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Chromium Pillared Clay Catalysed Allylic Oxidation And Oxidative Deprotection of Allyl Ethers And Amines : A Simple And Convenient Procedure+

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Abstract : *An efficient method for allylic oxidation of cyclic and acyclic alkenes to the corresponding α,β-unsaturated carbonyl compounds in good yields was described using catalytic amounts of chromia-pillared montmorillonite and equimolar quantities of tert-butyl hydroperoxide. This is also a convenient method for selective oxidative deprotection of allyl ethers and amines using same system. Incidentally this is the first heterogeneous system for the allylic oxidation as well as oxidative deprotection.*

Allylic oxidation of alkenes to enones offer a stimulating challenge for organic chemists in spite of number of methods available. Earlier large excess of chromium (VI) complexes were used for effecting allylic oxidations[1-4]. Later Chandrasekharan and his co-workers[5] reported a successful methodology for allylic oxidations using 2 mole equivalents of tert-butyl hydroperoxide (TBHP) and pyridinium dichromate (PDC) to the substrate. All these methods suffer drawbacks such as use of excess of chromium complex, large volume of solvent, tedious work-up procedures and the disposal of environmentally hazardous tary chromium residues. However, little efforts were made for the development of catalytic system, based on chromium for allylic oxidation. A recent discovery of Muzart[6] provided a catalytic method using a homogeneous system comprising chromium trioxide as catalyst and excess of TBHP as reoxidant for allylic oxidation affording moderate yields in case of cyclic alkenes and negligible yields in acyclic systems. A very serious problem inherently present in all the systems without exception is the migration of double bond during allylic oxidation[3,6] yielding a mixture of products. Thus it was felt that there is a need and scope for the development of efficient catalytic system for allylic oxidation.

Metal oxide pillared clays derived from smectites interlayered with polyoxocations exhibit attractive catalytic activity for organic transformations. As solid catalysts[7] are effective and industrially feasible in catalytic organic transformations in terms of ease of handling and adoptability, we designed and used several pillared clay catalysts in liquid phase reactions which exhibited unusual and novel selectivity. For example a novel vanadium pillared clay catalyst[8]

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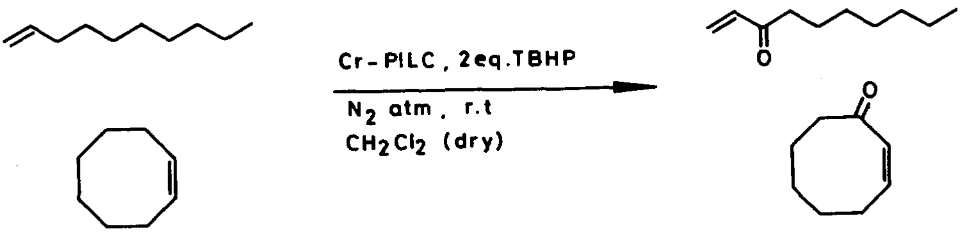
displayed high substrate selectivity in the oxidation of primary and p-benzyl alcohols discriminating secondary and ortho ones. The regioselective epoxidation of allyl alcohols using vanadium pillared clay catalyst[9] and asymmetric epoxidation of primary allyl alcohols using titanium pillared clay catalyst[10] were well demonstrated. Recently we presented a letter[11] on selective oxidation of secondary alcohols in presence of primary alcohols using chromium pillared clay catalyst (Cr-PILC) in conjunction with TBHP. In the present article we report an efficient catalytic system, Cr-PILC as catalyst and TBHP as reagent for allylic oxidations in good yields and compared with the best systems described earlier in order to put these results in right perspective.

Allylic oxidation reaction was carried out using Cr-PILC[12] and TBHP at room temperature under nitrogen atmosphere on various alkenes (Table 1) such as monocyclic, bicyclic and acyclic ones that led to the formation of α,β-unsaturated carbonyl compounds in very good yields (Scheme 1). The present catalytic system displayed an impressive performance in all the allylic oxidation reactions in terms of selectivity and yields over the best results reported so far.



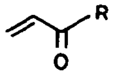
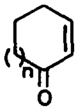
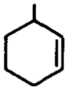
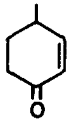
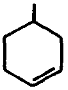
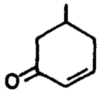
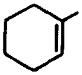
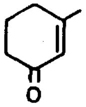
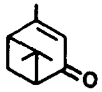
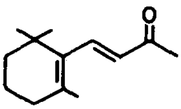
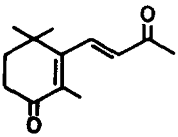
Scheme - 1

Allylic oxidation of terminal alkenes such as dec-1-ene, hept-1-ene and hex-1-ene (entries 1a, 1b and 1c) with the present catalytic system afforded 1-ene-3-ones are in the range of 88-91% yield. On the other other hand the catalyst reported by Muzart[6] afforded 20% yield only. This result indicate that there was no migration of terminal double bond during the allylic oxidation with the present catalytic system.

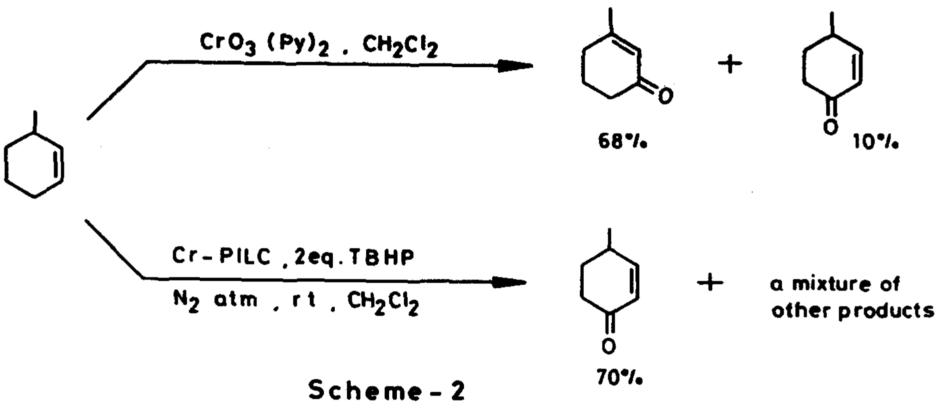
Similarly allylic oxidation of cyclic alkenes and monosubstituted cyclohexenes are also effective with the present catalytic system. Although marginal improvement was observed in the case of cyclic ones[5,6], the high selectivity in the oxidation of monosubstituted cyclohexene towards enones formed as a major product without concomitant isomerisation in good yields is significant. Thus the result supports that there was insignificant migration of double bond resulted into minor byproduct in case of cyclic ones. For example 3-methyl-1-cyclohexene on oxidation with pyridine chromate[13] gave 3-methyl-2-cyclohexene-1-one as isomerised product in 68% yield whereas the present system gave 70% of unisomerised product i.e. 4-methyl-2-cyclohexene-1-one (entry 3) (Scheme 2).

Table - 1

Allylic oxidation of alkenes to α,β-unsaturated carbonyl compounds using Cr-PILC and TBHP.

Entry	Substrate	Product	Time (hrs)	Yield[a] (%)
1				
	a R = n-heptyl		36	91
	b R = n-butyl		34	88
	c R = n-propyl		38	89
2				
	a n = 0		38	87
	b n = 1		39	85
	c n = 2		40	88
	c_1 2nd cycle		44	86
	c_2 3rd cycle		44	85
	c_3 4th cycle		45	82
	d n = 4 (E/Z)		35	92
3			36	70
4			37	76
5			39	68
6			42	76
7			46	68

[a] Isolation yield.



Scheme - 2

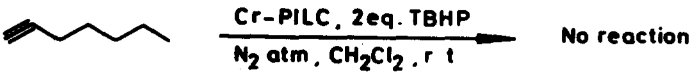
1-Methyl cyclohexene also gave 1-methyl-1-cyclohexene-3-one as a major product while the chromium pyridine complex gave 1-methyl-1-cyclohexene-6-one as a dominant product^3. Similarly 1-methyl-3-cyclohexene gave 1-methyl-3-cyclohexene-5-one with the present catalytic system in 76% yield.

When this method was applied to the highly strained systems like α-pinene and β-ionone (entries 6 and 7) gave the corresponding products 76% and 68% against 40% and 55% which were reported earlier^{5,28}. But on performing the reaction with the internal acyclic alkenes the selectivity was poor.

The catalyst recovered after the reaction by simple filtration was successfully reused in the allylic oxidation of cyclooctene (entries 3c$_1$, c$_2$ and c$_3$) which displayed consistant activity and selectivity for four cycles. Also the catalyst recovered after the reaction shows the same d_{001} spacing in the XRD indicating that the catalyst remain unchanged during the reaction.

In order to reduce the reaction times, we performed an allylic oxidation reaction using dry chloroform as solvent at reflux temperature under nitrogen atmosphere. Although the starting material was absent within 3 h, the selectivity towards the product is very low. When this reaction was performed with aqueous TBHP, though the reaction was taking place as usual, the catalyst was leaching which cannot be used for any recyclic reaction.

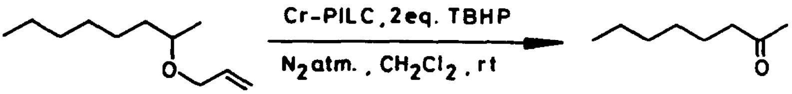
Since the present catalytic system is successful in the allylic oxidation of alkenes, we thought of applying the same system for the α-oxygenation of alkynes such as dec-1-yne, hept-1-yne to the corresponding conjugated acetylenic ketones, but to our surprise the starting material was recovered as such even the reaction was prolonged for longer times for about 50 h (Scheme 3).



Scheme - 3

The resounding success in allylic oxidation reactions in case of alkenes prompted us to apply the same method for the oxidative deprotection of O- and N- allyl group since there are no catalytic methods reported so far for the oxidative allylic deprotection to the best of our knowledge.

The deprotection of O- and N- allyl groups were usually achieved by catalytic hydrogenation, homolytic cleavage by lewis acids or bases, while oxidative deprotection method was applied rarely. Since most of these methods $CrO_3/AcOH$[14], $Ce_2SO_4/AcOH$[15] and Ag_2O[16] required excess of reagent and stringent conditions which of course led to the various side products[17]. We report here a successful catalytic methodology for the oxidative deprotection of O- and N- allyl compounds (Table 2) in good yields using the Cr-PILC and TBHP for the first time (Scheme 4).



Scheme - 4

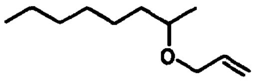
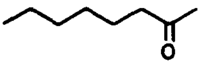
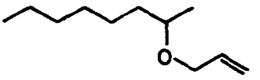
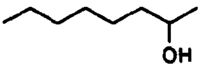
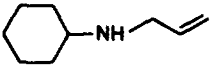
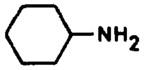
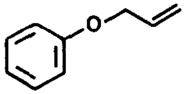
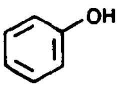
Oxidative allylic deprotection reaction was carried out with Cr-PILC and TBHP at room temperature under nitrogen atmosphere on various O-allyl and N-allyl compounds. When one mole of TBHP was used in case of O-allyl (entry 2, Table 2) the corresponding alcohol was obtained, while 2 moles of TBHP gave the carbonyl compound (entry 1, Table 2) in good yields. In case of N-allyl compounds 2 moles of TBHP were required to obtain the free amino compound in good yields.

Chromium intercalated in the form of oxy/hydroxy cations in montmorillonite is in III oxidation state as indicated in literature[18]. When molar excess quantities of Cr-PILC were used for the allylic oxidation, the reaction did not take place demonstrating that Cr(III) is inert as an oxidant. In order to increase the oxidation level of Cr(III) present in Cr-PILC to higher oxidation states which is proved to be good oxidant , an external oxidant like TBHP is required. Thus molar excess quantities of TBHP to the substrate were used to reoxidise the chromium from its lower oxidation level formed after oxidation of alkene to enones in each catalytic cycle and to sustain chromium always in higher oxidation state[6].

Generally 2 mole equivalents of TBHP for a mole of substrate is required for the oxidation of alkene to α, β-unsaturated carbonyl compounds. The reaction involves the hydroxylation

Table - 2

Oxidative deprotection of allyl esters and amines using Cr-PILC and TBHP.

Entry	Compound	Product	eq. TBHP	Time (hrs)	Yield[a] (%)
1			2	12	85
2			1	16	80
3			2	20	90
4			2	22	84
5			2	10	80

a. Isolated yields

of alkenes to form allyl alcohol which on subsequent oxidation gives enone. It is very difficult to stop the reaction at allyl alcohol stage, since the oxidation of alcohol to ketone is a facile reaction. The present studies in the oxidation of allylic oxidation of alkene (Table 1) using Cr-PILC indeed consumed 2 mole equivalents only per mole of the substrate and thus supporting the mechanism proposed by Muzart[19]. But in the case of oxidative deprotection reaction 1 mole equivalent of TBHP per mole of substrate is suffice for the simple deprotection of O-allyl group (entry 2, Table 2) while two mole equivalents of TBHP gave the corresponding ketone (entry 1, Table 2). On the other hand there was no deprotection in the absence of TBHP. These results indicate that the cleavage of allylic moiety takes place immediately after hydroxylation.

Montmorillonite obtained from various sources have been used as support for the chromium pillared catalyst. Natural montmorillonite, Kunipia, Japan pretreated with acid as described in experimental part and montmorillonite K_{10}, Fluka, Switzerland, originally pretreated with the acid are found to be very active for these allylic oxidation and O- and N- allylic deprotection reactions.

In conclusion, the present method described here is a mild, convenient and selective for the allylic oxidation as well as for the oxidative deprotection reactions and forms first report using heterogeneous catalyst. Although this method requires longer reaction times, the advantages inherently present such as easy work-up by simple filtration, reusability of the catalyst, requirement of molar equivalents of TBHP and environmentally safe project the use of Cr-PILC and TBHP as practical and viable alternative to the allylic oxidation and oxidative deprotection reactions.

Experimental

Preparation of the catalyst

Preparation of Na^+ - Montmorillonite : Montmorillonite prior to use was suspended as 1% weight slurry and was allowed to sediment for 24h to remove residual impurities like silicates, quartz etc. The Na^+-montmorillonite was prepared by centrifugation and washed free of chloride ions by deionised water as indicated by $AgNO_3$ test. Finally, it was dried in air.

Preparation of chromia-pillared montmorillonite catalyst (Cr-PILC) : For the preparation of Cr-PILC, a solution containing cationic polyoxychromium oligomers were 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 72h. To this hot solution, 1 wt.% suspension of Na^+-montmorillonite was added and the overall contents were stirred for 1.5h at room temperature. Finally, the product Cr-PILC was collected by centrifugation, washed free of excess chromium salt with deionised water and air-dried. The XRD of thus obtained Cr-PILC shows d_{001} spacing as 23.6 A° which gives the interlayer spacing as 14.0 A°. The amount of chromium pillared or exchanged in the Cr-PILC was determined by plasma analysis and found to be 2.5 mmol per gram.

General procedure for allylic oxidation

The allylic oxidation of alkenes (cyclooctene, 440 mg, 4 mmol) was performed by stirring initially Cr-PILC (40 mg, contains 0.1 mmol of chromium metal) in dry CH_2Cl_2 under nitrogen atmosphere for 1/2 hr. The dry tert-butylhydroperoxide (2.85 ml, c=2.8 M in iso-octane[29]) was then added and carried out the reaction for 42 h under stirring at room temperature. At the end of the reaction indicated in the TLC the catalyst was filtered off from the reaction mixture and the catalyst was washed with CH_2Cl_2. The filtrate was dried over Na_2SO_4 and concentrated under reduced pressure which on chromatography yielded (cycloocten-3-one, 436 mg, 88%) the product.

Preparation of dec-1-ene-3-one : The allylic oxidation of dec-1-ene (560 mg, 4 mmol) was performed by Cr-PILC (40 mg) and TBHP (2.85 ml, c=2.8 M in iso-octane[29]) under nitrogen atmosphere at room temperature for 36h. After completion of the reaction the catalyst was filtered off and washed with CH_2Cl_2. The filtrate was dried over Na_2SO_4, concentrated under reduced pressure and thus obtained compound was purified by column chromatography (98:2) petroleum ether and ethyl acetate gave the pure dec-1-ene-3-one (524 mg) in 91% yield. b.p. 188-190°C.

IR (Neat) : 2980, 1710, 1610, 1450, 1400, 1220, 1110, 1075, 1030, 990, 970, 825, 790 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ 6.5 - 6.2 (dd, 2H, J=10Hz, 2Hz); 5.9 - 5.8 (dd, 1H, J=10Hz, 10Hz); 2.5 (t, 2H, J=7Hz), 1.6 - 1.2 (m, 10H), 0.9 (t, 3H). Analysis for $C_{10}H_{18}O$: Found : C, 83.65; H, 10.92; Calc.: C, 83.33; H, 11.11%.

Preparation of hept-1-ene-3-one and hex-1-ene-3-one : These two compounds were prepared according to the procedure described earlier from hept-1-ene and hex-1-ene respectively. These compounds are having b.ps. 155-160°C and 125-130°C whereas literature reported[30] are 44-45°C and 25-26°C/11 atm. All the spectral data are similar to the dec-1-ene-3-one.

α-Pinene on oxidation with Cr-PILC and TBHP gave verbenone in 76% yield b.p. 220°-222°C (lit.[27] b.p. 227-228°C).

β-Ionone on oxidation under similar conditions gave 3-keto- -ionone as an oil in 68% yield. All the spectral data are compared with the literature values[28].

Physical characteristics of the products of Table - 1.
Cyclohexenone (entry 2a) b.p. 168-170°C (lit.[20] b.p. 169-171°C).
Cycloheptenone (entry 2b) b.p. 182-183°C (lit.[21] b.p. 186-188°C).
Cyclooctenone (entry 2c) b.p. 195-197°C (lit.[22] b.p. 89°C/14 atm).
Cyclodecene (entry 2d) b.p. 245-250°C (lit.[23] b.p. 59-62°C/0.3 atm).
4-Methyl-2-cyclohexene-1-one (entry 3) b.p. 170-172°C (lit.[24] b.p. 175-176°C).
1-Methyl-3-cyclohexene-5-one (entry 4) b.p. 180-185°C (lit.[26] b.p. 54°C/5 atm).
1-Methyl-1-cyclohexene-3-one (entry 5) b.p. 190-191 (lit.[25] b.p. 200-202°C).

General procedure for the oxidative deprotection of allyl group

The oxidative deprotection of alkyl allyl ethers (iso-octyl allyl ethr, 680 mg, 4 mmol) was performed by stirring initially Cr-PILC (40 mg, contains 0.1 mmol of chromium metal) in dry CH_2Cl_2 under nitrogen atmosphere for 1/2 hr. Then 2 equivalents of dry TBHP (2.85 ml, c=2.8 M iso-octane) were added and the reaction conducted for 12 h. The catalyst was filtered off from the reaction mixture at the end of the reaction as is indicated by TLC and the catalyst was washed with CH_2Cl_2. The filterate was dried over Na_2SO_4 and concentrated under reduced pressure which on purification by chromatography gave the (2-octanone, 435mg, 85% yield) product. BP, NMR, Mass and IR of all the products in Table-2 are very well compared with the Aldrich data.

Acknowledgement

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