Chromium-Pillared Clay as a Catalyst for Benzylic Oxidation and Oxidative Deprotection of Benzyl Ethers and Benzylamines: A Simple and Convenient Procedure†

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A mild and efficient method for benzylic oxidation of arylmethylenes to the corresponding carbonyl compounds in good yields is described using a catalytic amount of chromium-pillared montmorillonite and equimolar quantities of *tert*-butyl hydroperoxide. The method is very selective toward monocarbonyl compounds of the substrates prone to form dicarbonyl compounds. The present heterogeneous catalyst is inert toward the branched hydrocarbons and has been put to practice to obtain *p*-isobutylacetophenone selectively from *p*-isobutylethylbenzene. Further, the method is extended successfully to the oxidative debenzylation reactions for the first time. A striking feature of the oxidative deprotection with the present method is the deprotection of a benzyl group from the substrates having an alkyne moiety.

Introduction

Benzylic oxidation is an important transformation in organic synthesis. Although a variety of the reagents have been employed for benzylic oxidation, reagents based on chromium only could afford moderate yields.[1] Tedious workup and voluminous amounts of environmentally hazardous chromium residues formed as a result of the use of a large excess of chromium reagents in the benzylic oxidations are the main disadvantages associated with the use of chromium reagents.[2,3] Inspite of its importance, very little attention has been focused on the development of a catalytic method[4] for benzylic oxidation. Muzart, a pioneer in chromium-catalyzed oxidations[5] has developed a method for benzylic transformation using soluble 2,4-dimethylpentane-2,4-diol cyclic chromate[5] or CrO_3 in combination with *tert*-butyl hydroperoxide (TBHP),[6] affording moderate to poor yields. Oxidative deprotection of *O*- and *N*-benzyl groups using reagents developed for benzylic oxidation has not been well exploited. Earlier reports for the oxidative deprotection of the benzylic group with a few reagents such as CrO_3/AcOH,[7] $Ce(SO_4)_2$/AcOH,[8] etc., possess drawbacks such as a large excess of reagents, drastic conditions,[9] and an insufficient selectivity toward products that make the utility of these reagents as well as development of other methods limited.

Pillared clays have been used for selective organic transformations in the liquid phase in our laboratory. Unusual molecular recognition of primary and para-substituted benzyl alcohols discriminating against the secondary and ortho-substituted ones by use of vanadium-pillared clay catalysts[10] forms the first example in the area of pillared clays. Regio- and stereoselective epoxidation of allyl alcohols using vanadium-[11] and titanium-pillared[12] clays are other notable examples. Our success in the use of pillared clay catalysts for the selective organic transformations prompted us to attempt the selective benzylic oxidation reaction with pillared clay catalyst.

In this article, a very efficient and highly selective method for the benzylic oxidation using a heterogeneous catalyst, chromium-pillared clay catalyst[13,14] (Cr-PILC), in combination with a reoxidant TBHP is presented for the first time and compared to the best systems reported earlier. In addition to this, the employment of the same catalyst for selective oxidative deprotection of *O*- and *N*-benzyl groups is reported. A striking feature is the selective oxidative deprotection of a benzyl group in specially chosen substrates possessing an alkyne moiety.

Table I. Selective Benzylic Oxidation Using a Catalytic Amount of Cr-PILC/TBHP

entry	substrate	product	time (h)	yield (%)[a]
1	diphenylmethane	benzophenone	44	90
2	fluorene	fluorenone	38	88
3	tetralin	α-tetralone	45	91
	(a) 2nd cycle	α-tetralone	47	89
	(b) 3rd cycle	α-tetralone	47	88
	(c) 4th cycle	α-tetralone	47	85
4	bibenzyl	deoxybenzoin	47	92
5	deoxybenzoin	no reaction	48	
6	1,3-diphenyl-propane	1,3-diphenyl-1-propanone	40	86
7	1,3-diphenyl-1-propanone	no reaction	40	
8	indan	1-indanone	46	83
9	ethylbenzene	acetophenone	36	92
10	*n*-butylbenzene	butyrophenone	36	90
11	isobutylbenzene	no reaction	45	
12	isopropylbenzene	no reaction	45	
13	*p*-isobutylethyl-benzene	*p*-isobutylaceto-phenone	44	84
14	*p*-isopropylethyl-benzene	*p*-isopropylaceto-phenone	46	82
15	toluene	benzoic acid	45	89
16	*o*-xylene	*o*-toluic acid	48	87

[a] Isolated yield.

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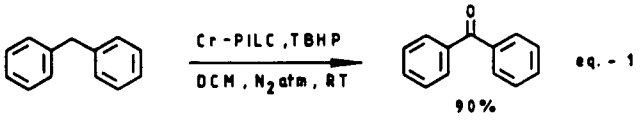
Table II. Comparative Data Demonstrating the Efficiency of the Present System

entry	substrate	product	% yield[a] method A	method B	method C	method D
1	diphenylmethane	benzophenone	90	87	53	76
2	tetralin	α-tetralone	91	65	64	78
3	indan	1-indanone	83	70	60	
4	bibenzyl	deoxybenzoin	92	29	21	
5	fluorene	fluorenone	88	57	95	90

[a] Method A: Cr-PILC and TBHP. Method B: cyclic chromate and TBHP.[5] Method C: catalytic CrO_3 and TBHP (hydrous).[6] Method D: pyridinium dichromate, TBHP.[3]

Results and Discussion

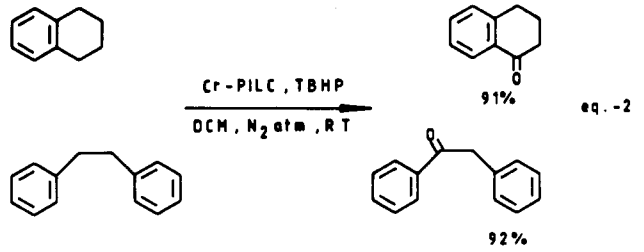
The oxidation of the benzylic methylene group was carried out at ambient temperature in dry CH_2Cl_2 containing a catalytic amount of chromium-pillared clay catalyst and 2 equiv of TBHP for 36–50 h giving the corresponding ketone in excellent yields in the range 85–95% (eq 1) (Table I). The selective oxidation of



eq. - 1

benzylic methylene groups is very impressive when compared with earlier methods. For example, oxidation of diphenylmethane with a catalytic amount of CrO_3 and excess TBHP gave benzophenone in 53% yield while the present method afforded the ketone in 90% yield.

Further, the most important feature of the present catalytic system is the selective benzylic oxidation to monocarbonyl compounds, especially of the substrates prone to form dicarbonyl compounds in very high yields (eq 2).



eq. -2

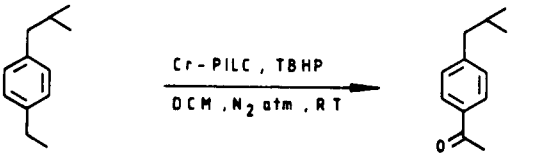
There was no formation of dicarbonyl compound even in the experiments conducted for prolonged times with monocarbonyl compounds as starting material and fresh amounts of Cr-PILC and excess of TBHP. Thus these results indicate that the total unreactivity of the monocarbonyl compounds formed during the reaction toward the present catalyst is reponsible for the display of high selectivity.

On the other hand, 2,4-dimethylpentane-2,4-diol cyclic chromate and anhdrous TBHP gave 65% and catalytic amount of CrO_3 and excess of TBHP gave 64% of α-tetralone from tetralin. Similarly, the benzylic oxidation of bibenzyl afforded deoxybenzoin in poor yields when 2,4-dimethylpentane-2,4-diol cyclic chromate or CrO_3 and TBHP were used.

Thus Table II clearly shows that the present method is selective, mild, and more efficient than the earlier methods.

The present catalytic procedure also exhibits good specificity toward ethylbenzene, *n*-butylbenzene, etc., giving the corresponding carbonyl compounds in almost 90% yields while the catalyst is inert toward the branched alkyl chains such as cumene, isobutylbenzene, etc. The starting materials in these cases were recovered even after prolonged reaction times.

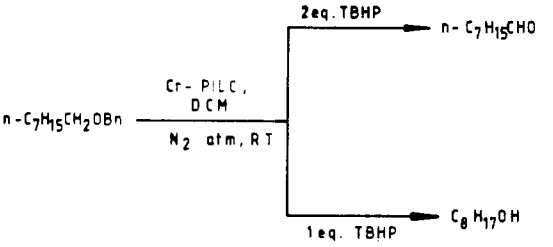
Further, this specificity was put to use and practically demonstrated in a specially chosen dialkyl substrates wherein branched hydrocarbon moieties were unaffected as shown in eq 3.



eq. -3

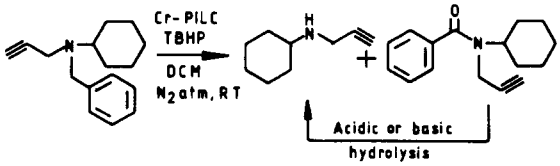
When the same reaction conditions were applied to the oxidation of benzylic methyls such as toluene, xylene, etc., it led to the formation of the corresponding acids.

The success of these benzylic oxidations prompted us to apply the same method for the oxidative deprotection of *O*- and *N*-benzyl groups. The oxidative benzylic deprotection reaction was carried out with Cr-PILC and TBHP at room temperature under a nitrogen atmosphere on various O- and N-benzylic compounds (Table III). The most attractive feature of the present benzylic deprotection method is that the final product can be directed either to the alcohol or the carbonyl compound by adding 1 equiv of TBHP or 2 equiv of TBHP, respectively (eq 4). The



eq. - 4

same result was observed even in the case of oxidative deprotection of *O*-allyl group.[15] When the same method was applied to the deprotection of *N*-benzyl groups, it led to the formation of two products, amine and benzyl amide, even when excess of TBHP was added (as shown in eq 5). The formed benzyl amide can be converted to amine by simple basic or acidic hydrolysis, giving higher yields in the oxidative deprotection.



eq.-5

The striking feature of the present catalytic method is the deprotection of the benzyl group from the substrates having an alkyne moiety, especially of amine since it is not possible with any other method reported so far to the best of our knowledge. Although the present catalytic system selectively oxidizes and subsequently cleaves the allylic

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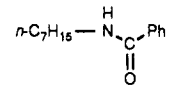
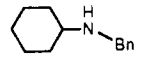
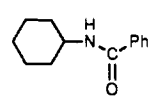
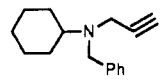
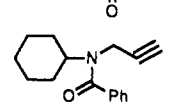
Table III. Oxidative Deprotection of the Benzyl Group Using a Catalytic Amount of Cr-PILC/TBHP

entry	substrate	product[a]	equiv of TBHP	time (h)	yield[b] (%)
1			2	12	96
	(a) 2nd cycle		2	14	91
	(b) 3rd cycle		2	14	89
	(c) 4th cycle		2	15	87
2	n-$C_8H_{17}OBn$	n-$C_8H_{17}OH$	1	14	91
3	n-$C_8H_{17}OBn$	n-$C_7H_{15}CHO$	2	18	88
4	n-$C_7H_{15}NBn$		3	26	48 (88)[c]
5			3	24	48 (86)[c]
6			excess	46	36 (65)[c]

[a] Amides can be converted to amines by acidic or basic hydrolysis. Heptylamine (40%), cyclohexylamine (38%), and *N*-propargylcyclohexylamine (29%) were also obtained in entries 4, 5, and 6, respectively. [b] Isolated yields. [c] Isolated combined yields in parentheses.

carbon attached to the amine,[15] it is totally inert toward alkynes attached to amines.

The catalyst recovered after the reaction by simple filtration was successfully reused in the benzylic oxidation of tetralin (entry 3, Table I) and oxidative deprotection of benzylic group (entry 1, Table III) which displayed consistent activity and selectivity for four cycles. The catalyst recovered after the reaction showed the same d_{001} spacing in the XRD, indicating that the catalyst remains unchanged during the reaction. When the reaction was performed with the commercially available 70% aqueous TBHP, though the reaction occurs as usual, the active catalyst species leached out from the support and the catalyst could not be reused. Hence, it is better to perform the reaction under anhydrous conditions which gave better yields, good selectivity, and reusability. This forms another successful story of pillared clays in the area of heterogeneous catalysts, which have emerged in the recent literature as successful practical alternatives for the selective organic transformations and solve most of the problems inherent in homogeneous catalysis.

Experimental Section

Melting points are uncorrected. CH_2Cl_2 was distilled from P_2O_5 and subsequently from CaH_2. All the arylalkanes were distilled before use. Commercially available aqueous TBHP was azeotropically distilled from isooctane.[17] Montmorillonite obtained from various sources was used as a support for the chromium-pillared catalyst. Natural montmorillonite, Kunipia, Japan, and even modified montmorillonite K_{10}, Fluka, Switzerland, are very active for these benzylic oxidation and O- and N-benzylic deprotection reactions. In the case where reusability by the catalyst is mentioned, the used catalyst was filtered, dried in vacuum for a few minutes, and reused.

Preparation of the Catalysts. Preparation of Na^+–Montmorillonite. Montmorillonite K_{10} (Fluka) prior to use was suspended as 1% weight slurry and was allowed to sediment for 24 h to remove residual impurities like silicates, quartz, etc. The Na^+–montmorillonite was prepared by suspending commercial K_{10} montmorillonite in excess aqueous NaCl solutions for 36 h. After that the clay suspension was subjected to centrifuge and washed free of chloride ions by deionized water as indicated by the $AgNO_3$ test. Finally it was dried in air.

Preparation of Chromium-Pillared Montmorillonite Catalyst (Cr-PILC). For the preparation of Cr-PILC, a solution containing cationic polyoxy chromium oligomers was prepared by the hydrolysis of 0.1 M chromium nitrate at 95 °C using Na_2CO_3 as the base. The base to chromium ratio (n) was maintained as 1.5, and the hydrolysis was carried out at 90 °C for 72 h. To this hot solution was added a 1 wt % suspension of Na^+–montmorillonite, and the overall contents were stirred for 1.5 h at room temperature. Finally, the product was collected by centrifugation, washed free of excess chromium salt with deionized H_2O, and air-dried. The XRD of this Cr-PILC showed d_{001} spacing of 23.6 Å, which gives the interlayer spacing of 14.0 A°.[16] The amount of chromium pillared or exchanged in the Cr-PILC was determined by plasma analysis and found to be 2.5 mmol/g.

Representative Procedure for the Oxidation of Arylalkanes. The benzylic oxidation of tetralin (529 mg, 4 mmol) was performed by stirring initially with Cr-PILC (40 mg, containing 0.1 mmol of chromium) in dry CH_2Cl_2 under a N_2 atmosphere for $^1/_2$ h. The addition of TBHP (2.9 mL, C = 2.8 M in isooctane) was then effected, and the reaction mixture was allowed to stir under N_2 at rt for 47 h. The reaction was monitored by TLC. After the completion of the reaction, the said catalyst was filtered and washed with CH_2Cl_2 and the filtrate concentrated under reduced pressure, and the crude mixture was subjected to the column chromatography to give α-tetralone (532 mg, 91% yield). Bp, mp, and spectral data of the products compared well with the authentic data available in the literature.[18]

Representative Procedure for the Oxidative Deprotection of Benzyl Group. The oxidative deprotection of benzylamines (*N*-benzylhexahydrobenzanilide, 4 mmol, 812 mg) was performed by stirring initially Cr-PILC (40 mg, containing 0.1 mmol of chromium) in dry CH_2Cl_2 under a N_2 atmosphere for $^1/_2$ h. Then 2 equiv of dry TBHP (2.85 mL, C = 2.8 M isooctane) was added, and the reaction mixture was allowed to stir for 24 h at rt. The catalyst was filtered off from the reaction mixture at the end of the reaction as indicated by TLC, and the catalyst was washed with CH_2Cl_2. The filtrate was dried over Na_2SO_4 and concentrated under reduced pressure which on purification by column chromatography gave the products, cyclohexylamine and benzoylhexahydrobenzamide. The bp and spectral data of the products compared well with the authentic data available in the literature.[18]

***N*-Cyclohexyl-*N*-propargylbenzamide**: mp 156–158 °C; IR (neat) 1670, 2100, 3350, cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.8 (m, 2 H), 7.3 (m, 3 H), 3.45 (d, J = 3 Hz, 2 H), 2.45 (m, 1 H), 1.85 (t, J = 3 Hz, 1 H), 1.1–1.7 (m, 10 H). Anal. Calcd for $C_{16}H_{19}NO$: C, 79.64; H, 7.93; N, 5.80. Found: C, 79.43; H, 7.6; N, 5.76.

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***N*-Propargylcyclohexylamine**: IR (neat) 3360, 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.4 (d, J = 3 Hz, 2 H), 2.3 (m, 1 H), 1.95 (t, J = 3 Hz, 1 H), 1.2-1.8 (m, 10 H). Anal. Calcd for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.20. Found: C, 78.60; H, 11.01; N, 10.39.

***N*-Cyclohexylbenzamide**: mp 144-145 °C (lit.[18b] mp 147 °C); IR (neat) 3340, 1660 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.7 (m, 2 H), 7.25 (m, 3 H); 2.4 (m, 1 H), 1.1-1.8 (m, 10 H). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.36; N, 6.88. Found: C, 76.4; H, 8.21; N, 6.74.

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Nonracemic Frontalin via Copper- and Palladium-Based Skeletal Construction and the Asymmetric Dihydroxylation[1]

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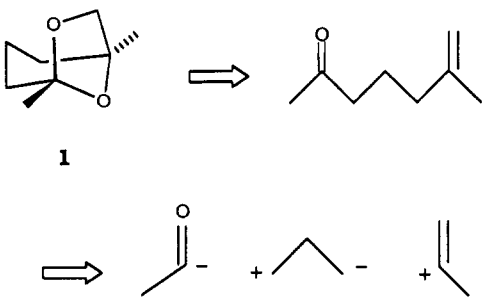
The new higher order organocuprate, $Li_2Cu(CN)(C(OMe):CH_2)_2$, prepared through a Sn → Li → Cu transmetalation sequence, was found to efficiently couple with allyl bromide producing 2-methoxy-1,4-pentadiene (**3**) which is efficiently converted to the ketal **4**. Hydroboration of **4** with 9-BBN-H and the selective oxidation of this adduct with trimethylamine *N*-oxide (TMANO) produces 9-oxa-10-borabicyclo[3.3.2]decane **5**, which undergoes Pd-catalyzed cross coupling with 2-bromopropene producing **6**, thereby accomplishing the construction of the frontalin carbon skeleton in 63% overall yield from allyl bromide. The Os-based dihydroxylation of **6** followed by ketalization either produces the racemic pheromone ((±)-**1**) or, with the Sharpless catalytic asymmetric dihydroxylation (dihydroquinine ligand) procedure, results in the selective formation of the *S* enantiomer in 35% ee. The de determined from the ^{13}C NMR spectra of the diastereomeric Mosher's monoesters (**9**) was found to provide useful corroborative information on the optical purity of the intermediate 1,2-diols **7**.

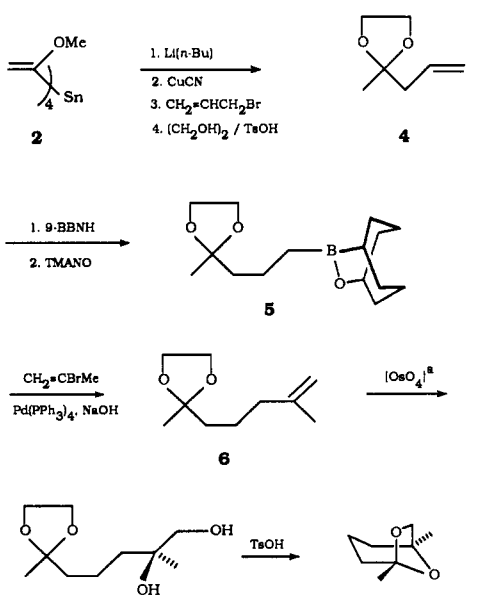
Our recent interest in new applications for the cross coupling of either higher order organocuprates[3] (Lipshutz reagents)[4] or organoboranes[5] (Suzuki coupling)[6] with electrophilic substrates led us to seek a simple synthetic target where the value of these reagents could be efficiently demonstrated. For this purpose, (*S*)-(−)-frontalin (**1**),[7] the aggregation pheromone of the southern pine beetle, *Dendroctonus frontalis*, was selected because both of these organometallic intermediates could be envisioned to play key roles in its novel 2 + 3 + 3 skeletal construction (Scheme I).

Historically, frontalin has been a popular synthetic target, whose asymmetric synthesis has been achieved through a variety of classic methods which employ chiral building blocks, auxiliaries, and reagents.[7] Considerable success with this last approach has been achieved with the Sharpless asymmetric epoxidation from either of two achiral allylic alcohol substrates.[7a] To adapt our synthetic approach to **1** to an asymmetric process would not have been feasible were it not for recent advances in the cata-

Scheme I



Scheme II[a]



[a] (±)-**7**: OsO_4, TMANO·$2H_2O$, *t*-BuOH; (*S*)-**7**: **8**, OsO_4, $K_3Fe(CN)_6$, K_2CO_3, *t*-BuOH.

(1) Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday in appreciation for his guidance and support over the years.

(2) Graduate student supported by the NIH-MBRS Program (RR08102).

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