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THE PREPARATION OF α-HYDROXYORGANOSILANES FROM α-BORYLORGANOSILANE INTERMEDIATES [1]

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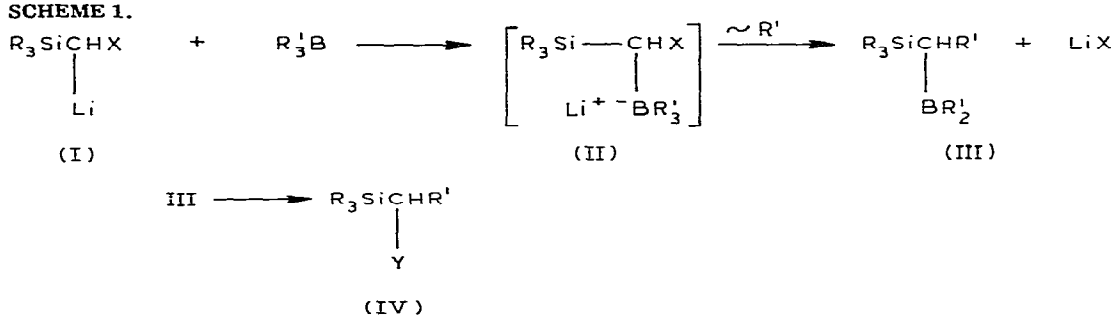
Summary

The generation of α-silyl-α-borylmethane derivatives as intermediates and their oxidation to α-hydroxyorganosilanes is reported. The formation of the intermediate α-silyl-α-borylmethane derivatives is via the type I transfer reaction of organoboranes with either (trimethylsilyl)bromomethyllithium and (phenyldimethylsilyl)chloromethyllithium in THF or in some cases hexane.

Introduction

In our interest in utilizing organoborane chemistry to generate carbo-functional organosilanes we have continued our investigation of the α-transfer reaction (type I transfer [2]) of organoboranes to both introduce an alkyl group from the organoborane into the organosilane and to utilize the newly created carbon—boron bond to introduce functionality in the α-position of the organosilane. This general concept is illustrated in Scheme 1. Thus, reaction of an

SCHEME 1.



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organoborane with an appropriately substituted α-silylmethyllithium reagent would allow formation of an intermediate complex, II, which would be expected to undergo type I transfer to form the α-boryl organosilane, III. Compound III could then be converted to various α-functionalized organosilanes via reaction of the carbon—boron bond. In our initial work reported herein [1], we chose to oxidize the organoborane, III, to the α-hydroxyorganosilanes, V (eq. 1). Two reasons lead us to first use the oxidation reaction: (1) this is a known reaction of organoboranes which proceeds in very high yield and (2) it was felt that the α-hydroxyorganosilanes could be converted to other α-substituted organosilanes (work now underway in our laboratories).

$$\underset{\text{(III)}}{R_3SiCHR'(BR'_2)} \xrightarrow[HO^-]{H_2O_2} \underset{\text{(V)}}{R_3SiCHR'(OH)} + 2\ R'OH \qquad (1)$$

Our attention thus turned to the generation of the α-silylmethyllithium reagents containing a leaving group, X. An investigation of the literature revealed that lithium reagents of the type I have been prepared where X = Cl [3,4], Br [5], SR [6] and $P(O)(OEt)_2$ [6]. Of these possibilities the chloro, bromo and sulfur derivatives seemed to offer the best chance for success in their reaction with boranes since all of these leaving groups had been utilized in type I transfer reactions with organoboranes [2,7]. It was recognized a priori that two major obstacles could work against the desired reaction: (1) the thermal instability of the appropriate lithium reagents, I, requiring low reaction temperatures and (2) the potentially large steric requirement of the silyl group. Both of these effects (low temperature and large steric effect) would slow down or stop the reaction of the lithium reagent with the organoborane, especially the more hindered organoboranes. With these points in mind the reaction sequence illustrated in eq. 2 was carried out in an attempt to ascertain the efficacy of the generation of the intermediate organoborane, IV, and to prepare α-hydroxyorganosilanes. The reaction sequence was carried out with representative organoboranes and (trimethylsilyl)bromomethyllithium, VI, (generated "in situ"), (phenyldimethylsilyl)chloromethyllithium, VII, (generated prior to borane addition or "in situ") and (trimethylsilyl)phenylthiomethyllithium, VIII, (generated prior to organoborane addition).

$$R_3SiCHX(Li) \xrightarrow[(2)\ H_2O_2/HO^-]{(1)\ R'_3B} R_3SiCHR'(OH) + 2\ R'OH \qquad (2)$$

(R_3Si = Me_3Si, X = Br, VI); (R_3Si = $PhMe_2Si$, X = Cl, VII); (R_3Si = Me_3Si, X = SPh, VIII)

Reaction of trimethyl(dibromomethyl)silane with lithium metal in the presence of an organoborane

Our initial efforts dealt with the straight-forward approach of adding trimethyl(dibromomethyl)silane, IX, to a THF mixture of lithium metal and the

$$\underset{\text{(IX)}}{Me_3SiCHBr_2} + 2\ Li + R_3B \xrightarrow{THF} \xrightarrow[HO^-]{H_2O_2} Me_3SiCHR \quad (3)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

organoborane as illustrated in eq. 3. It was felt that the desired lithium reagent, IV, would be generated "in situ" and that its reaction with the organoborane would be fast enough to compete with decomposition. Brown and coworkers have used similar "in situ" approaches to the type I transfer reactions of organoboranes in the alkylation of esters [8], ketones [9] and nitriles [10] and in the synthesis of tertiary alcohols from dichloromethylmethyl ether and organoboranes [11].

Good yields of the desired α-hydroxyorganosilanes were obtained for the less sterically hindered tri-n-alkyl and tricyclopentylboranes, with the yields diminishing with the more hindered tricyclohexyl and tri-*exo*-norbornyl boranes. Apparently, the more hindered organoboranes react with VI slowly enough to allow decomposition of the lithium reagent to occur. The reaction is independent of the type of lithium used, lithium wire or dispersion working equally well. Magnesium, however, gave considerably lower yields and sodium and zinc gave none of the desired product. One crucial drawback with this reaction is the problem of separating by distillation the α-hydroxyorganosilane from the non-silylated alcohol (ROH) obtained by the oxidation of the remaining two alkyl groups on the boron. The use of B-alkyl-9BBN derivatives gave a mixture of products.

The reaction of (trimethylsilyl)phenylthiomethyllithium with organoboranes

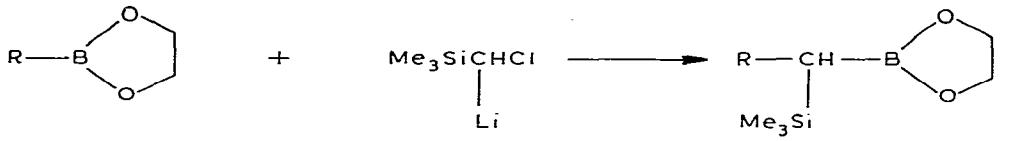
A report by Carey and Court [6a] on the formation of the lithium reagent, VIII, coupled with the work of Smith et al. [12] indicating that the phenylthio group could be used as a leaving group in the type I transfer reaction made this lithium reagent worthy of investigation. The admixture of the preformed lithium reagent, VIII, with tri-n-pentylborane in THF was not exothermic, nor did it produce any color changes. However, upon refluxing for several hours followed by treatment with an excess of iodomethane (addition of mercuric chloride gave poor yield and no electrophile addition gave no product) and oxidation a 60% yield of 1-trimethylsilyl-1-hexanol was produced (eq. 4). Similarly, tri-n-hexylborane was converted to 1-trimethylsilyl-1-heptanol in 71% yield. Several attempts, however, to carry out the reaction with tricyclopentylborane resulted in low yields of the corresponding α-hydroxyorganosilane and this approach was abandoned as a general method of preparing α-hydroxyorganosilanes.

$$Me_3SiCH_2SPh \xrightarrow[(4)\ H_2O_2/HO^-]{\substack{(1)\ n\text{-}BuLi \\ (2)(C_5H_{11})_3B \\ (3)\ CH_3I}} Me_3SiCH\text{-}n\text{-}C_5H_{11} + n\text{-}C_5H_{11}OH + MeSPh \quad (4)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

Reaction of (phenyldimethylsilyl)halomethyllithium reagents with organoboranes

Magnus and coworkers have reported the generation of trimethylsilylchloromethyllithium and its reaction with aldehydes and ketones [3] and alkylating

reagents [13]. Matteson and Majumdar [14] have recently used this interesting lithium reagent with boronic esters to yield the homologous α-trimethylsilyl boronic esters (eq. 5).



(5)

In order to avoid the separation problem encountered with the trimethylsilyl moiety it was decided to employ the phenyldimethylsilyl group, namely (phenyldimethylsilyl)chloromethyllithium, VII. Treatment of (chloromethyl)-phenyldimethylsilane with sec-butyllithium and TMEDA in THF at −78°C for 40 min followed by the addition of tri-n-hexylborane and oxidation gave a 38% yield of 1-(phenyldimethylsilyl)-1-heptanol (average of three reactions) (eq. 6). This approach was not pursued any further, except with variations on the formation of the lithium reagent, which did not enhance the yield of the α-hydroxyorganosilane.

$$PhMe_2SiCH_2Cl \xrightarrow[(3)\ H_2O_2/HO^-]{(1)\ \text{sec-BuLi TMEDA}\ (2)\ (n\text{-}C_6H_{13})_3B} PhMe_2SiC(OH)\text{-}n\text{-}C_6H_{13} + 2\ n\text{-}C_6H_{13}OH \qquad (6)$$

We have found that the lithium reagent, VII, can be generated by utilizing strong nitrogen bases like lithium diisopropylamide [4]. It seemed possible that via the use of a suitable lithium dialkylamide base, which would not for steric reasons attack the borane, VII could be generated in the presence of the organoborane. The results of this approach with tributylborane, which are sum-

TABLE 1

α-HYDROXYSILANES FROM ORGANOBORANES

R of R_3B	Product	Yield (%)
n-Pentyl	$Me_3SiCH(OH)\text{-}n\text{-}C_5H_{11}$ [a]	79 [b]
n-Hexyl	$Me_3SiCH(OH)\text{-}n\text{-}C_6H_{13}$ [a]	72 [b]
n-Octyl	$Me_3SiCH(OH)\text{-}n\text{-}C_8H_{17}$ [a]	69 [b]
c-Pentyl	$Me_3SiCH(OH)\text{-}cyclo\text{-}C_5H_9$ [a]	63 [b]
c-Hexyl	$Me_3SiCH(OH)\text{-}cyclo\text{-}C_6H_{11}$ [a]	43 [b]
exo-Norbornyl	$Me_3SiCH(OH)\text{-}exo\text{-}C_7H_{11}$ [a,c]	46 [b]
n-Butyl	$Phme_2SiCH(OH)\text{-}n\text{-}C_4H_9$ [d]	60 [e]
n-Hexyl	$PhMe_2SiCH(OH)\text{-}n\text{-}C_6H_{13}$ [d]	80 [e]
n-Octyl	$PhMe_2SiCH(OH)\text{-}n\text{-}C_8H_{17}$ [d]	78 [e]
3-Hexyl	$PhMe_2SiCH(OH)CH(CH_2CH_3)CH_2CH_3$ [d]	37 [e]
c-Pentyl	$PhMe_2SiCH(OH)\text{-}cyclo\text{-}C_5H_9$ [d]	72 [e]
c-Hexyl	$PhMe_2SiCH(OH)\text{-}cyclo\text{-}C_6H_{11}$ [a]	42 [e]
exo-Norbornyl	none isolated [d]	—

[a] Reaction of $Me_3SiCHBr_2$, lithium and the organoborane. [b] GLC yield using internal standard. [c] An apparent mixture of diastereomers. [d] Reaction of $PhMe_2SiCH_2Cl$, LTMP and the organoborane. [e] Yield of distilled material.

TABLE 2

EFFECT OF THE BASE ON THE REACTION OF (CHLOROMETHYL)-PHENYLDIMETHYLSILANE AND TRI-n-BUTYLBORANE

$PhMe_2SiCH_2Cl$	$\xrightarrow[Bu_3B]{\text{Base-solvent}} \xrightarrow[HO^-]{H_2O_2}$		$PhMe_2SiCH(OH)$-n-C_4H_9 [a]
Base	Solvent	$PhMe_2SiCH_2Cl$ (%) [b]	Product (%) [c]
Et_2NLi	THF	51	— [d]
Et_2NLi	Hexane	75	— [d]
i-Pr_2NLi	THF	48	20 [d]
i-Pr_2NLi	Hexane	75	— [d]
(cyclo-$C_6C_{11})_2NLi$	THF	65	32
(cyclo-$C_6H_{11})_2NLi$	Hexane	64	36
LTMP	THF	26	74
LTMP	Hexane	20	80
$(Me_3Si)_2Nli$	THF [e]	100	0

[a] $PhMe_2SiCH_2Cl$ (6 mmol), base (6.5 mmol), Bu_3B (5 mmol) at 0.25 *M*. [b] NMR analysis using CH_2Br_2 as internal standard. [c] NMR analysis; yield based on Bu_3B. [d] A mixture of products as adjudged by the numerous silicon-methyl resonances at ca. δ0. [e] Tri-n-hexylborane was used in this reaction.

marized in Table 2, range from no reaction (i.e. no apparent proton abstraction, lithium hexamethyldisilazide) to good yield of product (lithium 2,2,6,6-tetramethylpiperidide, LTMP). Clearly LTMP is the best base for this approach. Lithium hexamethyldisilazide is apparently not basic enough to abstract the proton. A change of solvent from THF to n-hexane did not influence the yield of product. We found it most convenient to employ THF since the organoboranes are readily prepared in this solvent. The use of (bromomethyl)phenyldimethylsilane or (iodomethyl)phenyldimethylsilane in this approach resulted in low yields (ca. 30%) of the desired product. It is to be noted that direct formation of LTMP from n-butyllithium and 2,2,6,6-tetramethylpiperidine in THF in an addition funnel attached to the reaction flask resulted in a drop of about 20% in the yield of product as compared to those reactions where the formation of the base was done at 0°C and transferred to the additional funnel.

The mechanism of this reaction could either be via attack of the lithium reagent, VII, on the organoborane or via attack of the phenyldimethylsilylcarbene on the organoborane. It is probable that the lithium reagent, VII, is the reactive species in THF and possible that the carbene is reacting in hexane, where trimethylsilylcarbene has been shown to be present under conditions very similar to those employed here [15].

Experimental

General considerations

The standard reaction apparatus consisted of a three-necked, round-bottom flask equipped with addition funnel, condenser, no-air stopper, nitrogen inlet and magnetic stirrer. This apparatus was flame dried under a vigorous stream of nitrogen and allowed to cool in a nitrogen atmosphere prior to charging it with

the various reagents. Nitrogen gas was passed through concentrated sulfuric acid and then over solid potassium hydroxide. n-Butyllithium was titrated prior to use, lithium wire and dispersion were washed with the same solvent to be used in the reaction. THF, hexane, ether and toluene were distilled from sodium benzophenone. Diisopropylamine, dicyclohexylamine, hexamethyldisilazane and *N,N,N',N'*-tetramethylethylenediamine were distilled from calcium hydride and stored over 4A molecular sieves prior to use, as was 2,2,6,6-tetramethylpiperidine.

Tri-n-butylborane was prepared from the reaction of n-butylmagnesium bromide with boron fluoride ethyletherate [16]. All other boranes were prepared via the hydroboration of the appropriate olefin with a THF solution of borane. These organoboranes were used as solutions without isolation. The various organosilane starting materials were prepared according to literature procedures as follows: (dibromomethyl)trimethylsilane [5], (thiophenoxymethyl)trimethylsilane [18], (chloromethyl)phenyldimethylsilane by the reaction of phenylmagnesium bromide with (chloromethyl)dimethylchlorosilane in ether (85% yield), (bromomethyl)phenyldimethylsilane [18,19] and (iodomethyl)phenyldimethylsilane [20] from (chloromethyl)phenyldimethylsilane and sodium iodide in refluxing acetone.

Spectral measurements were carried out using a Perkin—Elmer 237 infrared spectrophotometer (IR), Varian T60 or Perkin—Elmer R24B (NMR) and a Finnigan mass spectrometer (MS). GLC analyses were done using a Perkin—Elmer 3920 (analytical) and Varian 90P (preparative) gas chromatographs with 6′ × 1/8″ or 6′ × 1/4″ carbowax, diethyleneglycol succinate or SE-30 columns.

Preparation of α-hydroxytrimethylsilanes. General procedure

The standard apparatus of 100 ml volume was charged with 10 mmol of borane in THF and then 30 mmol of olefin in THF at 0°C. The total volume was 25 ml. The reaction mixture was stirred at room temperature to form the organoborane, after which time it was charged with 0.3 g (43 g-at) of lithium (wire or dispersion). The reaction mixture was cooled to 0°C during the dropwise addition of 2.36 g (10 mmol) of (dibromomethyl)trimethylsilane in 10 ml of THF. The reaction was stirred at 0°C for 1 h and at room temperature for an additional 1 h followed by the careful addition of a small amount of water to destroy the excess lithium present. Oxidation was accomplished by the addition of 7 ml of 3 *N* sodium hydroxide and the cautious addition of 7 ml of 30% hydrogen peroxide followed by warming to 40—50°C for 1 h. The two phase system was saturated with sodium chloride, the aqueous phase extracted with ether (2 × 20 ml) and the combined organic layers dried over magnesium sulfate. After distillation of the solvent at atmospheric pressure the residue was subjected to GLC analysis. Pure samples were obtained by preparative GLC. The proximity of the boiling points of the α-hydroxytrimethylsilanes and the alcohols produced by direct oxidation of the organoborane precluded a facile separation of the desired material by distillation.

Reaction of phenylthio(trimethylsilyl)methyllithium with organoboranes

The standard apparatus of 250 ml was charged with 1.96 g (10 mmol) of (phenylthiomethyl)trimethylsilane and 20 ml of THF. This was cooled to 0°C

and 5.59 ml of 1.79 *M* n-butyllithium (10 mmol) added followed by stirring at 0°C for 1.5 h. To the lithium reagent was then added 10 mmol of tri-n-pentylborane (from 30 mmol of 1-pentene and 10 mmol of borane in THF) in 20 ml of THF. The reaction was refluxed for 8 h and 4.26 g (30 mmol) of methyl iodide added. The reaction was stirred overnight at room temperature and then oxidized by the addition of 10 ml of 3 *N* sodium hydroxide and 10 ml of 30% hydrogen peroxide. The two phase system was saturated with sodium chloride separated and the aqueous layer extracted with pentane (2 × 25 ml). The combined organic layers were dried (Na_2SO_4) and the solvents removed by distillation. The product was isolated in 60% yield by column chromatography through silica gel using 2.5% ether/pentane.

Preparation of α-hydroxy(phenyldimethyl)silanes. General procedure

The standard apparatus of 100 ml was charged with 10 mmol of a borane/THF solution and 30 mmol of the appropriate olefin added at 0°C. After formation of the organoborane, 2.22 g (12 mmol) of (chloromethyl)phenyldimethylsilane was added followed by the rapid (2 min) addition of the lithium dialkylamide (12 mmol) (formed by the reaction of 12 mmol of n-butyllithium and the amine). The reaction mixture, which warmed slightly upon the addition of the base was refluxed for 16 h and then oxidized by the addition of 7 ml of 3 *N* sodium hydroxide and 7 ml of 30% hydrogen peroxide. The organic layer was separated and washed with 1 *M* citric acid (20 ml). The combined aqueous layers were extracted with ether (2 × 15 ml) and the organic layers combined and dried (Na_2SO_4). After removal of the solvents at reduced pressure the residue was distilled to first give the alcohol resulting from oxidation of the alkyl groups on the original borane and then the desired α-hydroxy(phenyldimethyl)silane.

1-Trimethylsilyl-1-hexanol: n_D^{23} 1.4381; NMR (CCl_4) δ 3.10 (m, 1H), 1.90—0.80 (m, 11H), variable (s, 1H), —0.13 (s, 9H); IR (neat) 3390 and 1235 cm^{-1}; MS 147 (7), 91 (15), 75 (53), 74 (10), 73 (100), 69 (8), 61 (5), 60 (8), 59 (7), 57 (10), 56 (21), 55 (14), 47 (6), 45 (22), 44 (9), 43 (22), 42 (11), and 41 (17).

1-Trimethylsilyl-1-heptanol: n_D^{24} 1.4421; NMR (CCl_4) δ 3.10 (m, 1H), 1.98—0.71 (m, 13H), variable (s, 1H), —0.08 (s, 9H); IR (neat) 3370 and 1245 cm^{-1}; MS 91 (17), 83 (7), 75 (55), 74 (9), 73 (100), 71 (8), 70 (13), 69 (17), 68 (8), 61 (5), 59 (16), 56 (18), 55 (20), 47 (5), 45 (19), 44 (8), 43 (21), 42 (10) and 41 (18).

1-Trimethylsilyl-1-nonanol: n_D^{23} 1.4443; NMR (CCl_4) δ 3.07 (m, 1H), 1.68—0.58 (m, 17H), variable (s, 1H), —0.15 (s, 9H): IR (neat) 3370 and 1245 cm^{-1}; MS 97 (5), 91 (19), 84 (7), 83 (14), 75 (55), 74 (10), 73 (100), 70 (14), 69 (17), 66 (11), 57 (13), 56 (18), 55 (17), 45 (14), 44 (5), 43 (17), 42 (7) and 41 (16).

Cyclopentyl(trimethylsilyl)carbinol: n_D^{23} 1.4665; NMR (CCl_4) δ 2.92 (d, 1H, *J* 3.5 Hz), 1.42 (broad m, 9H), variable (s, 1H), —0.12 (s, 9H); IR (neat) 3370 and 1240 cm^{-1}; MS 157 (7), 130 (6), 129 (52), 98 (8), 90 (11), 83 (12), 82 (9), 81 (12), 75 (78), 74 (15), 73 (100), 72 (9), 70 (6), 69 (14), 68 (12), 67 (62), 61 (10), 59 (10), 57 (13), 55 (21), 54 (32) and 53 (8).

Cyclohexyl(trimethylsilyl)carbinol: n_D^{23} 1.4711; NMR (CCl_4) δ 2.92 (m, 1H),

2.41—0.78 (m, 11H), variable (s, LH), —0.11 (s, 9H); IR (neat) 3370 and 1248 cm^{-1}; MS 186 (5), 147 (10), 129 (14), 112 (6), 95 (15), 94 (11), 93 (12), 90 (15), 89 (5), 83 (8), 82 (6), 81 (30), 77 (6), 76 (5), 75 (34), 74 (10), 73 (100), 69 (5), 68 (16), 67 (21), 57 (7), 55 (30).

exo-Norbornyl(trimethylsilyl)carbinol: This was obtained as two diastereomers separated by preparative GLC on a 6′ × 1/4″ β,β′-oxydipropionitrile column at 95°C. Diastereomer A (longer retention time) showed: n_D^{21} 1.4866; NMR (CCl_4) δ 3.47 (m, 1H), 2.70—0.93 (m, 11H), variable (s, 1H) 0.29 (s, 9H); IR (neat) 3460 and 1247 cm^{-1}: MS 183 (16), 165 (9), 155 (6), 130 (18), 129 (89), 117 (10), 109 (14), 108 (16), 95 (37), 93 (28), 80 (32), 79 (60), 77 (15), 75 (84), 74 (20), 73 (100), 67 (56), 66 (45), 59 (10), 57 (15), 55 (14), 54 (14) and 53 (12). Diastereomer B (shorter retention time) showed: n_D^{21} 1.4847: NMR (CCl_4) δ 3.47 (m, 1H), 2.60—0.87 (m, 1H), variable (s, 1H), 0.37 (s, 9H); IR (neat) 3413 and 1242 cm^{-1}; MS 183 (20), 169 (6), 165 (14), 155 (7), 130 (17), 129 (75), 109 (16), 108 (35), 96 (42), 95 (100), 94 (22), 93 (52), 91 (20), 81 (21), 80 (53), 79 (65), 77 (30), 75 (72), 74 (20), 73 (82), 68 (34), 67 (77), 66 (63), 57 (30), 55 (44), 54 (30) and 53 (31).

1-(Phenyldimethylsilyl)-1-pentanol: B.p. 65—85°C/1.2 mmHg; n_D^{26} 1.5044: NMR (CCl_4) δ 7.57—7.07 (m, 5H), 3.33 (m, 1H), 1.70—0.58 (m, 10H), 0.29 (s, 6H); IR (neat) 3625, 3500 and 1252 cm^{-1}; MS 222 (0.1), 207 (9), 165 (12), 137 (25), 136 (11), 135 (100), 105 (7) and 75 (14).

1-(Phenyldimethylsilyl)-1-heptanol: B.p. 114—120°C/0.3 mmHg; n_D^{23} 1.5038; NMR (CCl_4) δ 7.50—6.97 (m, 5H), 3.33 (broad t, 1H), 1.62—0.57 (m, 13H), variable (s, 1H), 0.27 (s, 6H); IR (neat) 3676, 3521 and 1245 cm^{-1}; MS 235 (6), 165 (7), 152 (7), 138 (8), 137 (52), 136 (14), 135 (100), 107 (5), 105 (8), 75 (10), 55 (5), 43 (8) and 41 (5).

1-Phenyldimethylsilyl-1-nonanol: B.p. 130—150°C/0.01 mmHg; n_D^{24} 1.5665; NMR (CCl_4) δ 7.68—7.17 (m, 5H), 3.42 (broad t, 1H), 1.27 (m, 18H), 0.30 (s, 6H); IR 3640 and 1248 cm^{-1}; MS 265 (5), 165 (8), 152 (9), 137 (65), 136 (12), 135 (100) and 105 (5).

Cyclopentyl(phenyldimethylsilyl)carbinol: B.p. 109—116°C/0.5 mmHg; n_D^{23} 1.5307; NMR (CCl_4) δ 7.53—7.03 (m, 5H), 3.23 (d, 1H, *J* 7 Hz), variable (s, 1H), 2.20—0.77 (m, 10H), 0.28 (s, 6H); IR (neat) 3676, 3546 and 1244 cm^{-1}; MS 219 (4), 191 (8), 166 (9), 165 (55), 158 (10), 138 (11), 137 (65), 136 (42), 135 (100), 134 (8), 121 (11), 120 (10), 119 (13), 117 (5), 109 (5), 107 (21), 106 (5), 105 (35), 98 (17), 93 (9), 91 (18), 83 (9), 82 (6), 81 (23), 77 (10), 76 (6), 75 (26), 69 (8), 67 (19), 61 (7), 59 (11), 58 (10), 57 (15), 55 (13), 54 (7), 53 (13), 45 (15), 43 (36), 42 (5), 41 (35) and 39 (17).

Cyclohexyl(phenyldimethylsilyl)carbinol: B.p. 111—121°C/0.30 mmHg; n_D^{23} 1.5278; NMR (CCl_4) δ 7.60—7.13 (m, 5H), 3.22 (d, 1H, *J* 4 Hz), variable (s, 1H), 2.00—0.90 (m, 11H), 0.30 (s, 6H); IR (neat) 3676, 3534 and 1241 cm^{-1}; MS 247 (0.3), 165 (29), 152 (5), 137 (56), 136 (13), 135 (100), 95 (6), 75 (10), 55 (7), 43 (9) and 41 (6).

1-(Phenyldimethylsilyl)-2-ethylpentanol: B.p. 112—130°C/0.5 mmHg; n_D^{26} 1.5050; NMR (CCl_4) δ 7.7—7.17 (m, 5H), 3.55 (m, 1H), 1.62—0.60 (m, 14H), 0.33 (s, 6H); IR (CCl_4) 3619, 3450 and 1257 cm^{-1}; MS 250 (0.1), 235 (8), 193 (17), 166 (10), 137 (36), 136 (12), 135 (100), 107 (5), 105 (6), and 89 (5).

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