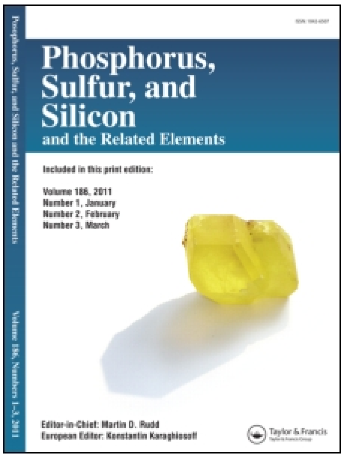

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TRIMETHYLSILICON(IV) DERIVATIVES OF ANILIC ACIDS

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TRIMETHYLSILICON(IV) DERIVATIVES OF ANILIC ACIDS

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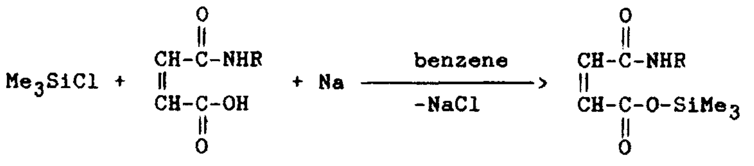
Treatment of sodium salts of maleanilic and chloromaleanilic acids (prepared *in situ*) with trimethylsilicon(IV) chloride in 1:1 molar ratio yields trimethylsilicon(IV) maleanilate and trimethylsilicon(IV) chloromaleanilate, respectively. Similar treatment of sodium salts of phthalanilic and chlorophthalanilic acids with trimethylsilicon(IV) chloride in 1:1 molar ratio yields trimethylsilicon(IV) phthalanilate and trimethylsilicon(IV) chlorophthalanilate, respectively.

Keywords: Maleanilic acid; phthalanilic acid; trimehtylsilicon(IV) chloride; trimethylsilicon(IV) anilates

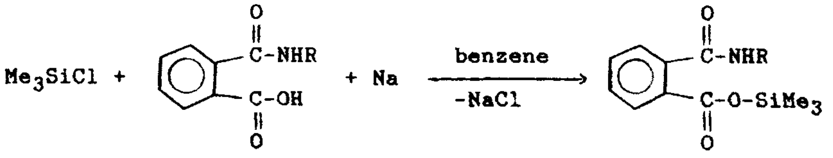
The chemistry of organosilicon molecules has attracted the attention of chemists in the past 3–4 decades as evidenced by a number of monographs and large number of reviews.[1,2] These organosilicon derivatives are becoming more and more important for industrial applications, and many organic synthesis have been improved by use of them.[3] From the point of new applications, chemical vapor deposition has been widely applied to obtain thin films using organometal halides.[4] More recently metal organic derivatives have been used as a metal gas source for the chemical vapor deposition.[5]

Among the ligands containing both N and O atoms, anilic acids are important from biochemical[6] and analytical[7] points of view. Their complexes with metals have been found to be of great industrial and biochemical importance.[8] Keeping in view the above promising facts and continuing our earlier work,[9,10] we report here some new trimethylsilicon(IV) derivatives of anilic acids, which may be useful as molecular precursor for chemical vapor deposition.[11]



1a, R = C_6H_5 **2a**, R = C_6H_5

1b, R = $C_6H_4.Cl(p)$ **2b**, R = $C_6H_4.Cl(p)$



3a, R = C_6H_5 **4a**, R = C_6H_5

3b, R = $C_6H_4.Cl(p)$ **4b**, R = $C_6H_4.Cl(p)$

RESULTS AND DISCUSSION

The reaction of the sodium salt of maleanilic acids **1a**, **1b** (prepared *in situ*) with trimethylsilicon(IV) chloride in dry benzene gives solid crystalline compounds identified as trimethylsilicon(IV) maleanilates, **2a** and **2b**, respectively. Similar treatment of the sodium salt of phthalanilic acids **3a**, **3b** with trimethylsilicon(IV) chloride in dry benzene gives white crystalline solids characterised as trimethylsilicon(IV) phthalanilates **4a** and **4b**, respectively.

Intermolecular nucleophilic substitution with elimination of chloride ion leads to the formation of products **2** and **4** which were characterised on the basis of satisfactory elemental analyses, molecular weights and spectral (IR, NMR) studies.

These new complexes are soluble in common organic solvents like benzene, chloroform, carbon tetrachloride, dichloromethane and coordinating solvents like DMSO and DMF etc. but are insoluble in water and appear to be highly susceptible to hydrolysis.[12] The molecular weight determination in chloroform solution shows the monomeric nature of these complexes at room temperature.

The comparison of I.R. spectra of these complexes with ligands show bands at 1645–1625 cm^{-1} due to amide carbonyl and in the region 3340–3150 cm^{-1} due to-NH group, and does not show any discernible shift in the complexes indicating non-involvement of the amide group in coordination. A sharp new band appears in the region 1105–1090 cm^{-1} in the spectra of the complexes, which may be due to (Si-O-C) mode[13] indicating the bonding through the carboxylate group. This fact is further supported by the disappearance of the band at 3000–2800 cm^{-1} (responsible for ν(O-H) in ligand) in the complexes.

The PMR spectra of the complexes are devoid of any signal at δ 11.66 ppm suggesting deprotonation of the -COOH group and its subsequent involvement in coordination. The resonance due to -NH protons appears in the region at δ 5.60–6.30 ppm with negligible shift ($\pm$0.13 ppm) compared to the respective ligand position, suggesting the monodentate nature of the ligand. Remaining signals due to different types of protons appear at expected positions (Table I).

On the basis of the above spectral data it may be concluded that the ligands are acting as monodentate moieties, bonded to the silicon atom through the oxygen of carboxylate group. Thus, we may tentatively suggest tetra-coordinated, ester type structures for the trimethyl silicon(IV) derivatives of anilic acids.

EXPERIMENTAL

Due to the highly hygroscopic nature of the compounds, moisture is carefully excluded throughout the experimental manipulations. Solvents (benzene, isopropanol etc.) are used after drying by standard methods.[14] All the melting points are uncorrected. The IR and NMR spectra are recorded on a Perkin-Elmer model 557 and JEOL JNM FX-90 Q spectrophotometers, respectively. The microanalyses are carried out using Coleman Carbon, Hydrogen and Nitrogen analysers for C, H, and N, respectively. Silicon and Chlorine have been estimated gravimetrically by reported method.[14]

Synthesis of Anilic Acids

Maleanilic, chloromaleanilic, Phthalanilic and chlorophthalanilic acids are synthesised by an already reported method.[15] Compounds are characterised on the basis of satisfactory elemental analyses and spectral studies.

Reaction Between Chlorotrimethylsilane and Sodium Salt of Maleanilic and Chloromaleanilic Acids in 1:1 Molar Ratio

0.23g (10 mmole) of sodium metal and 20 ml of isopropanol are taken in a round bottom flask and refluxed for about half an hour till a clear solution of sodium isopropoxide is obtained. After cooling, 1.91g (10 mmole) maleanilic

TABLE I Microanalytical and spectral data for complexes 2 and 4

Compound	*Mol.Formula/ Mol.Wt. Found (Calcd.)*	*Analysis % Found/(Calcd.)*					*I.R. (KBr, cm^{-1})*				*PMR (δ ppm)*
		C	*H*	*N*	*Si*	*Cl*	*ν(NH)*	*ν(C=O) Carboxylate*	*ν(C=O) Amide*	*ν(Si-O-C)*	
2a	$C_{13}H_{17}NO_3Si$ 292 (264)	59.32 (59.07)	6.46 (6.23)	5.32 (5.18)	10.65 (10.24)	—	3300–3200	1710 1500	1625	1100	1.25 (s,9H,CH_3); 2.60 (d,2H,CH = CH); 5.60 (s,1H,NH) and 7.00–7.70 (m,5H,arom.).
2b	$C_{13}H_{16}NO_3ClSi$ 306 (298.5)	52.44 (52.22)	5.38 (5.13)	4.70 (3.93)	9.41 (9.06)	11.93 (11.54)	3340–3210	1700 1515	1645	1090	1.20 (s,9H,CH_3); 2.70 (d,2H,CH = CH); 6.20 (s,1H,NH) and 6.80–7.60 (m,4H,arom.).
4a	$C_{17}H_{19}NO_3Si$ 356 (314)	65.17 (64.94)	6.07 (5.82)	4.47 (4.22)	8.95 (8.73)	—	3300–3150	1720 1525	1635	1095	1.25 (s,9H,CH_3); 6.30 (s,1H,NH) and 6.90–8.00 (m,9H,arom.).
4b	$C_{17}H_{18}NO_3ClSi$ 376 (348.5)	58.70 (58.56)	5.18 (5.02)	4.02 (3.75)	8.05 (7.84)	10.21 (9.76)	3340–3210	1695 1505	1640	1105	1.20 (s,9H,CH_3); 6.15 (s,1H,NH) and 7.20–7.95 (m,8H,arom.).

acid dissolved in 20 ml of benzene is added to it and the contents are refluxed for an hour on an oil bath. Now 1.09g (10 mmole) chlorotrimethylsilane is added and the contents relfuxed for 3 hours. Sodium chloride thus precipitated is filtered off. Volatiles are removed under reduced pressure. The light green colored solid, 1.32g (48%), m.p. 145°C is obtained. Similar treatment of chlorophthalanilic acid (1.91g) with chlorotrimethylsilane (0.92g) gave a brown colored solid, 1.57g (63%) m.p. 142°C.

Reaction Between Chlorotrimethylsilane and Sodium Salt of Phthalanilic and Chlorophthalanilic Acids in 1:1 Molar Ratio

In place of maleanilic acid in the above procedure sodium metal (0.23g; 10 mmole) in 20 ml of isopropanol is treated with chlorotrimethylsilane (1.09g; 10 mmole) and phthalanilic acid (2.41g; 10 mmole) in dry benzene to give a white crystalline solid, 1.21g (50%), m.p. 162–64°C. Similar treatment of chlorophthalanilic acid (2.76g; 10 mmole) with chlorotrimethylsilane (1.09g; 10 mmole) yielded a white crystalline solid, m.p. 160–161°C.

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