

Preliminary communication

The reaction of some perhalosilanes with benzaldehyde

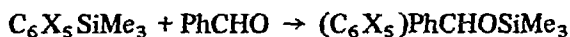
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We have been interested in preparing perhaloorganometallic compounds¹. It appeared² that the C—SiMe₃ units in perhalo compounds might partake of some of the characteristics of C—M units, for example, addition to a carbonyl group of compounds such as benzaldehyde. This we have found to be the case with such compounds as C₆F₅SiMe₃ and C₆Cl₅SiMe₃.

A precursory compound formed in such reactions is the trimethylsiloxy derivative, of which the following is illustrative:



(where X = F or Cl)

The trimethylsiloxy derivatives are hydrolyzed to the corresponding carbinols, products that are formed by reaction of the Grignard reagents or lithium compounds with benzaldehyde³. Authentic specimens prepared by such reactions were used to help complete identification (by mixed m.p. and infrared) of the reaction products of hydrolysis.

It should be mentioned that under corresponding experimental conditions the non-halogenated phenyltrimethylsilane is essentially recovered². In these orienting experiments pentafluorophenyltrimethylsilane was heated with benzaldehyde in an oil bath at 165–170° for 4 days to give 62% yield of the silyl ether. Under similar conditions, pentachlorophenyltrimethylsilane yielded 89% of the siloxy compound. However, when phenyltrimethylsilane was heated for 7 days, no silylated compound appeared to have formed and the recovery of phenyltrimethylsilane was 87%.

The infrared analyses were carried out on a Perkin–Elmer PE21 instrument; the NMR spectra were determined on a Varian A 60, spectrophotometer, mass spectra on an Atlas CH4 spectrometer.

The following spectral data were obtained:

(C₆F₅)PhCHOSiMe₃:

IR: 3048, 2949 cm⁻¹ (C–H); 1950, 1885 cm⁻¹ (benzene ring overtones); 1600, 1504, 749, 696 cm⁻¹ (mono-substituted phenyl); 1250, 844 cm⁻¹ (–SiMe₃); 1070, 1030 cm⁻¹ (Si–O); 995 cm⁻¹ (–C₆F₅).

NMR: τ 2.58, 2.69, 2.76, 2.82, 2.87 ($-\text{C}_6\text{H}_5$); τ 3.80 ($-\text{CH}-$); τ 9.90 ($-\text{SiMe}_3$).



Mass spec.: 346 (molecule ion, calcd. 346); 331 (loss of $-\text{CH}_3$); 257 (loss of $-\text{OSiMe}_3$); 179 (loss of $-\text{C}_6\text{F}_5$); 77 ($-\text{C}_6\text{H}_5$); 73 ($-\text{SiMe}_3$).

$(\text{C}_6\text{Cl}_5)\text{PhCHOSiMe}_3$:

IR: 3058, 3030, 2950 cm^{-1} (C-H); 1949, 1890, 1805, 1764 cm^{-1} (benzene ring overtones); 1600, 1496, 748, 685 cm^{-1} (monosubstituted phenyl); 1250, 840, 755 cm^{-1} ($-\text{SiMe}_3$); 1067, 1028 cm^{-1} (Si-O); 784, 725 cm^{-1} ($-\text{C}_6\text{Cl}_5$).

NMR: τ 2.70, 2.75, 2.83 ($-\text{C}_6\text{H}_5$); τ 3.27 ($-\text{CH}-$); τ 9.87 ($-\text{SiMe}_3$).



Mass spec.: 426, 428, 430, 432, 434 (molecule ions with the correct intensity ratio for a molecule containing one Si and five Cl atoms, calcd. 428.3 taking Cl = 35.45); showed mass spectral molecular ions with the expected intensity ratio corresponding to the loss of $-\text{CH}_3$, $-\text{OSiMe}_3$ and $-\text{C}_6\text{Cl}_5$; 77 ($-\text{C}_6\text{H}_5$); 73 ($-\text{SiMe}_3$).

The recent¹ availability of $\text{Me}_3\text{Si}(\text{CF}_2)_n\text{SiMe}_3$ types suggests them as candidates for the related reactions now under investigation.

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