While the biphenylylsilanes are somewhat unstable at higher temperatures, they have been noted as products of pyrolyses carried out from 530°–665°. These pyrolyses have been carried out using both standard sealed-vial and flow techniques.

In further investigation of individual steps in the overall decomposition mechanism, it has been found that the triphenylbiphenylylsilanes can be produced almost exclusively at lower temperatures by means of the reaction of tetraphenylsilane with benzil. Benzil is known to be a source of phenyl radicals[4]. Thus, it seems probable that the reaction proceeds via a free radical mechanism. In a typical experiment, 8.9×10^{-5} moles of benzil and 4.44×10^{-4} moles of tetraphenylsilane were heated to 448° for 100 minutes in an evacuated, sealed-vial having a volume of 47 cc. Chromatographic analysis of the reaction products showed approximately a 60 percent yield of triphenylbiphenylylsilanes with the *ortho*-, *meta*-, and *para*-isomers in a ratio of approximately 1:4:2. In this connection it is of interest to note the report by Rondestvedt and Blanchard[5] that decomposition of benzoyl peroxide in phenyltrimethylsilane gave biphenyltrimethylsilanes ($o:m:p = 31:45:24$).

Analyses were carried out on a 6 ft × 1/4-in. stainless column packed with 5 percent SE-30 on Anachrom-ABS. Retention times at 225° and a helium flow rate of 100 cc/min were 7, 10, 38, and 57 minutes, respectively, for tetraphenylsilane, triphenyl-*o*-biphenylylsilane, triphenyl-*m*-biphenylylsilane, and triphenyl-*p*-biphenylylsilane. Certification of the identities of these materials was further made by means of infrared spectroscopy and mass spectrometry.

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1 H. GILMAN AND K. OITA, *J. Org. Chem.*, 20 (1955) 862.
2 L. SPIALTER, D. O. PRIEST AND C. W. HARRIS, *J. Am. Chem. Soc.*, 77 (1955) 6227.
3 F. B. DEANS AND C. EABORN, *J. Chem. Soc.*, (1959) 2299.
4 M. T. JAQUISS AND M. SZWARC, *Nature*, 170 (1952) 312.
5 C. S. RONDESTVEDT AND H. S. BLANCHARD, *J. Org. Chem.*, 21 (1956) 229.

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