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Preliminary communication

The reaction of some perhalosilanes with benzaldehyde

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We have been interested in preparing perhaloorganometallic compounds[1]. It appeared[2] that the C–$SiMe_3$ 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 $C_6F_5SiMe_3$ and $C_6Cl_5SiMe_3$.

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

$$C_6X_5SiMe_3 + PhCHO \rightarrow (C_6X_5)PhCHOSiMe_3$$

(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 benzaldehyde[3]. 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 recovered[2]. 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:

$(C_6F_5)PhCHOSiMe_3$:

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} (–$SiMe_3$); 1070, 1030 cm^{-1} (Si–O); 995 cm^{-1} (–C_6F_5).

NMR: τ 2.58, 2.69, 2.76, 2.82, 2.87 ($-C_6H_5$); τ 3.80 ($-\underset{\underset{\diagdown}{O}}{\underset{|}{C}}H-$); τ 9.90 ($-SiMe_3$).

Mass spec.: 346 (molecule ion, calcd. 346); 331 (loss of $-CH_3$); 257 (loss of $-OSiMe_3$); 179 (loss of $-C_6F_5$); 77 ($-C_6H_5$); 73 ($-SiMe_3$).

(C_6Cl_5)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} ($-SiMe_3$); 1067, 1028 cm^{-1} (Si–O); 784, 725 cm^{-1} ($-C_6Cl_5$).

NMR: τ 2.70, 2.75, 2.83 ($-C_6H_5$); τ 3.27 ($-\underset{\underset{\diagdown}{O}}{\underset{|}{C}}H-$); τ 9.87 ($-SiMe_3$).

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 $-CH_3$, $-OSiMe_3$ and $-C_6Cl_5$); 77 ($-C_6H_5$); 73 ($-SiMe_3$).

The recent[1] availability of $Me_3Si(CF_2)_nSiMe_3$ types suggests them as candidates for the related reactions now under investigation.

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