

A New Crystal Engineering Approach for the Synthesis of {[K.18-Crown-6]I₃}_n as a Nanotube-Like and Recyclable Catalyst for the Chemoselective Silylation of Alcohols

M.A. Zolfigol^{a,*}, E. Kolvari^a, N. Koukabi^a, S. Salehzadeh^a, G. Chehardoli^b, I.S. Tidmarsh^c and K. Niknam^d

^a*Faculty of Chemistry, Bu-Ali Sina University, P. O. Box 4135, Hamedan 6517838683, Iran*

^b*School of Pharmacy, Hamedan University of Medical Sciences, Hamedan, Iran*

^c*Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK*

^d*Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr 75169, Iran*

(Received 10 July 2010, Accepted 4 October 2010)

Reaction of 18-crown-6 with KI in ethanol solution followed by addition of iodine (I₂) afforded a unique triiodide salt with a nanotube-like structure ([K.18-Crown-6]I₃)_n. It is shown that this reagent may be used for the chemoselective trimethylsilylation of alcohols. The synthesis of the crystalline reagent is a good example of crystal engineering. Reagent was recycled and reused.

Keywords: {[K.18-Crown-6]I₃}_n, 18-Crown-6, Triiodide, Nanotube-like, Silylation of alcohols, Host-guest chemistry

INTRODUCTION

Crown ethers are heterocycles that, in their simplest form, are cyclic oligomers of dioxane and they have attracted significant interest from various fields of science [1]. Crown ether moieties are popular host compounds in host-guest chemistry and corresponding ligands have shown a remarkable ability to form strong complexes with organic and inorganic cations [2-10] or anions [11-12], in a selective manner. Among the crown ethers, 18-crown-6 forms a very stable complex with K⁺ which has a maximum stability constant when combined with other alkali complexes involving metal cations [13-15].

The design of both organic and inorganic structures and being able to organize them in a predicted manner to form tubular structures is also an area of great active interest. The idea is to assemble well-established paradigms of crystal engineering and supramolecular chemistry nanospaces of suitable dimension to carry out host-guest chemistry,

reversible binding of smaller species for storage purposes [16], crystal packing control over molecular structure [17], or to use them for rational development of novel predictable bulk structure with special properties [18]. Recently, nanotubes and nanoribbons have been synthesized *via* supramolecular assembly [19] or by self-assembly of suitable ligands [20]. Various organic triiodides (OTIs) [21-28] and polyiodides (OPIs) [29-34] have been reported.

Following our studies of the host-guest chemistry of crown ether **1** [35-39], nitrosation of azacrown ethers **2** [40-43] (Fig. 1) and the synthesis of the unique tribromide reagent **3** [44], we now report the synthesis and application of a triiodide salt with a nanotube-like structure ([K.18-Crown-6]I₃)_n **4**.

EXPERIMENTAL

General

Chemicals were purchased from Merck. Substrates, Silylated products were characterized by comparison of their spectral (IR, UV, ¹H NMR and ¹³C NMR) and physical data with those of known samples.

*Corresponding author. E-mail: zolfi@basu.ac.ir

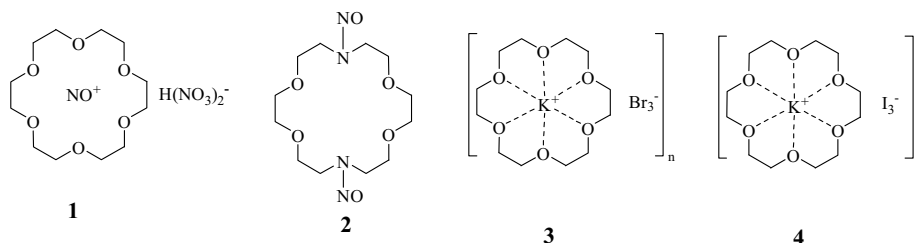


Fig. 1. Some microcycle structures.

Preparation of {[K.18-Crown-6]I₃}_n

In a round-bottomed flask (100 ml) equipped with a magnetic stirrer, KI (1.32 g, 8 mmol) was added to a solution of 18-crown-6 (1.32 g, 5 mmol) in ethanol (30 ml) and the mixture was stirred for 1 h, then filtered. Iodine (1.27 g, 5 mmol) was added to the solution. After filtration over a sintered glass funnel, a fine dark brown powder was obtained and recrystallized from CH₃CN to give dark brown crystals [m.p.: 207-210 °C].

General Procedure for the Trimethylsilylation of Alcohols

To a solution of the alcohol (1 mmol) in CH₂Cl₂ (4 ml), HMDS (0.8 mmol) and {[K.18-Crown-6]I₃}_n **4** (0.1 mmol) were added. The solution was vigorously stirred at room temperature. After completion of the reaction, dichloromethane was removed by water-bath distillation. The residue was dissolved in *n*-hexane (5 ml) and filtered off. The filtrate was washed with *n*-hexane (2 × 10 ml). *n*-Hexane was removed by distillation to yield pure products.

General Procedure for Deprotection of Trimethylsilyl Ethers Catalyzed by {[K.18-Crown-6]I₃}_n

{[K.18-Crown-6]I₃}_n (0.1 mmol) was added to a mixture of TMS ethers (1 mmol) in CH₂Cl₂ (4 ml) moistened by three drops of water and then the mixture was stirred at room temperature for the specified time (see Table 5). The progress of the reaction was monitored by TLC. On completion of the reaction, column chromatography on short pad of silica gel afforded pure products.

Experimental Description of Structure

An orange crystal (0.40 × 0.20 × 0.10 mm³) was mounted on a Bruker SMART-1000 diffractometer. Crystal data:

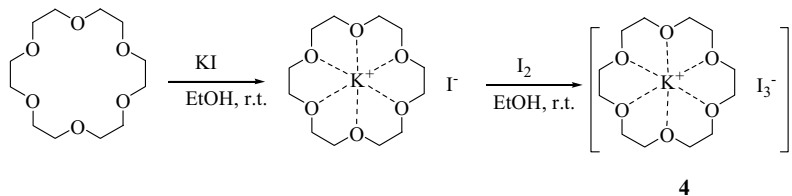
C₁₂H₂₄I₃KO₆, *M* = 684.11, monoclinic, space group *Cc*, *a* = 8.381(11), *b* = 14.973(19), *c* = 17.322(2) Å, β = 98.612(2)°, *V* = 2149.2(5) Å³, *Z* = 4, *D_c* = 2.114 mg m⁻³, μ (Mo-Kα) = 4.576 mm⁻¹, *T* = 150 K. Refinement of 199 parameters with 4408 unique reflections afforded a final *R*1 value [for selected data with *I* > 2σ(*I*)] of 3.09% and a final *wR*2 value (all data) of 5.01%.

RESULTS AND DISCUSSION

The crystalline reagent with a nanotube-like structure was made through the packing of [K.18-Crown-6]⁺ cations- and bridging symmetrical multi nuclear linear anions. We found that the reaction of I₂ with complex [K.18-Crown-6]I, easily produces the triiodide reagent **4** (Scheme 1). Recrystallization of the latter compound in acetonitrile gave brownish crystals, suitable for X-ray crystallography (Fig. 2).

Crystallographic analysis confirmed the formulation of these crystals as {[K.18-Crown-6]I₃}_n, in which the [K.18-Crown-6]⁺ cations are aligned in columnar stacks separated by bridging triiodide anions (Figs. 3, 4). Each triiodide ligand interacts with two K⁺ ions, although the coordination is far from linear, with I-I-K angles of 83.1°. The latter bond angle is very similar to the corresponding Br-Br-K angle, 83.2°, in the {[K.18-Crown-6]Br₃}_n [44]. Thus, the columnar stacks are infinite one-dimensional polymeric chains of alternating cations and anions. This is in close agreements with the reported crystallographic data by Bock *et al.* [45]. The coordination geometry in the [K.18-crown-6]⁺ cation is unremarkable.

To the best of our knowledge, silylation of alcohols and polyols is one of the simplest methods used for their protection [46]. Trimethylsilylation is a classic way to produce volatile derivatives of alcohols and polyols, as required for their vapor



Scheme 1. Schematic synthesis of {[K.18-Crown-6]I₃}_n (**4**)



Fig. 2. Crystals of (**4**).

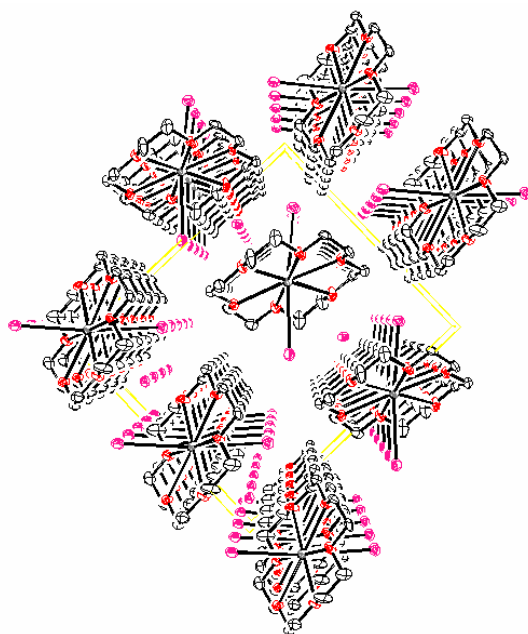


Fig. 3. X-Ray structure of {[K.18-Crown-6]I₃}_n (**4**).

phase chromatography/mass spectrometry analysis [47]. Another application is conversion of trimethylsilyl ethers into the corresponding ethers [48], so that the described procedure due to its special ability has been selected by the American Chemical Society (ACS) as heart-cut [49]. Generally, the formation of trimethylsilyl ethers has been carried out by treatment of alcohols with trimethylsilyl chloride or trimethylsilyl triflate in the presence of base [50], Li₂S [51], and sometimes a nonionic super base catalyst [52]. However, some of those methods have frequently suffered from drawbacks, such as a lack of reactivity or the difficulty in removal of amine salts derived from the reaction of by-produced acid and co-bases during the silylation reaction. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a stable, commercially available, and cheap reagent for trimethylsilylation of hydrogen-labile substrates [53], giving ammonia as the only by-product.

On the other hand, silylation, using this silazan-type reagent, is nearly neutral and does not need any special precautions. However, the low silylating power of HMDS is the main drawback for its application which needs forceful conditions and long reaction times etc. A variety of catalysts such as (CH₃)₃SiCl [54], silica chloride [55], ZnCl₂ [56], zirconium sulfophenyl phosphonate [57], LiClO₄ [58], K-10 montmorillonite [59], H-β zeolite [60], tungstophosphoric acid [61], poly(*N*-bromobenzene-1,3-disulfonamide) [62], CuSO₄·5H₂O and Cu(OTf)₂ [63], MgBr₂·OEt₂ [64], iodine [65], Al(HSO₄)₃ [66], KBr [67], Al(OTf)₃ [68], magnesium triflate [69], silica supported perchloric acid [70], sulfonic acid-functionalized ordered nanoporous silica [71], trichloroisocyanuric acid [72] and 1,3-dibromo-5,5-diethylbarbituric acid [73] have been reported for the silylation of hydroxyl groups using HMDS [54-73]. However, in most of these cases a long reaction time, drastic reaction conditions, and the use of hazardous solvents or tedious work-up are

needed. In addition, many of these reagents are moisture sensitive or expensive.

The lack of a facile and general synthetic methodology for the silylation of alcohols, under essentially neutral conditions, promoted us to develop an efficient procedure for the protection of hydroxyl groups using $\{[K.18\text{-Crown-6}]I_3\}_n$ as a novel and recyclable catalyst for this purpose. Herein we wish to report the first application of $\{[K.18\text{-Crown-6}]I_3\}_n$ as an excellent and recyclable catalyst for the chemoselective trimethylsilylation of various alcohols without observation any side products (Scheme 2).

Firstly, we investigated the effect of various solvents on

the progress of reactions. As illustrated in the Table 1, we have found that dichloromethane is the best solvent for the above mentioned reactions due to fast reaction times and high yields.

The trimethylsilylation of hydroxyl groups is easily carried out at room temperature under mild conditions. A good range of alcohols were subjected to the trimethylsilylation in the presence of a catalytic amount of $\{[K.18\text{-Crown-6}]I_3\}_n$ as an efficient catalyst and HMDS as a silylating system. The corresponding trimethylsilyl ethers were obtained in good to excellent yields under mild and homogeneous conditions (Table 2 and Scheme 2).

Table 1. Silylation of Benzyl Alcohol with HMDS in the Presence of $\{[K.18\text{-Crown-6}]I_3\}_n$ (**4**), as a Catalyst at Room Temperature in Various Solvents

Entry	Solvent ^a	Substrate		Time (h:min)	Yield (%) ^b
		HMDS	Catalyst		
1	<i>n</i> -Hexane	0.8	0.1	06:00	65
2	Dichloromethane	0.8	0.1	00:15	100
3	Chloroform	0.8	0.1	00:50	95
4	Ethyl acetate	0.8	0.1	03:00	100
5	Diethyl ether	0.8	0.1	06:00	85
6	Acetonitrile	0.8	0.1	00:20	100
7	CCl ₄	0.8	0.1	6:00	92

^aThe amount of solvent was chosen 2 ml. ^bGC yields.

Table 2. Silylation of Alcohols (1 mmol), with HMDS (0.8 mmol) in the Presence of (**4**), as a Catalyst (0.1 mmol) at Room Temperature

Entry	Substrate	Product	Time (h:min)	Yield (%) ^a
1			00:16	100
2			00:12	100
3			00:20	100
4			00:37	100
5			00:10	100

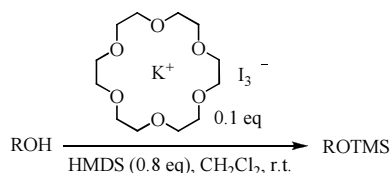
Table 2. Continued

6			00:35	100
7			00:20	100
8			00:15	100
9			00:15	100
10			01:30	100
11			00:15	100
12			00:16	100
13			00:25	100
14			00:22	100
15			3:25	100
16			00:40	100
17			01:15	95 ^b
18			00:15	100
19			00:25	100
20			1:30	100
21			09:00	74 ^b

^aGC Yield. ^bIsolated yield.

To investigate the recyclability of the [K.18-Crown-6]I₃, the residue after work-up was washed with *n*-hexane and the brown solid was obtained. {[K.18-Crown-6]I₃}_n was recycled and reused for the silylation of alcohols successfully (Table 3).

In order to investigate the selectivity of the catalyst, various reactions have been carried out using different types of alcohols and other functional groups (Table 4). The catalyst shows good selectivity for 1° alcohols in the presence of 2°



Scheme 2. Silylation of alcohols in the presence of {[K.18-Crown-6]I₃}_n (**4**), as catalyst

Table 3. Silylation of Alcohols (1 mmol), with HMDS (0.8 mmol) in the Presence of Recovered {[K.18-Crown-6]I₃}_n (**4**), as a Catalyst (0.1 mmol) at Room Temperature

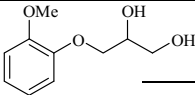
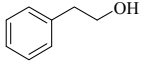
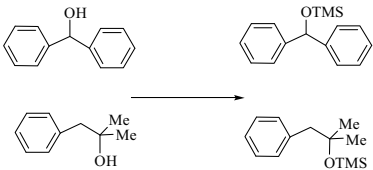
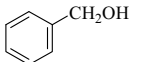
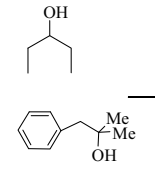

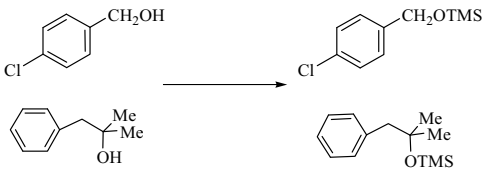

Entry	Substrate	Product	Run 1		Run 2	
			(h:min)	Yield (%) ^a	(h:min)	Yield (%) ^a
1			00:45	100	01:20	100
2			00:25	100	00:20	100
3			01:35	100	06:00	60
4			00:33	100	06:00	84
5			00:20	100	06:00	90

^aGC Yield.

Table 4. Selective *O*-Trimethylsilylation of Alcohols in the Presence of HMDS and (**4**) as Catalyst at Room Temperature^a

Entry	Substrate	Product binary mixture	Time (h:min)	Yield (%) ^b
1			00:30	100
				0
2			00:35	100
				0

Table 4. Continued

3		Mix of Products	2:00	-
4		100	00:40	0
5		100	00:20	0
6		100	00:15	0
7		100	00:30	0
8		90	00:25	10
9		100	00:15	0
10		100	00:25	0

^aMolar ratio, substrate 1/substrate 2/HMDS/catalyst: 1/1/0.8/0.1; ^bGC yields.

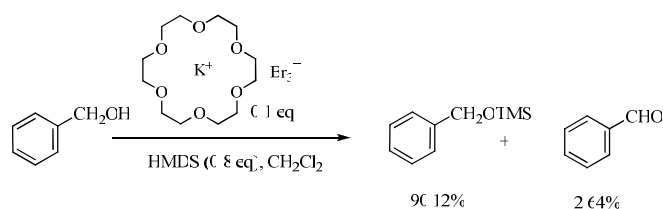
and 3° alcohols. The amines will mainly remain intact in the presence of alcohols under silylation conditions (Table 4, entry 6). Interestingly we found that 2-thionaphthol is converted to 2-naphthyl disulfide under silylation condition in the presence of benzyl alcohol, so no silylated product was observed (Table 4, entry 11).

We also decided to use {[K.18-Crown-6]Br₃}_n for the silylation of alcohols but the reaction was not applicable for this purpose due to the side product and oxidation of alcohols (Scheme 3).

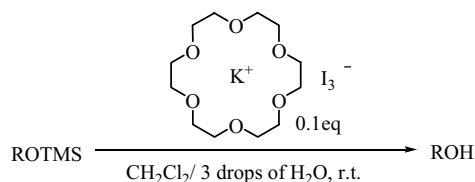
In addition, we investigated the possibility of deprotection of trimethylsilyl ethers using (4) as a catalyst in wet dichloromethane (Scheme 4). We successfully converted selected TMS ethers to the parent hydroxyl compounds in the presence of catalytic amount of {[K.18-Crown-6]I₃}_n at room temperature. The results are summarized in Table 5.

The following mechanism for the silylation reaction may be suggested, according to the previously reported reagents [44,65] and the obtained results (Scheme 5).

In conclusion, the mildness and recycle ability of {[K.18-



Scheme 3. Silylation of benzyl alcohol in the presence of {[K.18-Crown-6]Br₃}_n (3), as a catalyst

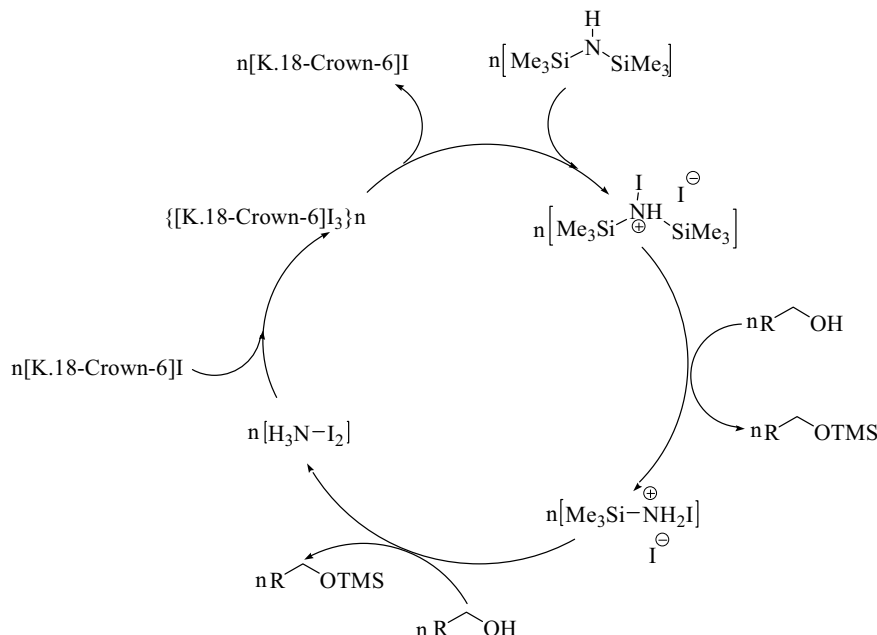


Scheme 4. Desilylation of benzyloxytrimethylsilane in the presence of {[K.18-Crown-6]I₃}_n (4), as catalyst

Table 5. Deprotection of Trimethylsilyl Ethers (1 mmol) in the Presence of Catalytic Amount of (4) as Catalyst in CH₂Cl₂ (5 ml) Moistened by 3 Drops of Water at Room Temperature

Entry	Substrate	Product	Time (h:min)	Yield(%) ^a
1			00:20	100
2			00:40	100
3			00:25	100
4			00:35	100
5			00:18	100

^aGC Yield.



Scheme 5. A reasonable mechanism for the silylation reaction with [K.18-Crown-6]I₃

Crown-6]I₃]_n is the major advantage of the described nano-tube like reagent making it an attractive and useful reagent for organic functional group transformations [77-79].

ACKNOWLEDGMENTS

Financial support of this work by the Research Deputy of Ministry of Science, Research and Technology of I.R. Iran, Center of Excellence in Development of Chemical Methods (CEDCM) of Bu-Ali Sina University, Hamedan, Iran, and Professor Michael D. Ward for supporting the X-ray crystallography structure from the University of Sheffield, Sheffield, S3 7HF, UK, is gratefully acknowledged.

REFERENCES

- [1] G.W. Gokel, W.M. Leevy, M.E. Weber, Chem. Rev. 104 (2004) 2723.
- [2] Z.B. Huang, S.H. Chang, Synlett (2005) 1703.
- [3] Z.B. Huang, S.H. Chang, Synlett (2005) 2257.
- [4] Z.B. Huang, T.J. Kang, S.H. Chang, Tetrahedron Lett. 46 (2005) 3461.
- [5] Z.B. Huang, S.H. Kim, S.H. Chang, Synlett (2006) 1707.
- [6] Z.B. Huang, S.H. Chang, Tetrahedron Lett. 46 (2005) 5351.
- [7] Z.B. Huang, S.H. Kim, S.H. Chang, Bull. Korean Chem. Soc. 27 (2006) 893.
- [8] Z.B. Huang, S.H. Chang, J. Inclus. Phenomen. Marocycl. Chem. (2006) 341.
- [9] Z.B. Huang, T.J. Kang, S.H. Chang, New. J. Chem. 29 (2005) 1616.
- [10] J.C.W. Gray, K. Barry, E.J. Lindberg, T.A. Houston, Tetrahedron Lett. 48 (2007) 2683.
- [11] L.F. Lindoy, J. Iran. Chem. Soc. 1 (2004) 1.
- [12] J. Hua, Y.G. Wang, Chem. Lett. 34 (2005) 98.
- [13] R.M. Izatt, K. Pawlak, J.S. Bradshaw, Chem. Rev. 91 (1991) 1721.
- [14] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, Chem. Rev. 85 (1985) 271.
- [15] D. Braga, M. Polito, E. Dichiaranti, K. Rubini, F. Grepioni, Chem. Commun. (2007) 1594.
- [16] D. Pasini, M. Ricci, Curr. Org. Chem. 4 (2007) 59.
- [17] J.W. Steed, E. Sakellariou, P.C. Junk, M.K. Smith,

- Chem. Eur. J. 7 (2001) 1240.
- [18] V.V. Ponomarova, K.V. Domasevitch, *Crystal Engineering* 5 (2002) 137.
- [19] Y. Luo, H. Liu, F. Xi, L. Li, X. Jin, C.C. Han, C. Chan, *J. Am. Chem. Soc.* 125 (2003) 6014.
- [20] Y. Cui, S.J. Lee, W. Lin, *J. Am. Chem. Soc.* 125 (2003) 6447.
- [21] I. Tornieporthoetting, T. Kalapotke, *Ang. Chem. It. Ed. Eng.* 29 (1990) 677.
- [22] D.J. Tudela, *Chem. Edu.* 79 (2002) 558.
- [23] A.J. Blake, R.O. Gould, S. Parsons, C. Radek, M. Schroder, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* 52 (1996) 24.
- [24] C. Walbaum, I. Pantenburg, G. Meyer, *Z. Anorg. Allg. Chem.* 633 (2007) 1609.
- [25] A.N. Chekhlov, *Russ. J. Coord. Chem.* 30 (2004) 8.
- [26] C. Runschke, G. Meyer, *Z. Anorg. Allg. Chem.* 623 (1997) 1493.
- [27] A.K. Nurtaeva, G. Hu, E.M. Holt, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* 54 (1998) 594.
- [28] K.F. Tebbe, M. Elessawi, S.A. Elkhaliq, *Z. Anorg. Allg. Chem.* 50 (1995) 1429.
- [29] I. Pantenburg, I. Muller, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* 59 (2003) M 427.
- [30] I. Pantenburg, K. Tebbe, *Z. Anorg. Allg. Chem.* 628 (2002) 1780.
- [31] L. Kloo, P.H. Svensson, M.J. Taylor, *J. Chem. Soc. Dalton Trans.* (2000) 1066.
- [32] C.C. Hines, C.B. Bauer, R.D. Rogers, *New J. Chem.* 31 (2007) 762.
- [33] P.H. Svensson, L. Kloo, *Chem. Rev.* 103 (2003) 1649, and references cited therein.
- [34] H. Chown, P.A.W. Dean, D.C. Craig, N.T. Lucas, M.L. Scudder, *New J. Chem.* 27 (2003) 704.
- [35] M.A. Zolfigol, A. Ghorbani-Choghamarani, H. Hazarkhani, *Synlett* (2002) 1002.
- [36] M.A. Zolfigol, A. Bamoniri, *Synlett* (2002) 1621.
- [37] M.A. Zolfigol, D. Habibi, B.F. Mirjalili, A. Bamoniri, *Tetrahedron Lett.* 44 (2003) 3345.
- [38] M.A. Zolfigol, K. Niknam, F. Nazari, *J. Chin. Chem. Soc.* 53 (2006) 669.
- [39] K. Niknam, M.A. Zolfigol, *J. Iran. Chem. Soc.* 3 (2006) 59.
- [40] M.A. Zolfigol, M.H. Zebarjadian, G. Chehardoli, H. Keypour, S. Salehzadeh, M. Shamsipur, *J. Org. Chem.* 66 (2001) 3619.
- [41] M.A. Zolfigol, M.H. Zebarjadian, G. Chehardoli, S.E. Mallakpour, M. Shamsipur, *Tetrahedron* 57 (2001) 1627.
- [42] M.A. Zolfigol, M.H. Zebarjadian, M.M. Sadeghi, I. Mohammadpoor-Baltork, H.R. Memarian, M. Shamsipur, *Synth. Commun.* 31 (2001) 929.
- [43] M.A. Zolfigol, M.H. Zebarjadian, I. Mohammadpoor-Baltork, M. Shamsipur, *Synth. Commun.* 32 (2002) 2803.
- [44] M.A. Zolfigol, G. Chehardoli, S. Salehzadeh, H. Adams, M.D. Ward, *Tetrahedron Lett.* 48 (2007) 7969.
- [45] M. Sievert, V. Krenzel, H.Z. Bock, *Kristallogr.* 211 (1996) 794.
- [46] T.W. Green, P.G.M. Wuts, *Protective Groups in Organic Synthesis*, 3th ed., Wiley, New York, 1999.
- [47] G. Van Look, G. Simchen, J. Heberle, *Silylating Agents*, 2th ed., Fluka, Buches, Switzerland, 1995.
- [48] M.A. Zolfigol, I. Mohammadpoor-Baltork, D. Habibi, B.F. Mirjalili, A. Bamoniri, *Tetrahedron Lett.* 44 (2003) 8165.
- [49] See: <http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=heartcut>.
- [50] E.J. Corey, B.B. Sinder, *J. Am. Chem. Soc.* 94 (1972) 2549.
- [51] G.A. Olah, B.G.B. Gupta, S.C. Narang, R. Malhotra, *J. Org. Chem.* 44 (1979) 4272.
- [52] B.A.D. Sa, D. McLeod, J.G. Verkade, *J. Org. Chem.* 62 (1997) 5057.
- [53] M. Lalonde, T.H. Chan, *Synthesis* (1985) 817.
- [54] P. Gauttret, S. El-Ghamarti, A. Legrand, D. Coutrier, B. Rigo, *Synth. Commun.* 26 (1996) 707.
- [55] F. Shirini, M.A. Zolfigol, K. Mohammadi, *Phosphorus Sulfur, and Silicon* 178 (2003) 1567.
- [56] H. Firouzabadi, A.R. Sardarian, Z. Khayat, B. Karimi, S. Tangestaninejad, *Synth. Commun.* 27 (1997) 2709.
- [57] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, U. Constantino, *Synth. Commun.* 29 (1999) 541.
- [58] N. Azizi, R. Yousefi, M.R. Saidi, *J. Organomet. Chem.* 691 (2006) 817.
- [59] Z.H. Zhang, T.S. Li, F. Yang, C.G. Fu, *Synth.*

- Commun. 28 (1998) 3105.
- [60] V.H. Tillu, V.H. Jadhav, H.B. Borate, R.D. Wakharkar, *Arkivoc* (2004) 83.
- [61] H. Firouzabadi, N. Iranpoor, K. Amani, F. Nowrouzi, J. Chem. Soc., *Perkin Trans. 1* (2002) 2601.
- [62] R. Ghorbani-Vaghei, M.A. Zolfigol, M. Chegeny, H. Veisi, *Tetrahedron Lett.* 47 (2006) 4505.
- [63] B. Akhlaghinia, S. Tavakoli, *Synthesis* (2005) 1775.
- [64] M.M. Mojtahedi, H. Abbasi, M.S. Abaee, *J. Mol. Catal. A: Chem.* 250 (2006) 6.
- [65] B. Karimi, B. Golshani, *J. Org. Chem.* 65 (2000) 7228.
- [66] F. Shirini, M.A. Zolfigol, M. Abedini, *Bull. Chem. Soc. Jpn.* 78 (2005) 1982.
- [67] F. Shirini, E. Mollarazi, *Synth. Commun.* 36 (2006) 1109.
- [68] H. Firouzabadi, N. Iranpoor, S. Sobhani, S. Ghassamipour, *Synthesis* (2005) 595.
- [69] H. Firouzabadi, N. Iranpoor, S. Sobhani, S. Ghassamipour, *J. Organomet. Chem.* 689 (2004) 3197.
- [70] H.R. Shaterian, F. Shahrekipoor, M. Ghashang, *J. Mol. Catal. A: Chem.* 272 (2007) 142.
- [71] D. Zareyee, B. Karimi, *Tetrahedron Lett.* 48 (2007) 1277.
- [72] A. Khazaei, M.A. Zolfigol, A. Rostami, A. Ghorbani Choghamarani, *Catal. Commun.* 8 (2007) 543.
- [73] A. Khazaei, M.A. Zolfigol, Z. Tanbakouchian, M. Shiri, K. Niknam, J. Saïen, *Catal. Commun.* 8 (2007) 917.
- [74] M.A. Zolfigol, F. Shirini, G. Chehardoli, E. Kolvari, *J. Mol. Catal. A: Chem.* 265 (2006) 271.
- [75] M.A. Zolfigol, F. Shirini, A.G. Choghamarani, *Synthesis* 12 (2006) 2043.
- [76] M.A. Zolfigol, M. Bagherzadeh, S. Mallakpour, G. Chehardoli, A. Ghorbani-Choghamarani, N. Koukabi, M. Dehghanian, M. Doroudgar, *J. Mol. Catal. A: Chem.* 270 (2007) 219.
- [77] P. Salehi, M.A. Zolfigol, F. Shirini, M. Baghbanzadeh, *Curr. Org. Chem.* 10 (2006) 2171.
- [78] E. Kolvari, A. Ghorbani-Chghamarani, P. Salehi, F. Shirini, M.A. Zolfigol, *J. Iran. Chem. Soc.* 4 (2007) 126.
- [79] F. Shirini, M.A. Zolfigol, P. Salehi, M. Abedini, *Curr. Org. Chem.* 12 (2008) 183.