

NOTE

ORGANOSILICON COMPOUNDS XI*. THE REACTION OF SALICYLANILIDE WITH DIMETHYLDI- CHLOROSILANE AND HEXAMETHYLCYCLOTRISILAZANE

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INTRODUCTION

Generally *O*-silylated carbonamides are described as highly unstable, and silylation leads with few exceptions to *N*-substituted species as main products^{1,2}. Continuing earlier investigations concerning silylation of β -hydroxycarbonyl compounds³ we studied the reaction of dimethyldichlorosilane or hexamethylcyclotri-silazane with a β -hydroxycarbonamide (salicylanilide). Under certain conditions from this reaction we isolated in high yield a thermally stable cyclic compound, the IR spectrum of which indicates the *O*-silylated structure (II) (Fig. 1). An *N*-silylated species was not observed in the reaction products.

RESULTS AND DISCUSSION

Fig. 1 indicates the possible products of the reaction of dimethyldichlorosilane with salicylanilide. From the reaction of salicylanilide with dimethyldichlorosilane in a mole ratio of 2 : 1 the primary product (I) can be isolated in good yield as a highly viscous liquid which slowly crystallized. As expected the compound is hydrolytically unstable. Its thermal stability however is high. The compound is distillable at 187° (2 mm) and no decomposition into salicylanilide and (II) was observed up to 250°. The IR spectrum of (I) shows the characteristic features of a *N*-monoarylsubstituted aromatic carbonamide (Fig. 2) with $\nu(\text{NH})$ at 3420 cm^{-1} , amide band I at 1675 cm^{-1} , amide band II at 1535 cm^{-1} measured in dilute CCl_4 solution. The corresponding frequencies of free salicylanilide are 3445, 1660 and 1520 cm^{-1} . Further prominent IR absorptions of (I) are 1315 cm^{-1} (typical for nitrogen bound to an aromatic nucleus), 1215 and 925 cm^{-1} (typical for aromatic C–O–Si bonding). The absence of siloxane bands in the region 1000–1100 cm^{-1} indicates that no hydrolysis occurred during preparation of the sample.

* For Part X see ref. 3.

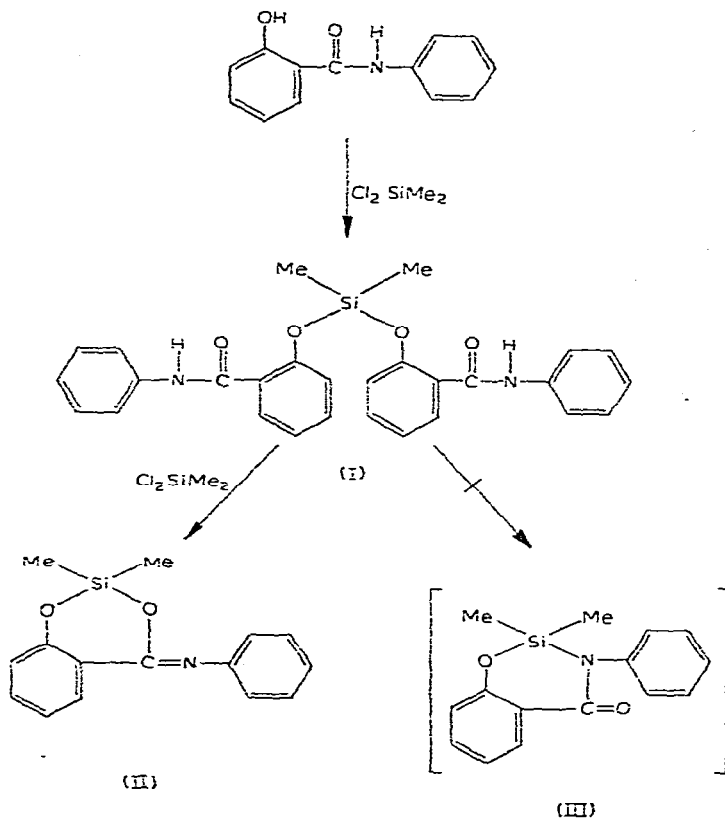


Fig. 1.

Salicylanilide and dimethyldichlorosilane in molar ratio of 1:1 yielded a crystalline compound, which is hydrolytically unstable and distillable without decomposition. The IR spectrum of this compound (Fig. 3) exhibits only slight absorption in the range of NH vibrations due to a trace of (I). A strong band at 1672 cm^{-1} may be attributed to a C=O as well as to a C=N vibration. The fact, that only a single

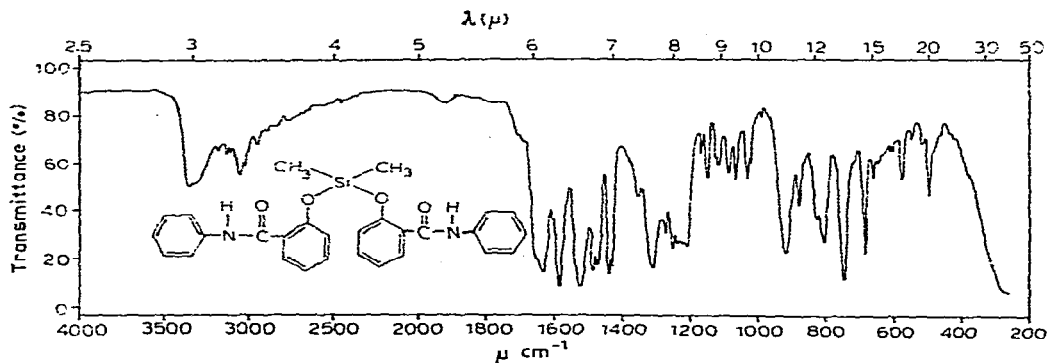


Fig. 2. IR spectrum of compound I.

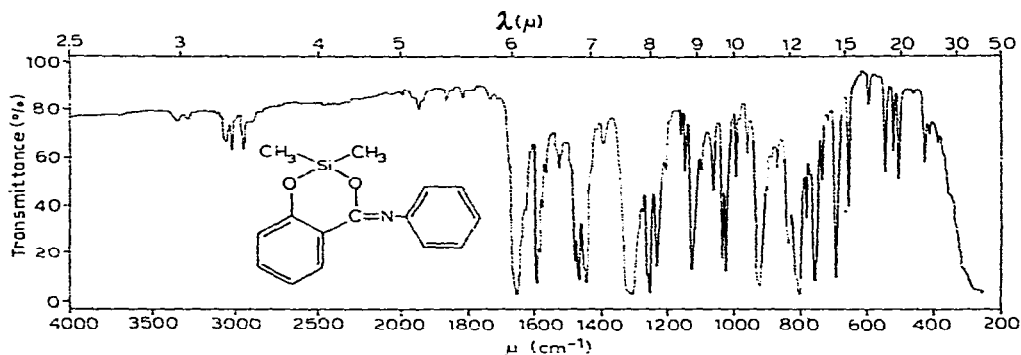


Fig. 3. IR spectrum of a crystalline compound yielded from the reaction of salicylanilide and dimethyldichlorosilane.

absorption appears in this range however indicates, that only one of the two possible species (II) or (III) is present. In the range of Si-O-C stretching vibrations the spectrum resembles closely those of the compounds described earlier². The frequencies of the aromatic Si-O-C bond (1238 and 928 cm^{-1}) remain nearly unchanged compared with (I). Additional strong absorptions at 1030, 1038 and 1136 cm^{-1} may be attributed to an additional Si-O-C band rather than to a Si-N-C band. The range below 900 cm^{-1} , where Si-N vibrations are to be expected exhibits no fundamental change compared with (I). These observations confirm the structure (II) rather than (III).

Probably the unusual structure of an *O*-silylated imino ether in this case is stabilized by resonance through two aromatic nuclei in conjugation to the C=N bond.

An earlier work³ reports that silylation of carbonamides with chlorosilanes is difficult but possible through reaction with silazanes. In our case the reaction of salicylanilide with hexamethylcyclotrisilazane in molar ratio of 3:1 produced a mixture of compounds (I) and (II).

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen in a three-necked flask equipped with reflux condenser, sealed stirrer and dropping funnel.

IR spectra were obtained from capillary films or dilute solutions in CCl_4 , using a Perkin-Elmer grating spectrometer, model 521.

The reaction of salicylanilide with dimethyldichlorosilane

(a). *Mole ratio 1 : 1.* To a mixture of 21.3 g (0.1 mole) of salicylanilide and 16 g (0.2 mole) of pyridine a solution of 12.9 g (0.1 mole) of dimethyldichlorosilane in 25 ml of dry benzene was added dropwise under stirring. After refluxing for 5 h the separated pyridine hydrochloride was filtered off. Fractionation of the liquid phase under reduced pressure yielded 19.1 (71%) of the crystalline compound (II), b.p. 182–184° (2 mm), m.p. 105°. (Found: C, 66.8; H, 5.54; N, 5.42; Si, 10.6. $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{Si}$ calcd.: C, 67.0; H, 5.58; N, 5.21; Si, 10.4%.)

(b). *Mole ratio 2 : 1.* Similarly 6.45 g (0.05 mole) of dimethyldichlorosilane in

100 ml of dry toluene were added to a mixture of 21.3 g (0.1 mole) of salicylanilide and 8 g (0.1 mole) of pyridine. After refluxing for several hours and separation of pyridine hydrochloride fractionation of the liquid phase yielded 16.8 g (70%) of a highly viscous liquid (I), b.p. 187–190° (2 mm). (Found: C, 69.5; H, 5.29; N, 5.79; Si, 5.96. $C_{28}H_{26}N_2O_4Si$ calcd.: C, 69.7; H, 5.39; N, 5.81; Si, 5.81%.)

The reaction of salicylanilide with hexamethylcyclotrisilazane (mole ratio 3:1)

A mixture of 42.65 g (0.2 mole) of salicylanilide with 14.6 g (0.07 mole) of hexamethylcyclotrisilazane was heated without solvent to 120°. After 1 h the evolution of NH_3 ceased. The obtained product was distilled, 34.5 g, b.p. 182–187° (2 mm), and consisted of comparable amounts of (I) and (II).

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