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Synthesis of novel aryloxysilylethers using hexamethyldisilazane and laponite RD[®] catalyst

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ABSTRACT

The synthesis and characterization of some novel aryloxysilylethers from structurally diversified phenols and biphenols bearing alkyl-, alkoxy-, benzyl-, and ketone substituents is reported. Laponite RD[®] was found to be a simple versatile catalyst for the conversion.

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KEYWORDS

Phenols;
Organosilicon;
Aryloxysilylethers;
HMDS;
Laponite RD[®].

INTRODUCTION

Organosilicon compounds have proved to be important building blocks in organic synthesis^[1,2]. This is due to the large number of regio- and stereo-specific transformations they undergo^[3,4]. There are several classes of organosilicon compounds. One important class is aryloxysilylethers. The silyl- group in these compounds acts as a masking agent for the aryloxy- anion. The compounds serve as synthetic intermediates in several synthesis^[5,6].

There are several methods reported in the literature to prepare aryloxysilylethers^[7,8]. Most of the preparations employ halosilanes, silyltriflates, silylazides, silylamines etc., and suitable catalyst as starting reagents for the protection of the aryloxyanions^[9-11].

Our laboratory is basically interested in the preparation and reactions of novel organosilyl- based reagents. For our reactions, we have employed large quantities of chlorotrimethylsilane. Chlorotrimethylsilane is sensitive to moisture and all reactions have to be carried under completely anhydrous conditions^[12].

The reagent HMDS (hexamethyldisilazane)^[13] in contrast is a clear colourless liquid. It is commercially available and hydrolyses slowly in water. Due to its easy availability, the reagent has been used for the conversion of phenols and alcohols to their respective aryloxytrimethylsilyl- and silylenol- ethers, giving ammonia as the only by-product.

Literature shows that Laponite RD[®] has not been used as solid support for conversion of phenols to aryloxysilylethers. Laponite RD[®] is proved to be nanoparticulate in nature with layered interlamellar covalently anchored cations. Laponite RD[®] is environmentally compatible, commercially available synthetic clay used in waterborne formulations^[14,15].

In continuation of our basic interest in the preparation and reactions of novel organosilicon compounds, we performed the silyl- protection reactions to phenols and biphenols in presence of Laponite RD[®]. We have found that Laponite RD[®] clay is an excellent catalyst for the conversion of a wide variety of phenols to the corresponding aryloxysilylethers with HMDS.

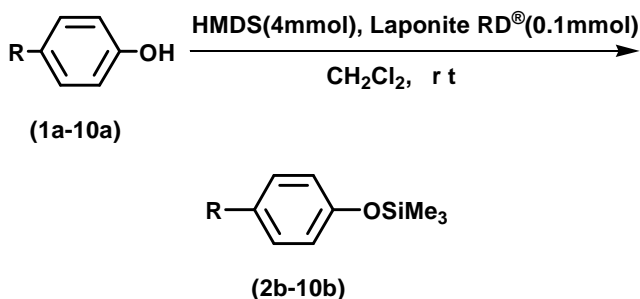
EXPERIMENTAL

Materials and methods

The phenols (**1a**) to (**10a**) were synthesized according to reported literature procedures^[16-23]. All the compounds were purified by column chromatography using silica gel (60-120 mesh size), and 2% ethyl acetate with hexane (60°C-80°C fraction) as eluent. The chemical structures of the phenols and target compounds were determined by standard spectroscopic techniques. HMDS, Laponite RD[®] and all solvents were procured from commercial suppliers and used without further purification. IR was recorded on Shimadzu FTIR-8400 spectrophotometer. NMR spectra were recorded in CDCl₃ with a Bruker AMX 400 spectrometer using tetramethylsilane (TMS) as an internal standard. The chemical shifts are reported in δ values with reference to CDCl₃. Microanalysis was carried by Shimadzu GC-MS QP 5050A instrument equipped with a 30 m length and 0.32 mm diameter BP-5 capillary column, and elemental analysis by (Carlo-Erba 1106 analyser). The transition temperatures (melting points) of all compounds was determined using polarizing optical microscopy (POM) using Olympus BX50 microscope equipped with a heating hot stage Mettler FP82HT and a central processor Mettler FP80. All melting and boiling points remain uncorrected.

General procedure for the synthesis of aryloxysilylethers

HMDS (4 mmol) was added to a mixture of phenol (1 mmol) and Laponite RD[®] (0.010g) in 5 ml of dichloromethane and stirred at room temperature for 30 minutes (Scheme 1).



Scheme 1 : General synthetic path for preparation of novel aryloxysilylethers.

The progress of the reaction was monitored by

TLC, using hexane (80°C-100°C) as mobile phase. After completion of the reaction, the mixture was left aside for five minutes to allow the clay to settle. The clay was removed by filtration, and concentrated under vacuum. The crude material was washed with water (10 mL), and aqueous sodium hydroxide (5%, 5 mL), and extracted into hexane (10 mL). The organic extract was re-washed with water (10 mL) and dried over anhydrous magnesium sulphate. Removal of solvent under vacuum gave pure aryloxysilylethers.

Spectral data for novel aryloxysilylethers

1-[2-Ethyl-4-(trimethylsilyloxy)phenyl]ethanone (**1b**)

IR (KBr): 2960, 2871, 1679, 1600, 1492, 1245, 1130, 997, 848, 655 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.67 (t, 1H, Ar-H, J = 8.2 Hz), 6.74 (d, 1H, Ar-H, J = 8.2 Hz), 6.66 (d, 1H, Ar-H, J = 7.4 Hz), 2.91 (q, 2H, J = 7.4 Hz, Ar-CH₂-), 2.70 (s, 3H, -CO-CH₃), 1.20 (t, 3H, CH₃, J = 7.3 Hz), 0.30 (s, 9H, -OSi(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 200.9, 159.4, 148.8, 133.1, 129.2, 117.4, 112.4, 29.2, 27.7, 15.4, 0.30; Elemental analysis: C₁₃H₂₀O₂Si requires C, 66.05; H, 8.53; Found C, 66.31; H, 8.79.

3-(Benzyloxy)phenoxytrimethylsilane (**2b**)

IR (neat) 2958, 2869, 1593, 1487, 1379, 1288, 1253, 1149, 1028, 844, 688 cm⁻¹; ¹H NMR δ ppm: 7.35 (s, 5H, Ar-H), 7.12-6.43 (m, 4H, Ar-H), 5.05 (s, 2H, Ar-CH₂-), 0.25 (s, 9H, -OSi(CH₃)₃); ¹³C NMR δ ppm: 159.8, 156.2, 136.9, 130.0, 129.7, 128.5, 127.8, 127.4, 112.7, 108.0, 107.2, 102.4, 69.9, 0.15; Elemental analysis: C₁₆H₂₀O₂Si requires C, 70.54; H, 7.50; Found C, 70.13; H, 7.30.

1-[4'-(Trimethylsilyloxy)biphenyl-4-yl]ethanone (**3b**)

IR: 1678, 1597, 1527, 1492, 1454, 1377, 1290, 1203, 1020, 916, 844 cm⁻¹; ¹H NMR δ ppm: 8.01 (d, 2H, Ar-H, J = 8.6 Hz), 7.64 (d, 2H, Ar-H, J = 8.6 Hz), 7.52 (d, 2H, Ar-H, J = 8.6 Hz), 6.94 (d, 2H, Ar-H, J = 8.6 Hz), 2.63 (s, 3H, -CO-CH₃), 0.30 (s, 9H, -OSi(CH₃)₃); ¹³C NMR δ ppm: 197.7, 155.7, 135.3, 132.9, 128.9, 128.5, 128.3, 126.5, 120.5, 115.9, 30.8, 26.5, 0.23; GC-MS, m/z : 284, 43 (100%); Elemental analysis: C₁₇H₂₀O₂Si requires C, 71.79; H, 7.09; Found C, 71.50; H, 6.91.

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Methyl-[4'-(trimethylsilyloxy)biphenyl]-4-carboxylate (4b)

IR: 1649, 1587, 1496, 1458, 1402, 1300, 1273, 1215, 1136, 1016, 846 cm^{-1} ; ^1H NMR δ ppm: 8.07 (d, 2H, Ar-H, $J = 8.6$ Hz), 7.62 (d, 2H, Ar-H, $J = 8.6$ Hz), 7.52 (d, 2H, Ar-H, $J = 8.6$ Hz), 6.93 (d, 2H, Ar-H, $J = 8.6$ Hz), 3.93 (s, 3H, $-\text{OCH}_3$), 0.30 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); Elemental analysis: $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Si}$ requires C, 67.96; H, 6.71; Found C, 67.67; H, 6.43.

Ethyl-[4'-(trimethylsilyloxy)biphenyl]-4-carboxylate (5b)

IR: 1710, 1678, 1591, 1496, 1462, 1454, 1400, 1271, 1255, 1109, 1026, 1003 cm^{-1} ; ^1H NMR δ ppm: 8.08 (d, 2H, Ar-H, $J = 8.6$ Hz), 7.61 (d, 2H, Ar-H, $J = 8.6$ Hz), 7.51 (d, 2H, Ar-H, $J = 8.6$ Hz), 6.93 (d, 2H, Ar-H, $J = 8.6$ Hz), 4.41 (qr, 2H, $-\text{OCH}_2-$, $J = 7.0$ Hz), 1.41 (t, 3H, $-\text{CH}_3$, $J = 7.0$ Hz), 0.30 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); Elemental analysis: $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Si}$ requires C, 68.75; H, 7.05; Found C, 68.56; H, 6.64.

7-(Benzyloxy)naphthalene-2-yloxy-trimethylsilane (6b)

IR: 2923, 2852, 1627, 1512, 1461, 1375, 1253, 1207, 1164, 1008, 844 cm^{-1} ; ^1H NMR δ ppm: 7.65 (t, 2H, Ar-H, $J = 9.5$ Hz), 7.10 (s, 5H, Ar-H), 7.07 (d, 2H, Ar-H, $J = 9.5$ Hz), 6.92 (dd, 2H, Ar-H, $J = 9.5$ Hz), 5.20 (s, 2H, Ar- CH_2-), 0.30 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); ^{13}C NMR δ ppm: 157.2, 153.6, 136.9, 135.8, 129.1, 128.5, 127.9, 127.5, 124.9, 119.6, 116.8, 114.2, 106.2, 0.30; GC-MS, m/z : 322, 91 (100%); Elemental analysis: $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Si}$ requires C, 68.75; H, 7.05; Found C, 68.56; H, 6.79.

4-(Decyloxy)phenoxytrimethylsilane (7b)

IR: 2923, 2854, 1504, 1471, 1388, 1251, 1099, 912, 758, 684 cm^{-1} ; ^1H NMR δ ppm: 6.75 (s, 4H, Ar-H), 3.89 (t, 2H, $-\text{OCH}_2-$, $J = 6.6$ Hz), 1.75 (m, 2H, $-\text{OCH}_2-\text{CH}_2-$), 1.49-1.20 (m, 14H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$, $J = 6.6$ Hz), 0.23 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); ^{13}C NMR δ ppm: 153.8, 148.7, 120.6, 115.2, 68.4, 31.8, 29.5, 29.4, 29.3, 26.0, 22.6, 14.0, 0.11; GC-MS, m/z : 322, 43 (100%). Elemental analysis: $\text{C}_{19}\text{H}_{34}\text{O}_2\text{Si}$ requires C, 74.49; H, 6.88; Found C, 74.32; H, 6.47.

4-(3,7-Dimethyloctyloxy)phenoxytrimethylsilane (8b)

IR: 2954, 2952, 1506, 1475, 1231, 1251, 1099,

923, 846, 758 cm^{-1} ; ^1H NMR δ ppm: 6.75 (s, 4H, Ar-H), 3.95 (t, 2H, $-\text{OCH}_2-$, $J = 6.6$ Hz), 1.84-1.75 (m, 2H, $-\text{OCH}_2-\text{CH}_2-$), 1.72-1.62 (m, 1H, $-\text{CH}_2-\text{CH}-$), 1.60-1.47 (m, 1H, $-\text{CH}_2-\text{CH}-$), 1.37-1.24 (m, 4H, $-\text{CH}_2-$), 0.93 (d, 3H, $-\text{CH}_3$, $J = 6.6$ Hz), 0.87 (d, 6H, $-\text{CH}_3$, $J = 6.6$ Hz), 0.23 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); ^{13}C NMR δ ppm: 171.0, 153.8, 148.7, 120.5, 115.2, 66.7, 60.3, 39.2, 37.3, 36.3, 29.8, 27.9, 27.9, 24.6, 22.6, 20.9, 19.6, 14.1, 0.1; GC-MS, m/z : 322, 182 (100%). Elemental analysis: $\text{C}_{19}\text{H}_{34}\text{O}_2\text{Si}$ requires C, 70.75; H, 10.62; Found C, 70.87; H, 10.50.

4'-Pentylphenyl-4-(trimethylsilyloxy)benzoate (9b)

IR: 2956, 2858, 1737, 1602, 1510, 1465, 1263, 1163, 1070, 912, 846, 694 cm^{-1} ; ^1H NMR δ ppm: 8.11 (d, 2H, Ar-H, $J = 8.5$ Hz), 7.21 (d, 2H, Ar-H, $J = 8.5$ Hz), 7.10 (d, 2H, Ar-H, $J = 8.5$ Hz), 6.90 (d, 2H, Ar-H, $J = 8.5$ Hz), 2.61 (t, 2H, Ar- CH_2- , $J = 7.5$ Hz), 1.68 (m, 2H, Ar- CH_2-CH_2-), 1.38 (m, 4H, $-\text{CH}_2-$), 0.91 (t, 3H, $-\text{CH}_3$, $J = 4.0$ Hz), 0.31 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); ^{13}C NMR δ ppm: 165.2, 160.4, 148.8, 140.4, 132.5, 129.3, 122.0, 121.3, 115.3, 35.3, 31.4, 31.1, 22.5, 14.0; Elemental analysis: $\text{C}_{21}\text{H}_{28}\text{O}_3\text{Si}$ requires C, 70.74; H, 7.92 Found C, 70.53; H, 7.77.

4-(Tetradecyloxy)biphenyl-4-trimethylsiloxane (10b)

IR: 1606, 1498, 1465, 1454, 1377, 1276, 1551, 1170, 1039, 842, 750 cm^{-1} ; ^1H NMR δ ppm: 7.46 (d, 2H, Ar-H, $J = 8.8$ Hz), 7.41 (d, 2H, Ar-H, $J = 8.8$ Hz), 6.94 (d, 2H, Ar-H, $J = 8.8$ Hz), 6.88 (d, 2H, Ar-H, $J = 8.8$ Hz), 3.98 (t, 2H, $-\text{OCH}_2-$, $J = 6.6$ Hz), 1.80 (m, 2H, $-\text{OCH}_2-\text{CH}_2-$), 1.51-1.20 (m, 22H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$, $J = 6.5$ Hz), 0.28 (s, 9H, $-\text{OSi}(\text{CH}_3)_3$); Elemental analysis: $\text{C}_{29}\text{H}_{46}\text{O}_2\text{Si}$ requires C, 76.59; H, 10.20. Found: C, 76.93; H, 10.47.

RESULTS AND DISCUSSION

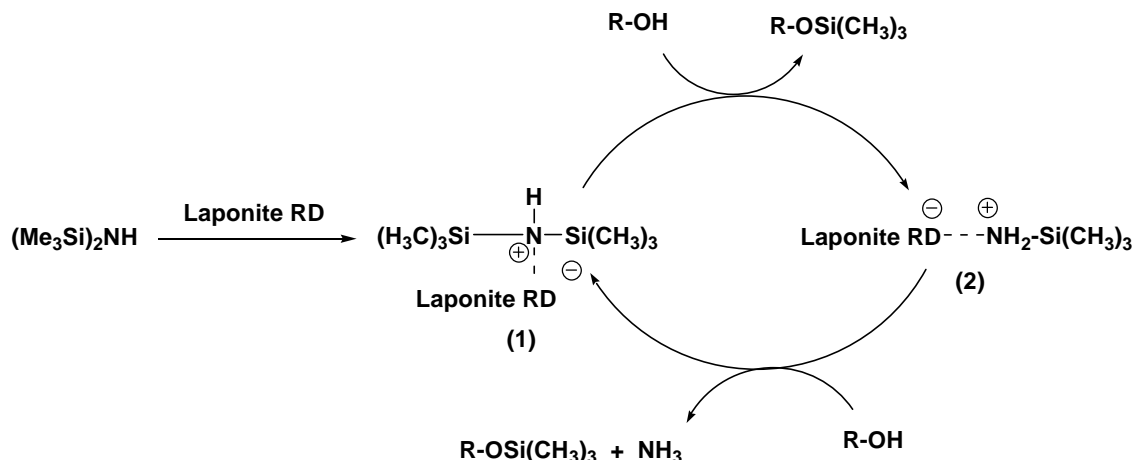
We have carried out the reactions with varying concentration of HMDS and Laponite RD® catalyst with a constant reaction time of thirty minutes for a wide variety of phenols (**1a**) to (**10a**) in dichloromethane solvent. The reaction gave highly pure and excellent yields of the novel aryloxytrimethylsilyl-ethers (**1b**) to (**10b**) as indicated in TABLE 1.

We have found that under our conditions only 4

equivalents of HMDS and 0.010g of Laponite RD[®] is required for all phenols to give expected products (**1b**) to (**10b**). The isolated yield of all prepared aryloxysilylethers was found to be generally more than 85%. The novel compounds prepared have been characterized completely by IR, NMR, GC-MS and elemental analysis.

Furthermore, we have examined the recovery and reuse of the catalyst on the silylation of decyloxyphenol

(Entry 7) under the same parameters, we found that, the conversion of phenol to corresponding aryloxysilylether and yields in the second and third use of the catalyst were almost same as that in the first use. In all cases more than 90% of the catalyst was recovered by filtration and washed with acetone dried at 130°C before use. The probable mechanism for the formation of aryloxysilylethers is depicted in Scheme 2.



Scheme 2 : Proposed mechanism for the preparation of aryloxysilylethers from phenols

TABLE 1 : Synthesis of some novel aryloxysilylethers using HMDS and laponite RD[®]

Entry	a	b	mp/bp* (°C)	Yield (%)
1			112-113	95
2			205-208*	92
3			114-115	85
4			214- 216	90
5			65-67	93
6			69-71	87
7			180-185*	94

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Entry	a	b	mp/bp*(°C)	Yield (%)
8			165-170*	90
9			140-142	84
10			54-56	96

Note : 1 *Indicates liquids (boiling points determined under reduced pressure at 10mm/Hg).

2 Boiling points and melting points remain uncorrected.

Laponite RD® is a cationic clay of a mixture of metaloxides, which polarizes the N-Si bond in HMDS by coordinating with nitrogen to form a intermediate 1, which effectively silylates the phenols to aryloxysilylethers and gives another reactive intermediate 2. Again this intermediate 2 reacts with another molecule of phenol to produce the second equivalent of corresponding aryloxysilylether (Scheme 2) with evolution of ammonia.

CONCLUSIONS

We hereby report Laponite RD® to be a mild and efficient catalyst for silylation of phenols using hexamethyldisilazane. All the ten novel aryloxysilylethers serve as masked aryloxyanions and may be used as important synthetic equivalents in organic chemistry.

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