A SIMPLE PHASE TRANSFER CATALYZED SYNTHESIS OF BENZYL AND HETARYLMETHYL SILACYCLOALKYL ETHERS FROM ACETATES

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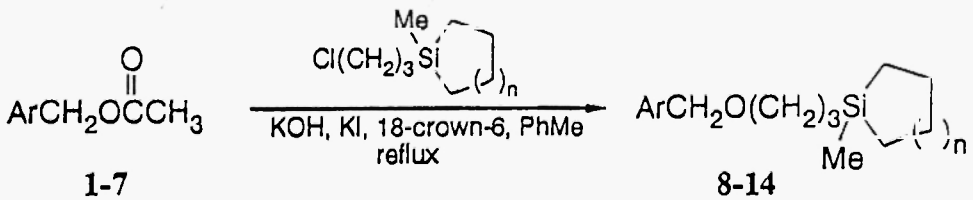
Abstract: Simple and one-pot phase transfer catalytic method for the preparation of benzyl and hetaryl silacycloalkyl ethers from corresponding acetates in the system chloropropylsilane / KOH / KI / 18-crown-6 was elaborated. The corresponding benzyl and hetaryl ethers were obtained in 56 → 78 % yield.

Introduction

Synthesis of O-trialkylsilylalkyl ethers under nucleophilic catalysis conditions are of interest in recent years. Application of Williamson ether synthesis to the preparation of benzyl trimethylsilylmethyl ether was unsuccessfull because of isomerization of (trimethylsilyl)methyl alcoholate to methoxytrimethylsilane (Brook rearrangement)[1,2]. It was also known that in the reaction with halogenomethyltrimethylsilanes the alkoxide anions generated from alcohols with NaH in THF/DMF/ n-Bu_4NI system produced only cleavage products, i.e., methyl and trimetylsilyl ethers with no traces of the expected trimethylsilylmethyl ether[3]. Therefore, we have elaborated a synthetic procedure starting from acetates and using phase transfer catalysis.

Results and Discussion

We have found that silacycle containing benzyl and hetarylmethyl ethers **8-14** [4-5] can be successfully obtained from the corresponding acetates **1-7** [6] in the phase transfer catalytic system 3-chloropropylsilane[7] /solid KOH / solid KI/ toluene/18-crown-6. Obviously, the formation of ethers **8-14** proceeds through the corresponding alcohols not detectable by GC-MS due to the rapid changes. The remarkable observation was that the etherification reactions with bulky chloropropylsilanes in the absence of added KI were very slow and the yields of the products obtained were usually low.[8] It suggests that this reaction proceeds via convertion of chloropropylsilane to the corresponding iodopropylsilane which is more reactive in the alkylation reaction.



1-7 **8-14**

Table 1. Synthesis of aryl and hetaryl ethers **8-14**

Starting acetate	Ar	Reaction time, h	Product	n	Bp (°C) at 10 mm Hg	Yield (%)[a]
1	Ph	3	**8a**	1	148-151	68
1	Ph	3	**8b**	2	168-170	67
2	2-furyl	5	**9a**	1	134-136	64
2	2-furyl	6	**9b**	2	145-146	63
3	2-thienyl	4	**10a**	1	146-148	72
3	2-thienyl	4	**10b**	2	150-152	71
4	2-pyridyl	7	**11a**	1	149-150	56
5	6-methyl-2-pyridyl	9	**12a**	1	182-183	67
5	6-methyl-2-pyridyl	9	**12b**	2	190-191	69
6	3-pyridyl	7	**13a**	1	146-147	63
7	4-pyridyl	6	**14a**	1	135-136	78
7	4-pyridyl	6	**14b**	2	150-152	71

[a]Isolated yield after purification

Thus, a simple and selective one-pot method for the preparation of benzyl and hetaryl silacycloalkyl ethers has been elaborated. The isolated yields of the products were 58 - 78 %.

References

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(4) **General procedure for synthesis of ethers 8-14**. To a solution of acetate **1-7** (5 mmol), chloropropylsilane (5 mmol) and 18-crown-6 (0.066 g, 0.25 mmol) in 8 ml of dry toluene were added powdered KI (3.32 g, 20 mmol) and powdered KOH (1.12 g, 20 mmol). The mixture was stirred 3-9 h at reflux temperature and cooled up to room temperature. The solid was filtered off and the solvent was removed under reduced pressure. The crude residue was purified by distillation in vacuo or chromatographed on silica (eluent benzene) to afford the pure products **8-14**.

(5) **Illustrative spectroscopic data**:

8a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.24 (s, 3H, CH_3), 0.73 (m. 6H, $(CH_2)_2\underline{CH_2}Si$ and silacycle $\underline{CH_2}(CH_2)_2\underline{CH_2}$), 1.70 (m, 6H, $CH_2\underline{CH_2}CH_2Si$ and silacycle $CH_2(\underline{CH_2})_2CH_2$), 3.62 (t, 2H, J = 6.8 Hz, $\underline{CH_2}(CH_2)_2Si$), 4.67 (s, 2H, CCH_2), 7.49 (m, 5H, Ph). MS m/z (rel. intensity) 248 (M^+, <1), 101 (80), 91 (100), 71 (10), 45 (10).

8b: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.22 (s, 3H, CH_3), 0.78 (m, 6H, $(CH_2)_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$), 1.77 (m, 8H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$). 3.67 (t, 2H, J = 6.8 Hz, $CH_2(CH_2)_2Si$), 4.73 (s, 2H, CCH_2), 7.56 (m, 5H, Ph). MS m/z (rel. intensity) 262 (M^+, <0.1), 160 (12), 113 (10), 101 (81), 91 (100), 43 (9).

9a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.07 (s, 3H, CH_3), 0.53 (m, 6H, $(CH_2)_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 1.60 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 3.44 (t, 2H, J = 7 Hz, $CH_2CH_2CH_2Si$), 4.47 (s, 2H, CCH_2), 6.33 (m, 2H, H-3 and H-4), 7.40 (m, 1H, H-5). MS m/z (rel. intensity) 238 (M^+, < 1), 101 (38), 81 (100), 71 (12), 53 (15), 45 (11).

9b: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.29 (s, 3H, CH_3), 0.86 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$), 1.64 (m, 8H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$), 3.76 (t, 2H, J = 7 Hz, $CH_2CH_2CH_2Si$), 4.73 (s, 2H, CCH_2), 6.62 (m, 2H, H-3 and H-4), 7.64 (m, 1H, H-5). MS m/z (rel. intensity) 252 (M^+, < 1), 101 (21), 81 (100), 53 (10).

10a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.18 (s, 3H, CH_3), 0.64 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 1.64 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 3.56 (t, 2H, J = 6.8 Hz, $CH_2(CH_2)_2Si$), 4.76 (s, 2H, CCH_2), 7.08 (m, 2H, H-4 and H-5), 7.35 (m, 1H, H-3). MS m/z (rel. intensity) 254 (M^+, < 1), 102 (25), 97 (100), 71 (12), 53 (10), 45 (21).

10b: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.20 (s, 3H, CH_3), 0.76 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$), 1.76 (m, 8H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_3CH_2$), 3.64 (t, 2H, J = 6.6 Hz, $CH_2(CH_2)_2Si$), 4.87 (s, 2H, CCH_2), 7.15 (m, 2H, H-4 and H-5), 7.42 (m, 1H, H-3). MS m/z (rel. intensity) 268 (M^+, < 1), 101 (21), 97 (100), 85 (19), 45 (15).

11a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.20 (s, 3H, CH_3), 0.71 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 1.64 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 3.42 (t, 2H, J = 6.8 Hz, $CH_2(CH_2)_2Si$), 4.71 (s, 2H, CCH_2), 7.13 (m, 1H, H-5), 7.60 (m, 1H, H-3), 8.09 (m, 1H, H-4), 8.62 (m, 1H, H-6). MS m/z (rel. intensity) 249 (M^+, 2), 220 (68), 192 (80), 178 (45), 165 (26), 152 (21), 136 (26), 101 (40), 93 (100), 65 (32), 43 (22).

12a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.29 (s, 3H, $SiCH_3$), 0.78 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 1.76 (m, 6H, $CH_2CH_2CH_2Si$ and silacycle $CH_2(CH_2)_2CH_2$), 2.67 (s, 3H, CH_3 in pyridine ring), 3.71 (t, 2H, J = 6.8 Hz, $CH_2(CH_2)_2Si$), 3.89 (s, 2H, CCH_2), 7.0-7.3 (m, 2H, H-3 and H-5), 7.71 (m, 1H, H-4). MS m/z (rel. intensity) 263 (M^+, 3), 234 (12), 206 (24), 192 (12), 150 (13), 122 (17), 107 (100), 79 (17).

12b: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.26 (s, 3H, $SiCH_3$), 0.84 (m, 6H, $CH_2CH_2C\underline{H}_2Si$ and silacycle $C\underline{H}_2(CH_2)_3C\underline{H}_2$), 1.86 (m, 8H, $CH_2C\underline{H}_2CH_2Si$ and silacycle $CH_2(C\underline{H}_2)_3CH_2$), 2.69 (s, 3H, CH_3 in pyridine ring), 3.76 (t, 2H, J = 6.8 Hz, $C\underline{H}_2(CH_2)_2Si$), 3.93 (s, 2H, CCH_2), 7.0-7.3 (m, 2H, H-3 and H-5), 7.82 (m, 1H, H-4). MS m/z (rel. intensity) 277 (M^+, 2), 234 (22), 206 (18), 192 (16), 179 (10), 122 (20), 107 (100), 85 (28), 59 (11), 43 (10).

13a: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.18 (s, 3H, CH_3), 0.64 (6H, $CH_2CH_2C\underline{H}_2Si$ and silacycle $C\underline{H}_2(CH_2)_2C\underline{H}_2$), 1.62 (m, 6H, $CH_2C\underline{H}_2CH_2Si$ and silacycle $CH_2(C\underline{H}_2)_2CH_2$), 3.55 (t, 2H, J = 6.8 Hz, $C\underline{H}_2(CH_2)_2Si$), 3.78 (s, 2H, CCH_2), 7.38 (m, 1H, H-5), 7.78 (m, 1H, H-4), 8.64 (m, 2H, H-2 and H-6). MS m/z (rel. intensity) 249 (M^+, 2), 220 (12), 192 (17), 101 (100), 92 (81), 65 (26), 39 (17).

14a: H NMR (90 MHz, $CDCl_3$) δ 0.13 (s, 3H, CH_3), 0.64 (m, 6H, $CH_2CH_2C\underline{H}_2Si$ and silacycle $C\underline{H}_2(CH_2)_2C\underline{H}_2$), 1.62 (m, 6H, $CH_2C\underline{H}_2CH_2Si$ and silacycle $CH_2(C\underline{H}_2)_2CH_2$), 3.56 (t, 2H, J = 6.8 Hz, $C\underline{H}_2(CH_2)_2Si$), 3.73 (s, 2H, CCH_2), 7.31 (m, 2H, H-3 and H-5), 8.60 (m, 2H, H-2 and H-6). MS m/z (rel. intensity) 249 (M^+, 3), 220 30), 207 (14), 192 (39), 150 (13), 101 (100), 65 (23), 45 (19).

14b: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.20 (s, 3H, CH_3), 0.78 (m, 6H, $CH_2CH_2C\underline{H}_2Si$ and silacycle $C\underline{H}_2(CH_2)_3C\underline{H}_2$), 1.73 (m, 8H, $CH_2C\underline{H}_2CH_2Si$ and silacycle $CH_2(C\underline{H}_2)_3CH_2$), 3.64 (t, 2H, J = 6.8 Hz, $C\underline{H}_2(CH_2)_2Si$), 3.84 (s, 2H, CCH_2), 7.44 (m, 2H, H-3 and H-5), 8.71 (m, 2H, H-2 and H-6). MS m/z (rel. intensity) 263 (M^+, 2), 220 (93), 207 (12), 192 (11), 178 (13), 150 (11), 113 (20), 101 (100), 92 (45), 65 (27), 43 (19).

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