SHORT PAPER

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Dioxomolybdenum(VI) complexes as catalytic neutral esterification agents†

Purnima Nag, Rakesh Bohra* and Ram C. Mehrotra

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

Esterification reactions of carboxylic acids with different alcohols in neutral nonaqueous media have been carried out in excellent yields using catalytic amounts of dioxomolybdenum(VI) complexes of the type $[MoO_2L_2]$ (where LH = acetylacetone, salicylaldehyde, *o*-aminophenol, 8-hydroxyquinoline, and 2-acetyl pyridoxime). The reactions of propionic acid with primary, secondary and tertiary alcohols in the presence of catalytic amounts of $MoO_2(acac)_2$ result in higher yields of the esters with primary alcohols, compared to those with secondary or tertiary alcohols. The results of the esterification reactions of propionic acid with methanol and tertiary butanol in the presence of different dioxomolybdenum(VI) complexes suggest that the homogeneous catalysts are better than heterogeneous analogues.

Keywords: dioxomolybdenum(VI) complexes, homogeneous catalysts, heterogeneous catalysts, acid number

The esterification reactions of carboxylic acids with various alcohols require a catalyst in order to obtain better yields of esters. Sulfuric acid, *p*-toluene sulfonic acid, organodistannoxanes and organostannyl oxides[1] are some of the most common catalysts which are generally employed in such reactions. Steliou and Poupart[2] as well as Muderawan *et al*.[3] reported some internal macrocylic esterification reactions using organostannyl oxides and cyclic allylic stannane compounds. Yang and coworkers[4] reported some nickel catalysed esterification reactions, yet efforts continue to be expended[5] in search of new, milder and more efficient methods for accomplishing esterification reactions.

There are many reactions which are facilitated by dioxomolybdenum(VI) complexes such as transformation of alkenes to epoxides,[6] sulfides to sulfoxides,[7] secondary alcohols to ketones,[8] aldehydes to carboxylic acids,[9] azobenzenes to azoxybenzenes,[10] N-heterocyclics to N-oxides,[11] amides to hydroxamates[12] and more complex reactions.[13]

Amongst dioxomolybdenum(VI) complexes, dioxomolybdenum(VI) acetylacetonate *i.e*., $[MoO_2(acac)_2]$ has been widely used as a catalyst in many organic transformations (due to its low cost and ease of handling) such as methoxymethylation of alcohols, protective tetrahydropyranylation of alcohols and phenols,[15] dehydration of tertiary alcohols to olefines,[16] β-selective epoxidation of cholesterol esters with molecular oxygen[17] and deprotection of acetals.[18]

We herein report on a synthetically useful new approach towards the preparation of a variety of esters using catalytic amounts of dioxomolybdenum(VI) complexes.

Esterification reactions of propionic acid with primary, secondary and tertiary alcohols in presence of catalytic amount of dioxomolybdenum(VI) acetylacetonate, $[MoO_2(acac)_2]$, have been carried out during the present investigations because of its good solubility in reaction mixtures under neutral conditions and without resorting to high dilution techniques:

$$C_2H_5COOH + ROH \xrightarrow[-H_2O]{[MoO_2(acac)_2],\Delta} C_2H_5COOR$$

(where R = CH_3, C_2H_5, $C_3H_7^i$, $C_4H_9^n$ and $C_4H_9^t$)

Results of these operationally convenient procedures are summarised in Table 1 along with the results of 'control' experiments carried out under similar conditions but without the presence of a catalyst. Employment of about ten fold excess of alcohol served very well as a solvent. Table 1 indicates that formation of esters take place with or without the presence of a catalyst. However, much better yields of esters were obtained in the presence of a catalyst. Good yields of esters were obtained from primary alcohols. Secondary and tertiary alcohols yielded esters in low yields which might be due to oxidation or dehydration of the corresponding alcohols. The chain lengthening of the alcohol moiety also lowers the amount of ester formed.

Esterification reactions of propionic acid with methanol in presence of different molar concentrations (*i.e*. 0.1, 0.05 and 0.02) of the catalyst, $[MoO_2(acac)_2]$, have also been carried out. Optimum yields of the ester were obtained with 0.05 molar concentration of the catalyst. Further addition of the catalyst does not change the yield of the ester appreciably. The reaction mixture of propionic acid, methanol and a catalytic amount of $[MoO_2(acac)_2]$ was refluxed and values of acid numbers were calculated after different time intervals (*i.e*. after 4, 8, 10 and 12 hours. refluxing). It has been observed that the optimum yield of the ester was obtained after 8 hours refluxing time. Further refluxing of reaction mixture does not affect the yield of the ester considerably.

A comparative study of the catalytic activities of different dioxomolybdenum(VI)complexes such as $[MoO_2(acac)_2]$, $[MoO_2(sald)_2]$, $[MoO_2(oap)_2]$, $[MoO_2(ox)_2]$ and $[MoO_2(acpy)_2]$ on the esterification reactions of propionic acid with methanol and tertiary butanol, has also been carried out and the results are summarised in Table 2.

$$C_2H_5COOH + CH_3OH \xrightarrow[-H_2O]{\text{Catalyst},\Delta} C_2H_5COOCH_3 \text{ (A)}$$

$$C_2H_5COOH + C_4H_9{}^tOH \xrightarrow[-H_2O]{\text{Catalyst},\Delta} C_2H_5COOC_4H_9{}^t \text{ (B)}$$

(where acacH = acetylacetone, saldH = salicylaldehyde, oap = o-aminophenol, oxH = 8-hydroxy quinoline, acpyH = 2-acetyl pyridoxime)

It has been observed that the yields of the esters formed using homogeneous catalysts (like $[MoO_2(acac)_2]$,

* To receive any correspondence. E-mail: rkbohra@satyam.net.in

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Table 1 Esterification of propinic acid with different alcohols
(A) Without catalyst
(B) Using $[MoO_2(acac)_2]$ as catalyst[a]

$$C_2H_5COOH + ROH \xrightarrow[-H_2O]{\Delta} C_2H_5COOR$$

Entry	R	Time of refluxing/ h	(A) Acid no.[b]	(A) Yield/%[e] Acid no.[c]	(A) Dist.[d]	(B) Acid no.[b]	(B) Yield/%[e] Acid no.[c]	(B) Dist.[d]
1.	CH_3	0	736			277		
		8	389	47	45	73	74	72
2.	C_2H_5	0	735			265		
		8	535	27	26	93	65	64
3.	$C_3H_7^i$	0	662			937		
		8	596	10	09	368	61	61
4.	$C_4H_9^n$	0	749			417		
		8	584	22	20	150	64	64
5.	$C_4H_9^t$	0	493			336		
		8	465	06	06	222	34	33

[a]Molar ratio of propionic acid and catalyst = 1: 0.05.
[b]mg of KOH consumed by per g of sample.
[c]Determined by acid number.
[d]Determined by distillation.
[e]GLC results of a few reaction mixtures also exhibit almost the same yield percent as determined by the above methods 'c' or 'd'.

Table 2 Esterification of propionic acid with (A) methanol and (B) tertiary- butanol in presence of homogeneous and heterogeneous catalysts

$$C_2H_5COOH + CH_3OH \xrightarrow[-H_2O]{\text{Catalyst, }\Delta} C_2H_5COOCH_3 \quad \text{(A)}$$

$$C_2H_5COOH + C_4H_9^tOH \xrightarrow[-H_2O]{\text{Catalyst, }\Delta} C_2H_5COOC_4H_9^t \quad \text{(B)}$$

Entry	Name of catalyst	Time of refluxing/ h	(A) Acid no.	(A) Yield/%[e] Acid no.[a]	(A) Dist.[b]	(B) Acid no.	(B) Yield/%[e] Acid no.[a]	(B) Dist.[b]
1.	$[MoO_2(acac)_2]$	0	277			336		
		8	73	74	72	222	34	35
2.	$[MoO_2(sald)_2]$	0	768			507		
		8	155	80	79	209	38	38
3.	$[MoO_2(oap)_2]$	–	–			508		
		8	–	–	70	311	39	39
4.	$[MoO_2(ox)_2]$	0	279			540		
		8	184	34	35	465	14	15
5.	$[MoO_2(acpy)_2]$	0	816			895		
		8	641	21	22	609	32	32

[a]Determined by acid number.
[b]Determined by distillation of ester.
GLC results of a few reaction mixtures also exhibit almost the same yield percent as determined by the above methods 'a' or 'b'.

$[MoO_2(sald)_2]$ and $[MoO_2(oap)_2]$) are better than those obtained using heterogeneous catalysts (like $[MoO_2(ox)_2]$ and $[MoO_2(acpy)_2]$). Amongst homogeneous catalysts, the order of catalytic activity appears to be: $[MoO_2(sald)_2] \geq [MoO_2(acac)_2] > [MoO_2(oap)_2]$.

The mechanistic aspect of the above work should be enlightening, but this requires extensive work on the mechanism of reactions, which we have initiated.

The above results indicate that the dioxomolybdenum(VI) complexes act as an efficient, simple, mild and neutral catalysts for esterification reactions in anhydrous conditions. As mentioned earlier, esterification and transesterification reactions are facilitated in the presence of a number of catalysts such as 1,3-disubstituted tetraorganodistannoxanes and cyclic allylic stannane compounds.[1-3] However, compared to dioxomolybdenum(VI) complexes such catalysts are not only

expensive but the time taken to complete the reaction is also much longer (20–24 hours). On the other hand due to low cost, ease of handling and less time taken, dioxomolybdenum(VI) complexes appear to be milder and more efficient catalysts in the above reactions. The applicability of this relatively simple method may be extended for the synthesis of natural products particularly of the macrolide type by internal macrocyclic esterification of ω-hydroxycarboxylic acids. Many of these compounds possess potent antibiotic, anti-tumoral, and other types of interesting biochemical activities.[2]

Experimental

Methanol, ethanol, isopropanol, *n*-butanol and tertiary butanol (Merk) were dried before use. Propionic acid (SRL) was used after distillation. $[MoO_2(acac)_2]$ and $[MoO_2(ox)_2]$ were synthesised according to literature methods.[19,20] New dioxomolybdenum (VI) complexes of the type $[MoO_2(sald)_2]$, $[MoO_2(oap)_2]$ and $[MoO_2(acpy)_2]$ have been synthesised by the reaction of an acidified aqueous solution of $Na_2MoO_4.2H_2O$ with corresponding ligands and characterised by elemental analysis and spectral (FTIR, NMR, electronic and FAB mass) studies.[21]

A mixture of propionic acid (4.77 g, 64.35 mmol), methanol (30 ml) and catalyst $MoO_2(acac)_2$ (1.05 gm, 3.22 mmol) was refluxed for 8 hours. 5 ml of the above mixture was titrated against standard KOH solution before and after the reaction. The percentage yield of ester formed was calculated from the change in the acid number [yield % = 100- (final acid no. × 100/initial acid no.)]. Water formed during the reaction was removed azeotropically as alcohol–water mixture. The methyl propionate formed during the reaction was distilled at 79° C. Results of the above as well as other investigations are summarised in Tables 1 and 2.

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