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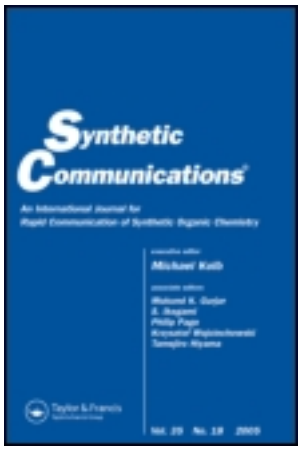

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Silica Chloride (SiO_2-Cl) and Trimethylsilyl Chloride (TMSCl) Promote Facile and Efficient Dehydration of Tertiary Alcohols

Habib Firouzabadi [a], Naser Iranpoor [a], Hassan Hazarkhani [a] & Babak Karimi [a]

[a] Chemistry Department, School of Sciences, Shiraz University, Shiraz, Iran

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Silica Chloride (SiO_2-Cl) and Trimethylsilyl Chloride (TMSCl) Promote Facile and Efficient Dehydration of Tertiary Alcohols

Habib Firouzabadi,* Naser Iranpoor,*
Hassan Hazarkhani, and Babak Karimi

Chemistry Department, School of Sciences,
Shiraz University, Shiraz, Iran

ABSTRACT

Silica chloride (SiO_2-Cl), as a heterogeneous reagent, has been used for the efficient dehydration of tertiary alcohols under mild reaction conditions. For comparison, we have also used trimethylsilyl chloride (TMSCl) as a homogeneous reagent for this purpose. We have found that silica chloride is a more efficient reagnet than trimethylsilyl chloride for this purpose. Handling of SiO_2-Cl is much safer and easier than TMSCl, especially for large-scale operation. The selectivity of the method is also demonstrated by several competitive reactions. Ether formation, rearranged products, and polymerization have not been observed in the reactions.

*Correspondence: Habib Firouzabadi and Naser Iranpoor, Chemistry Department, School of Sciences, Shiraz University, Shiraz 71454, Iran; Fax: +98-711-2286008; E-mail: firouzabadi@chem.susc.ac.ir; iranpoor@chem.susc.ac.ir.

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Key Words: Silica chloride; Trimethylsilyl chloride; Dehydration; Tertiary alcohols.

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Solid supports have found wide applications in organic reactions from different views.[1,2] They mostly facilitate the work-up of the reaction mixtures and usually high selectivity accompanied with high yields of the products is observed. Silica gel is one of the extensively used supports for different purposes in organic chemistry.[3–6] Modified silica supports for functional group transformation is also of interest. Silica chloride has been reported to be an efficient reagent for the transformation of sulfoxides to thioethers.[7] Recently, we have reported that silica chloride could also be conveniently used for the conversion of acetals to thioacetals.[8]

Conversion of alcohols to olefins is an important reaction in organic chemistry and a vast number of methods are documented in the literature for this purpose. These methods include conventional protic acid catalysis (H_2SO_4, H_3PO_4)[9] in which the major drawback is the formation of rearranged products and ether by products. Anhydrous $CuSO_4$,[10] Al_2O_3,[11] $FeCl_3$/silica gel,[4] TosOH/silica gel,[5a] H_2SO_4/silica gel,[5b] $BF_3{\cdot}OEt_2$,[12] $POCl_3$/pyridine,[13] HMPA,[14] Ph_3BiBr_2/I_2,[15] metallic sulfates/silica gel,[6] CH_3ReO_3,[16] CF_3COCCl_3,[17] sulfuranes.[18] Triflates have found useful applications in organic synthesis.[19] Copper(II) triflate has been used for dehydration of alcohols.[20] These methods suffer more or less from one of the following drawbacks: (1) unavailability of the reagent, (2) sometimes elevated temperatures are required, (3) fairly large amount of the catalyst or the reagent is needed, and (4) some of the reagents are expensive. Therefore, introduction of a new mild and inexpensive method for this aim could be a useful contribution in organic synthesis. In this article we have demonstrated a new application of silica chloride (SiO_2-Cl) as a cheap and an easily available reagent and trimethylsilyl chloride (TMSCl) for efficient dehydration of tertiary benzylic alcohols.

Preparation of silica chloride is reported in the literature.[21] We have modified this preparation in order to increase the capacity of the reagent.[8,22] According to this modification, the reagent can be prepared by the reaction of thionyl chloride ($SOCl_2$) and silica gel under reflux conditions for 48 h in a quantitative yield. SiO_2-Cl is a grayish and stable powder that should be stored in the absence of moisture.

Now in this article we report selective and efficient dehydration of tertiary benzylic alcohols to their corresponding olefins in $CHCl_3$ at room temperature with excellent yields (Sch. 1, Table 1). Saturated tertiary alcohols remained intact after prolonged reaction times. Surprisingly, 4-hydroxy-4-methyl-2-pentanone (Table 1, Entry 1k) was dehydrated to

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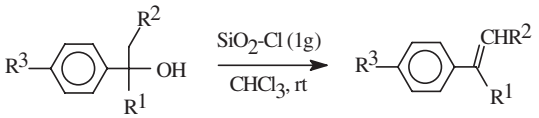
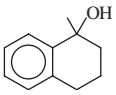
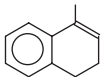
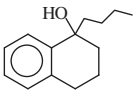
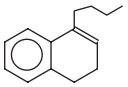
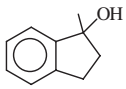
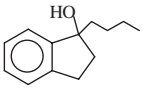
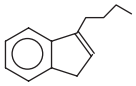
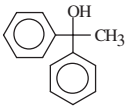
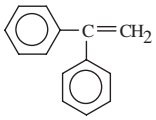
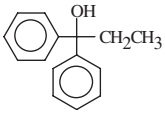
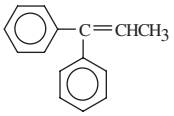
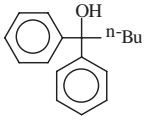
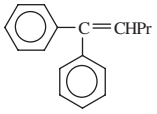


R^1 = Ph,Cyclohexyl, R^2 = H, Me, n-Pr, R^3 = H, Ph, Cl

Scheme 1.

Table 1. Dehydration of tertiary benzylic alcohols with SiO_2-Cl and TMSCl in $CHCl_3$.

Entry substrate	Time[a] (h) SiO_2-Cl, TMSCl	Product	Yield[b] (%) SiO_2-Cl, TMSCl	^{1}H-NMR (olefinic H)[e] δ ($CDCl_3$, ppm)
1a 	0.75, 1		95, 95	5.83
1b 	1, 1.25		89, 88[c]	5.82
1c 	0.66, 1.16		94, 92	6.16
1d 	1.16, 1.1		95, 94	6.13
1e 	0.5, 0.75		93, 94	5.51
1f 	0.75, 1		91, 90	6.15
1g 	1.2, 1.33		89, 88	6.12

(*continued*)

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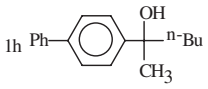
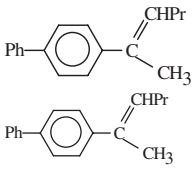
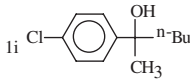
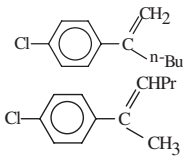
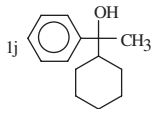
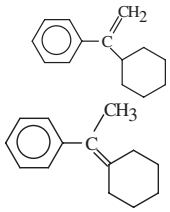
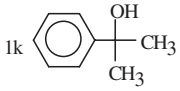
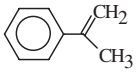
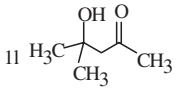
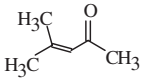
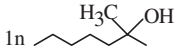
Table 1. Continued.

Entry substrate	Time[a] (h) SiO_2-Cl, TMSCl	Product	Yield[b] (%) SiO_2-Cl, TMSCl	^{1}H-NMR (olefinic H)[e] δ ($CDCl_3$, ppm)
1h 	3, 4		78.3, 79.2[d] 11.7, 8.7	5.85 5.85, 5.30[f]
1i 	4, 5.4		31.5[d], 25.4[d] 87.5, 52.6	5.18, 5.42[f] 5.70
1j 	3, 4		50, 44.9[d] 37, 41.1	4.97, 5.08[f] —
1k 	5, 5		78[d], 25[d]	6.02
1l 	5, 6		87[d], 80[d]	5.07, 5.36[f]
1m 	12, 12	N.R	—	—
1n 	12, 12	N.R	—	—

[a]Substrate/SiO_2-Cl 1 mmol/1.0 g/1 h and substrate/TMSCl 1 mmol 1/2 mmol.
[b]Isolated yields.
[c]10% of the exo-isomer has also been formed.
[d]Reactions were performed in refluxing $CHCl_3$.
[e]Some of the spectral data of the olefins produced in the reactions are given in Ref.[24]
[f]Two different olefinic protons.

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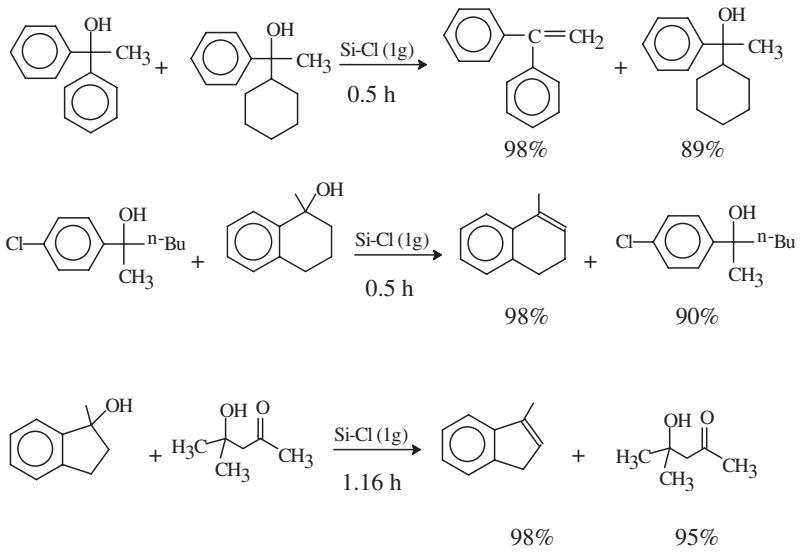
its corresponding conjugated enone after a prolonged reaction time. We believe the extension of conjugation by dehydration reaction provides the driving force for this reaction to occur.

We have also used trimethylsilyl chloride (TMSCl) as a homogenous reagent for this purpose in CH_2Cl_2. Dehydration of tertiary benzylic alcohols proceeded with TMSCl at room temperature and in some cases, refluxing of the reaciton mixture was obligatory for the completion of the reaction. In general, SiO_2-Cl is more reactive reagent than TMSCl for the dehydration of the tertiary alcohols in this study. Handling of SiO_2-Cl is easy and is a suitable reagent for the heterogeneous large-scale operation. The results are tabulated in Table 1.

In order to show the selectivity of SiO_2-Cl for the dehydration of structurally different tertiary alcohols, several competitive reactions proceeded (Sch. 2).

In conclusion, in this study we have shown new and useful applications of silica chloride (SiO_2-Cl) and trimethylsilyl chloride (TMSCl) for dehydration of tertiary benzylic alcohols. Solid silica chloride is a cheap reagent and its handling is much easier than highly reactive liquid trimethylsilyl chloride (TMSCl). Laboratory large-scale operation, even at elevated temperatures, can be conducted easily in the presence of solid silica chloride. Reactions are not time-consuming and the yields of the olefins are excellent.



Scheme 2.

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EXPERIMENTAL

General

Silica chloride (SiO_2-Cl) was prepared according of the reported procedure.[8] IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were run on a Bruker Avance DPX 250 MHz instrument.

Typical Procedure for Dehydration of Tertiary Alcohols

To a solution of 1,1-diphenylpropanol (Entry 1f, 5 mmol, 1.06 g), in $CHCl_3$ (25 mL), silica chloride (5 g) was added and the resulting heterogeneous mixture was stirred at room temperature. After completion of the reaction (0.75 h, TLC, *n*-hexane/EtOAc, 10/1), silica gel (5 g) was added to the reaction mixture and the solvent was evaporated under reduced pressure. The resulting powder was applied on a silica gel pad (5 cm thick) and washed with petroleum ether (100 mL). Evaporation of the solvent afforded 1,1-diphenylpropene in excellent yields (0.88 g, 91%, white crystals from methanol, m.p. 48–50°C, Lit.[23] 48–49°C, ^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 1.77 (d, 3H), 6.18 (q, 1H), 7.16–7.36 (m, 10H), ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ: 15.70, 124.14, 126.71, 126.82, 127.19, 128.05, 128.13, 130.05, 140.03, 142.43, 142.96 ppm.

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REFERENCES

1. McKillop, A.; Young, D.W. Synthesis **1979**, 401.
2. Cornelis, A.; Laszlo, P. Synthesis **1985**, 909.
3. Keinan, E.; Mazur, Y. J. Org. Chem. **1978**, *43*, 1020.
4. Tal, D.M.; Keinan, E.; Mazur, Y. Tetrahedron **1981**, *37*, 4327.
5. (a) Onofrio, F.D.; Scettri, A. Synthesis **1985**, 1159; (b) Chavez, F.; Suarez, S.; Diaz, M.A. Synthetic Commun. **1994**, *24*, 2325–2339.
6. Nishiguchi, T.; Kamio, C. J. Chem. Soc. Perkin Trans. I **1989**, 707.

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7. Mohanazadeh, F.; Momeni, A.R.; Ranjbar, Y. Tetrahedron Lett. **1994**, 6127.
8. Firouzabadi, H.; Iranpoor, N.; Karimi, B.; Hazarkhani, H. Synlett **2000**, 263.
9. March, J. *Advanced Organic Chemistry*, 3rd Ed.; Wiley Interscience: New York, 1985; 344–345, 901–902.
10. Hoffman, R.V.; Bishop, R.D.; Fitch, P.M.; Hardenstein, R. J. Org. Chem. **1980**, *45*, 917.
11. Knozinger, H. Synthesis **1968**, 791.
12. Posner, G.H.; Shulman-Roskes, E.M.; Oh, C.h.; Carry, J.C.; Green, J.V.; Clark, A.B.; Dai, H.; Anjeh, T.E.N. Tetrahedron Lett. **1991**, 6489.
13. Runk, C.S.; Haverty, S.M.; Klein, D.A.; McCrea, W.R.; Strobel, E.D.; Klein, D.D. Tetrahedron Lett. **1992**, 2665.
14. Monson, R.S.; Priest, D.N. J. Org. Chem. **1971**, *36*, 3826.
15. Dorta, R.L.; Suarez, E. Tetrahedron Lett. **1994**, 5035.
16. Zhu, Z.; Espenson, J.H. J. Org. Chem. **1996**, *61*, 324.
17. Abdel-Baky, S.; Moussa, A. Synthetic Commun. **1988**, *18*, 1795.
18. Martin, J.C.; Arhart, R.J. J. Am. Chem. Soc. **1971**, *93*, 4327.
19. (a) Firouzabadi, H.; Karimi, B.; Eslami, S. Tetrahedron Lett. **1999**, 58 and the references cited therein; (b) Corey, E.J.; Shimoji, K. Tetrahedron Lett. **1983**, *24*, 169.
20. Laali, D.; Gerzina, R.J.; Flajnik, C.M.; Geric, C.M.; Dombroski, A.M. Helv. Chem. Act. **1987**, *70*, 607 and the references cited therin.
21. Saunders, D.H.; Barford, R.A.; Magidman, P.; Olszewski, L.T.; Rothbart, H.L. Anal. Chem. **1974**, *46*, 834–838.
22. (a) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon **2002**, *177*, 2847–2858; (b) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon **2001**, *176*, 165; (c) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H., Tetrahedron Lett. **2002**, *43*, 7139; (d) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. Phosphorus, Sulfur and Silicon **2003**, *178*, 149–153; (e) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H.; Karimi, B. J. Org. Chem. **2002**, *67*, 2572.
23. Bruson, H.A.; Plant, H.L. J. Org. Chem. **1967**, *32*, 3356–3362.
24. Some spectral data of the isolated olefins:
1a. IR (liquid film): 3080, 3040, 2950, 2900, 2840, 1500, 1460, 1380, 1250, 1080, 1050, 820, 800, 760, 740. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 2.05 (s, 3H), 2.27 (m, 2H), 2.71 (t, 2H), 5.83 (t, 1H), 7.09–7.16 (m, 4H) ppm.
1b. IR (liquid film): 3080, 3040, 2940, 2870, 1480, 1460, 1280, 1040, 770, 740. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.89 (t, 3H), 1.47–1.51

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(m, 4H), 2.24 (m, 2H), 2.39 (m, 2H), 2.68 (t, 2H), 5.82 (t, 1H), 7.11–7.25 (m, 4H) ppm.

1c. IR (liquid film): 3060, 3020, 2980, 2940, 2900, 1620, 1460, 1440, 1400, 1380, 1290, 1110, 1000, 950, 770, 720. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 2.14 (t, 3H), 3.28 (t, 2H), 6.16 (t, 1H), 7.20–7.43 (m, 4H) ppm.

1d. IR (liquid film): 3060, 3030, 2960, 2940, 2880, 1610, 1490, 1460, 1290, 1030, 940, 760, 740. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.98 (t, 3H), 1.43 (m, 2H), 1.66 (m, 2H), 2.52 (t, 2H), 3.26 (d, 2H), 6.13 (t, 1H), 7.12–7.36 (m, 4H). ^{13}C-NMR ($CDCl_3$, 62.89 MHz): δ 13.51, 22.63, 27.34, 30.09, 37.41, 118.73, 123.46, 124.26, 125.57, 127.07, 144.16, 144.51, 145.35 ppm.

1e. IR (liquid film): 3080, 3060, 3040, 1610, 1580, 1490, 1450, 1330, 1070, 1030, 900, 780, 700. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 5.51 (s, 2H), 7.26 (m, 5H) ppm.

1k. IR (liquid film): 3020, 2980, 2920, 1690, 1620, 1450, 1360, 1220, 1170, 970, 760. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.87 (s, 3H), 2.17 (d, 6H), 6.02 (m, 1H). ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ: 27.47, 31.33, 123.98, 154.17, 197.11 ppm.

1l. IR (liquid film): 3100, 3080, 3040, 3000, 2940, 1610, 1500, 1450, 1380, 1270, 1080, 900, 790, 770, 710. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 2.14 (d, 3H), 5.07 (m, 1H), 5.36 (m, 1H), 7.28–7.47 (m, 5H) ppm.

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