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$[H_2$-Cryptand 222$]^{2+}(Br_3^-)_2$ as a Tribromide-Type Catalyst for the Trimethylsilylation/Tetrahydropyranylation of Alcohols

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ABSTRACT

A stable organic tribromide, $[H_2$-cryptand 222$]^{2+}(Br_3^-)_2$ was utilized as an active catalyst for the trimethylsilylation/tetrahydropyranylation of alcohols. The method is general for the preparation of OH-protected aliphatic (acyclic and cyclic), aromatic, primary, secondary and tertiary alcohols.

KEYWORDS

$[H_2$-cryptand 222$]^{2+}(Br_3^-)_2$, trimethylsilylation, tetrahydropyranylation, alcohols, tribromide, TMS-ether, THP-ether.

1. Introduction

Crown ethers have attracted significant attention from various fields of science. Crown ether moieties are popular host compounds in host–guest chemistry and these ligands have shown a remarkable ability to form strong complexes with organic and inorganic cations[1] or anions[2]. Among the crown ethers, cryptand 222 as a macrobicyclic compound has a variety of applications such as: formation of conductometric mercury [II] sensor based on poly aniline,[3] encapsulation of alkali metal especially K^+,[4] acceptor ligand for the formation of complexes containing 7,7,8,8-teracyanoquinodimethane (TCNQ),[5] extraction of uranium(VI),[6] exchanging cations of micas[7] and extraction of copper(II) with erythrosine B.[8]

Organic tribromide reagents (OTBs) are preferable as oxidants to molecular bromine, owing to the hazards associated with elemental bromine. Several tribromides have been reported, i.e. tetramethylammonium tribromide,[9] phenyltrimethylammonium tribromide,[10] cetyltrimethylammonium tribromide, tetrabutylammonium trihromide,[11] 1,8-diazabicyclo[5,4,0]-tetrabutylammonium tribromide,[12] pyridine hydrobromide perbromide,[13] hexamethylenetetramine-bromine[14] and *1,4-diazabicyclo[2.2.2]octane* (DABCO)-bromine.[15] Also, some ionic liquid tribromides (IL-Br_3^-), for the preparation of bromoesters from aromatic aldehydes[16] and bromination of aromatic substrates,[17] were reported.

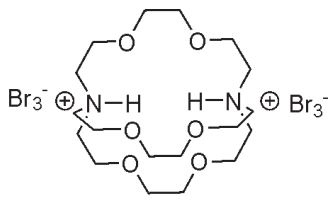
Recently, we reported $\{[K.18\text{-crown-}6]Br_3\}_n$ as a unique tribromide type with a columnar nanotube-like structure.[18]

We concluded that it would be extremely useful to develop further synthetic protocols for the synthesis of OTBs.[19]

Trimethylsilylation and tetrahydropyranylation are popular methods widely used for the protection of the hydroxyl group.[20] Among the many silylating agents which have been used for the silylation of alcohols, hexamethyldisilazane (HMDS), a cheap, stable and commercially available reagent,[21] is selected as one of the best candidates for this purpose. Its handling does not need special precaution, and the work-up is not time-consuming, as the by-product of the reaction is ammonia, which is simple to remove from the reaction medium. However, its poor silylating power is the main drawback of its application.[22] A variety of catalysts have been used for the activation of HMDS;[23] however, low selectivity, forcing conditions, tedious work-ups and long reaction times have been described in many of these reports. Consequently, a new procedure that addresses these drawbacks is desirable.

Also, due to the remarkable stability of tetrahydropyranyl ethers (THP-ethers) towards a variety of reaction conditions such as strongly basic media, reactions involving Grignard reagents and lithium alkyls, reduction with hydride, oxidation, oxidative alkylation and acylation reactions, and due to its low cost and ease with which it can be removed, 3,4-dihydro-2*H*-pyran (DHP) is the reagent of choice for hydroxyl group protection in multi-step organic synthesis.[24] Although, there are several reagents available for the tetrahydropyranylation of alcohols,[25] many of these methods are associated with several drawbacks, which include use of strongly acidic media, expensive reagents, tedious and time-consuming work-up procedures, refluxing conditions, long reaction times, poor selectivity, formation of polymeric by-products of the dihydropyran and isomerization. Thus there is still a need for mild and selective methods, especially using heterogeneous catalysts for this purpose.

In continuation of our studies on the host-guest chemistry of crown ethers,[26] synthesis and application of trihalides reagents[18,27] and based on our experiences on the protection of some organic functional groups,[28] herein we report that $[H_2$-cryptand 222$]^{2+}(Br_3^-)_2$[27,29] (**I**) can be used as an excellent catalyst for the selective trimethylsilylation and tetrahydropyranylation of alcohols.



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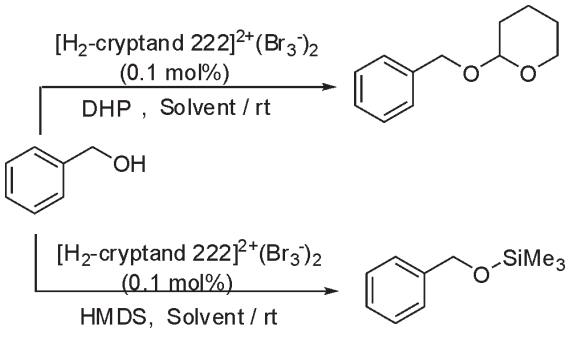


Scheme 1

Table 1 Compared performances of various solvents in the trimethylsilylation (**A**) and tetrahydropyranylation (**B**) of benzyl alcohol at room temperature.

Entry	Solvent	Time		Yields/%	
		A/min	B/min	A	B
1	CH_3CN	4	80	80	75
2	$CHCl_3$	240	360	70	50
3	$CHCl_3/CH_3CN$ (4/1)	30	180	60	60
4	CH_2Cl_2	120	390	75	50
5	CH_2Cl_2/CH_3CN (4/1)	20	390	70	60
6	*n*-Hexane	120	600	50	50
7	*n*-Hexane/CH_3CN (4/1)	40	480	55	65
8	Acetone	120	300	–	–
9	1,4-Dioxane	30	300	65	60
10	EtOAC	20	300	30	65

2. Results and Discussion

We initially studied the conversion of benzyl alcohol (1 mmol) to its corresponding TMS-ether or THP-ether derivative using the $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ catalyst (0.001 mmol) and HMDS (1.5 mmol)/DHP (1 mmol) in a variety of solvents at room temperature (Table 1). The results show that acetonitrile is the best solvent in terms of time and product yield (Scheme 1).

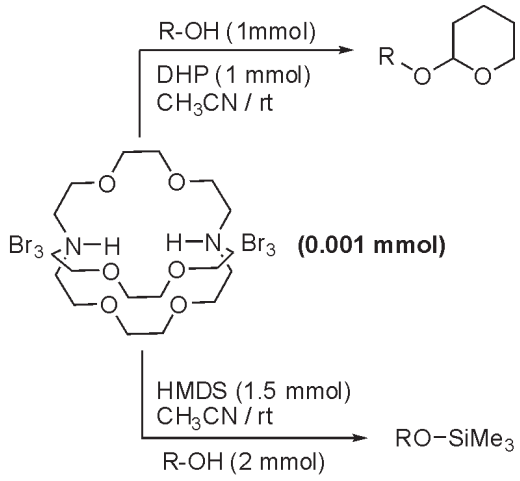
We then prepared a range of TMS or THP-ethers under the following reaction conditions: alcohol (2 mmol), HMDS (1.5 mmol), $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ (0.001 mmol) and acetonitrile (4 mL). Also, the condition for tetrahydropyranylation reaction is: alcohol (1 mmol), DHP (1 mmol), $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ (0.001 mmol) and acetonitrile (4 mL) (Scheme 2, Table 2).

A wide range of various alcohols undergo trimethylsilylation and tetrahydropyranylation using this procedure to provide the corresponding TMS-ethers and THP-ethers in moderate to excellent yields.

We also applied our new reaction protocols for the protection of some new alcohols (Table 2, entries 13-b, 18-b, 19-b, 32-b and 33-b). Spectral and physical data for the obtained products are in close agreement with their structures.

According to the previously reported papers[18,27,28] and the obtained results, the following mechanism for the trimethylsilylation and tetrahydropyranylation may be suggested in which the catalytic role of $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ (as a Br^+ source) in a catalytic cycle are clarified.

For tetrahydropyranylation, the Br_3^- reacts with alcohol to form ROBr species and HBr. Then tetrahydropyran reacts with HBr to form tetrahydropyrylium bromide. The tetrahydropyrylium bromide further reacts with ROH to form THP-ether and HBr. Resulted HBr in the presence of dihydropyran (DHP)

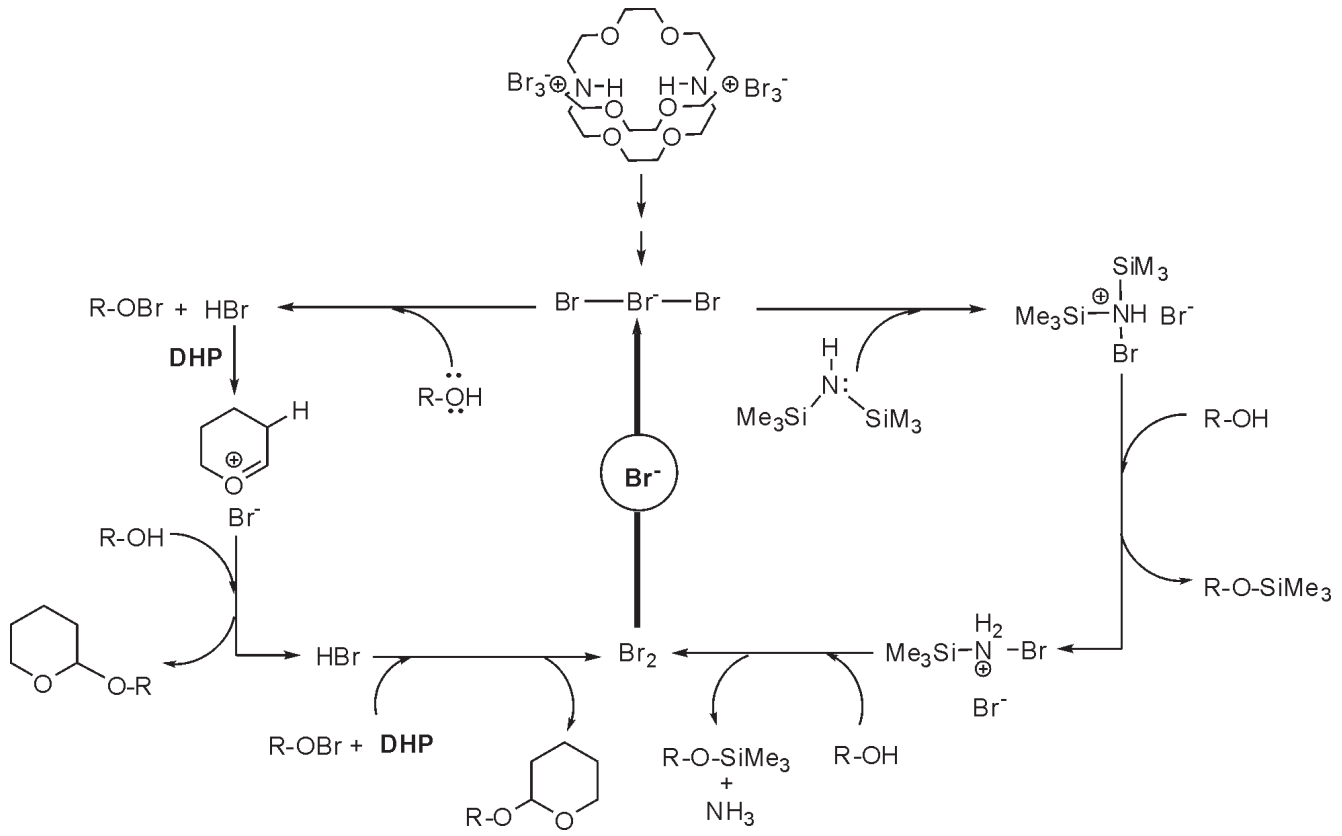


Scheme 2

Table 2 Protection of alcohols with HMDS (**A**) or DHP (**B**) using $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ as catalyst in acetonitrile at room temperature under mild conditions.

Entry	ROH	Time		Yields/%	
		A/min	B/min	A	B
1	2-Phenylethanol	5	180	81	98
2	Benzyl alcohol	60	120	–[c]	–[c]
3	Benzyl alcohol	4	80	75	80
4	Diphenylmethanol	2	120	76	95
5	(4-Chlorophenyl)methanol	3	120	89	85
6	5-Isopropyl-2-methylcyclohexanol	1	210	81	79
7	1-Adamantanol	25	300	82	68
8	2-Adamantanol	5	180	90	70
9	Heptan-1-Ol	2	45	55	88
10	Cyclododecanol	5	100	92	95
11	Cyclohexanol	1	60	55	65
12	1-Indanol	60	120	–[c]	–[c]
13	1-Indanol	2	60	89	91
14	(2,4-Dichlorophenyl) methanol	3	180	70	85
15	2-(4-Methylcyclohex-3-enyl)propan-2-ol	360	180	91	–[d]
16	2-Phenylpropan-1-ol	1	60	80	95
17	(4-Methoxyphenyl)methanol	2	60	92	95
18	3-Methylpent-1-yn-3-ol	15	240	50	32
19	2-Methyl-1-phenylpropan-2-ol	120	240	78	75
20	Cholesterol	15	240	95	–[d]
21	5-Phenylpentan-1-ol	3	300	97	98
22	1-Phenylethanol	5	360	60	75
23	1-Cyclohexylethanol	4	25	90	86
24	(4-Fluorophenyl)methanol	1	150	86	89
25	(4-Nitrophenyl)methanol	5	120	NR	80
26	Tetra hydroxymethyl methane	15	120	–[d]	–[d]
27	Thiophen-2-ylmethanol	5	240	–[d]	–[d]
28	Furan-2-ylmethanol	1	240	60	55
29	2,2′-(Phenylazanediyl)diethanol	5	240	–[d]	–[d]
30	Pyridin-2-ylmethanol	5	240	–[d]	–[d]
31	3-Phenylprop-2-en-1-ol	5	240	–[d]	–[d]
32	4-Chloro-2,6-dimethanolphenol	6	60	90	80
33	4-Bromo-2,6-dimethanolphenol	7	180	87	76
34	Phenol	3	60	–	–
35	2,6-Dimethoxyphenol	3	60	–	–

[c] Reaction in the absence of catalyst.
[d] Undesired product.



Scheme 3

Suggested mechanism for trimethylsilylation and tetrahydropyranylation of alcohols in the presence of a catalytic amount of $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$.

and ROBr generates THP-ether and Br_2. For trimethylsilylation, the Br_3^- reacts with HMDS and then two molecules of ROH to generate two molecules of TMS-ether and Br_2. In two routs, the generated Br_2 reacts with Br^- to regenerate Br_3^- (Scheme 3, right side for trimethylsilylation and left side for tetrahydropyranylation).

3. Chemoselectivity

In order to establish the scope of $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ in the chemoselective TMS- or THP-protection of alcohols in the presence of phenolic hydroxyl group, we reacted 4-bromo- and 4-chloro-2,6-dimethanolphenol with the HMDS and DHP (Table 2, entries 33, 34) at room temperature using 0.1 mol % of $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ under reaction condition. As seen in Scheme 4, alcoholic -OH has been protected and phenolic -OH remained intact during the protection reaction (Scheme 4).

4. Experimental

4.1. General

Chemicals were purchased from Merck. OH-protected products were characterized by comparison of their spectral (IR, ^{1}H-NMR and ^{13}C-NMR) and physical data with those of known samples.[23,25]

4.2. Preparation of $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$

In a round-bottomed flask (100 mL) equipped with a magnetic stirrer, bromine (0.494 g, 3.1 mmol) was added to a solution of cryptand 222 (0.376 g, 1 mmol) in ethanol (30 mL) and the mixture was stirred for 0.5 hour, and then filtered by sintered glass. After filtration, a fine yellow powder was obtained and recrystallized from CH_3CN to give red crystals [Mp: 145].[27,29]

4.3. General Procedure for the Tetrahydropyranylation or Trimethylsilylation of Alcohols

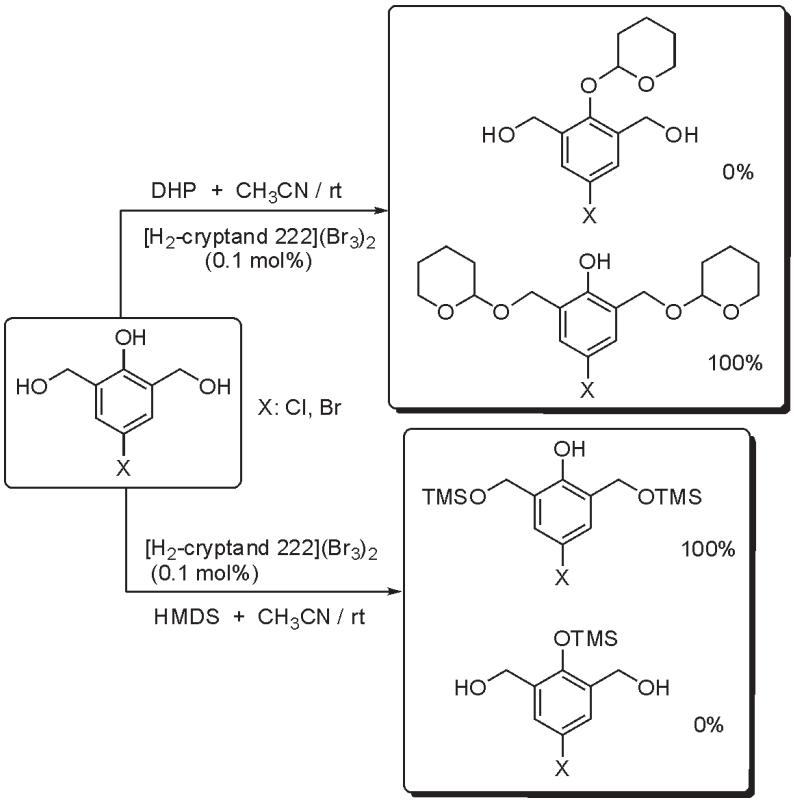
To a solution of the DHP (1 mmol) or HMDS (1.5 mmol) in CH_3CN (4 mL), were added $[H_2\text{-cryptand } 222]^{2+}(Br_3^-)_2$ (0.001 mmol). The solution was stirred at room temperature for one minute. Then alcohol (1 mmol for tetrahydropyranylation and 2 mmol for silylation) was added and solution was stirred at room temperature for appropriate time (see Table 2). After the reaction was over, CH_3CN was removed by water-bath distillation. *n*-Hexane or ethyl acetate (5 mL) was added to the residue and the mixture was filtered. The filtrate was washed with *n*-hexane or ethyl acetate (2 × 10 mL). Solvent was removed by distillation to yield pure products.

5. Spectroscopic Data for Novel Products

Entry 13-b: Yellow oil, yield 91 %; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.5 (br, 8H), 2.8 (m, 2H), 3.5–3.8 (m, 2H,), 4.8 (s, 1H), 5 (m, 1H), 7.4 (s, 4H); IR (KBr): 2944, 1440, and 1033 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): 19.4, 25.3, 29.7, 31.8, 34.0, 62.2, 78.9, 80.4, 96.3, 97.8, 124.7, 126.1, 127.8, and 143.1.

Entry 18-b: Colourless oil, yield 32 %; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.5 (br, 10H), 3.5 (br, 7H), and 4.5 (s, 1H). IR (KBr): 3263 (sp CH), 2941, 1464, and 1076 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): 8.2, 18.9, 24.8, 28.5, 29.9, 35.8, 61.8, 70.3, 72.9, 93.6, and 95.1.

Entry 19-b: Colourless oil yield 32 %; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.2 (br, 12H), 2.8 (s, 2H), 3.4 (br, 1), 3.8 (br, 1), 4.7 (s, 1) and 7.2 (s, 5H). IR (KBr): 3263 (sp CH), 2966, 1461, and 1031 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): 19.1, 25.1, 28.7, 30.2, 31.8, 49.5, 62.0, 70.1, 76.0, 93.1, 125.9, 127.7, 130.1, and 137.8.



Scheme 4

Entry 32-b: Yellow oil, yield 80 %; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.4 (br, 16H), 3.4 (br, 2H), 3.7 (br, 2), 4.3–4.7 (br, 3), and 7.0 (s, 2H). IR (KBr): 3361, 2926, 1587, and 1036 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): 19.1, 24.8, 30, 62.3, 64.8, 98.1, 123.8, 125.6, 127.6, and 151.8.

Entry 33-b: Orange oil, yield 76 %; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.4 (br, 16H), 3.4–3.7 (br, 4H), 4.5–4.7 (m, 3H,), and 7.1 (s, 2H). IR (KBr): 3469, 2945, 1505, and 1074 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): 19.2, 24.9, 30.1, 62.5, 64.9, 98.3, 111.2, 126.0, 130.7, and 152.5.

6. Conclusion

In summary, we have used a crystalline tribromide catalyst based on cryptand 222 which has high active bromine content per molecule and which acts as an excellent bromine carrier capable of catalyzing the chemoselective protection of alcohols to TMS-ethers or THP-ethers. The reaction is carried out under mild conditions and yields of products are good to excellent.

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