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Olefins by Transition Metal Catalyzed Elimination Reactions from Tertiary Alcohols and Acetates

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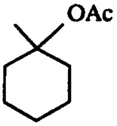
Abstract: *The elimination reaction of water or acetic acid from tertiary alcohols and acetates is catalyzed by transition metal complexes. Olefins are obtained in high yields with catalyst dependent regioselectivity. β-Cedrene **6b** can be prepared as major product from cedryl acetate **5**.*

A wide variety of methods is available for olefin formation by elimination of water or HX (X = leaving group). Many of these reactions proceed under acid catalysis[1] via carbenium ions, often giving rise to rearrangement products. Usually, the thermodynamically most stable olefins are formed preferentially. To obtain other isomers, e.g. 1,1-disubstituted alkenes, pyrolytic elimination processes[2] in the gas phase have been employed.

Only in very few cases transition metals have successfully been used to catalyze this kind of olefin forming reactions. For example, Pd(0) catalysts cause the formal elimination of acetic acid from allylic acetates to form conjugated dienes, with a π-allyl palladium complex as reactive intermediate.[3a] An analogous reaction has been reported using $Mo(CO)_6$ after treatment of allylic acetates with excess O,N-bis(trimethylsilyl)acetamide.[3b] Some heterogeneous reactions using almost stoichiometric amounts of anhydrous copper(II) sulfate[4] or ferric chloride[5] on silica gel as dehydrating agents also result in alkene formation.

As will be shown here, catalytic amounts (0.5-2.0 mol-%) of ionic or neutral transition metal complexes are sufficient to achieve elimination of water or acetic acid. In contrast to known reactions, even saturated tertiary alcohols and acetates are converted to the corresponding olefins in high yields after simple workup. Although the reaction proceeds smoothly in dioxane under reflux, it is advantageous to use a solvent of lower boiling point (Et_2O or THF) in a stainless steel autoclave, especially when volatile olefins are formed (Table 1, entry 1 - 4).



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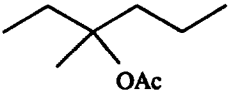

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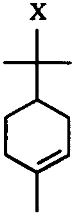
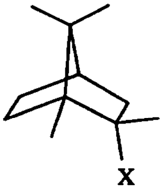
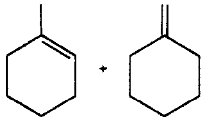
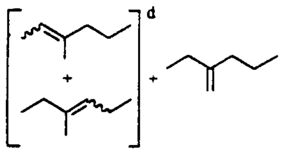
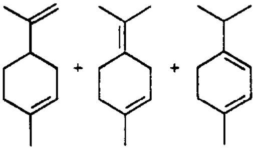
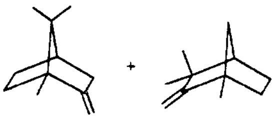


3a, X = OH
3b, X = OAc



4a, X = OH
4b, X = OAc

Table 1. Elimination Reactions of Tertiary Alcohols and Acetates

Entry	Starting Material	Conditions^{a}	Yield [%] (Conversion)^{b}	Products^{c}	(Relative Amount)
1	**1**	A (1) HOAc (10)	80 (96)		(13:1)
2	**1**	A (1) t-BuCOOH (100)	86 (100)		(19:1)
3	**2**	A (1)	98 (99)		(8:1)
4	**2**	A (1) HOAc (30)	96 (98)		(7:1)
5	**3a**	A (0.5) HOAc (20)	96 (46)		(8:5:1)
6	**3a**	B (0.5)	90 (93)		(4:2:1)
7	**3a**	C (4)	63^{e} (100)		(0.2:0.3:1)
8	**3b**	A (1)	95 (96)		(13:8:1)
9	**3b**	A (1) HOAc (30), 48 h	98 (96)		(4:4:1)
10	**4a**	A (1) HOAc (30), 48 h	87 (100)		(1.18:1)
11	**4b**	A (1)	90 (100)		(1.25:1)
12	**4b**	C (4)	83 (100)		(0.95:1)

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[a] standard reaction conditions unless otherwise stated: solvent Et_2O, 20 h, 100-110°C, amounts given in brackets (mol-%), catalysts: A = $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5CH_3)]BF_4$, B = $Mo_2(OAc)_4$, C = 50% HBF_4 in H_2O; [b] obtained by GC analysis of the product; [c] structure assignment based on comparison with authentic samples or additional ^1H-/^{13}C-NMR and mass spectral investigations; [d] mixture of regio- and E/Z-isomers; [e] two additional hydrocarbon products (26%) not identified.

The metal complexes used act as precatalysts, they are modified in the course of the reaction by the water or acetic acid (HOAc) formed. No reaction at all occurs without the precatalyst even in the presence of acetic acid or under basic conditions. Besides from $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5CH_3)]BF_4$,[6] which is superior to its synthetic precursor $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$, $Mo_2(OAc)_4$[7] can be used. The analogous $[Cr(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$ and the neutral complex $Mo(CO)_6$ that forms $Mo_2(OAc)_4$ *in situ* in the presence of acetic acid,[7] also catalyze the reaction. Yields are generally lower in the latter cases, as is the regioselectivity. In the presence of catalytic amounts (0.1 - 0.6 equivalents) of acetic acid, the rate of reaction increases, but smaller amounts of the 1,1-disubstituted olefins are formed (Table 1, entry 9). Increased steric demand of the acid (e.g. use of t-BuCOOH) has little influence on the product distribution (Table 1, entry 2).

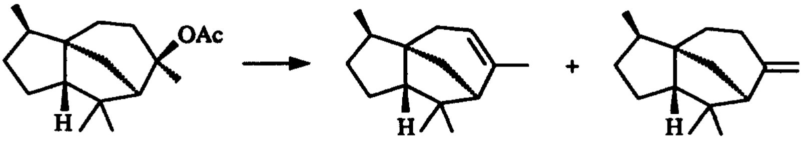
Generally, when **1** and **2** are used as substrates, a clear preference for the formation of trisubstituted olefins is observed. Even by gas phase pyrolysis of **1** at 450°C, only a 20% yield of methylene-cyclohexane was reported.[8] With **3a** and, more clearly, **3b**, the above selectivity is reversed and the geminal disubstituted terpene product limonene is preferentially formed. The tetrasubstituted olefin α-terpinolene occurs as a minor product. In contrast to the acid catalyzed reaction (Table 1, entry 7) only small amounts of the double bond migration product α-terpinene are formed in the reactions with molybdenum catalysts. Even with **4a** and **4b**, the amount of product arising from carbocationic skeletal rearrangement is smaller in the metal catalyzed reactions.

In order to investigate the preparative usefulness of the above reaction in more detail, an appropriate substrate was choosen for a study on the regioselectivity and its variability.

The tertiary cedryl acetate **5** as well as the corresponding alcohol (+)-cedrol are known to produce the tricyclic sesquiterpenoid hydrocarbon α-cedrene **6a** in the course of acid catalyzed elimination reactions.[9] Besides from **6a** naturally occurring cedrene contains minor amounts of a second isomer, β-cedrene **6b**. This compound with a 1,1-disubstituted double bond is the thermodynamically less stable elimination product of **5**. Racemic **6b** is available via total synthesis,[10] but its preparation by pyrolytic cis-elimination from tertiary and primary esters or amine oxide[11] as well as an isomerization procedure (hydrochlorination/elimination) starting from α-cedrene[12] only results in relatively low yields of cedrene mixtures. Therefore, a number of different transition metal catalysts have been tested and optimized towards a maximum yield of β-cedrene.

As can be seen from Table 2, the results obtained range from the exclusive production of α-cedrene **6a** to the formation of a mixture of the isomers with 70% β-cedrene at a conversion of 62%. This represents a synthetic improvement even in comparison with pyrolytic methods. At the moment, $Mo(CO)_6$ in the presence of acetic acid (HOAc) (Table 2, entry 8) is the most effective and selective catalyst for the preparation of **6b**. $Mo_2(OAc)_4$ results in a lower yield but comparable product ratio. In contrast to this, $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5CH_3)]BF_4$, although a very active catalyst, produces mainly or exclusively **6a**, depending on the reaction conditions. Only **6a** is also obtained with Pd/phosphite catalysts and the neutral tungsten complex[13] $(\eta^4\text{-}[R\text{-}(+)\text{-pulegone}])_2W(CO)_2$. No reaction at all occurs with $Pd(PPh_3)_4$, $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo) or $(\eta^6\text{-}C_6H_6)Mo(CO)_3$, even in the presence of acetic acid. These results demonstrate that the presence of any Pd-, Mo- or Cr-complex is not sufficient for obtaining the catalytic elimination.

Table 2. Catalyzed Elimination Reactions of Cedryl Acetate 5.

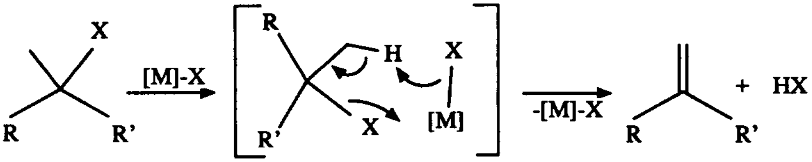


5 **6a** **6b**

Entry	Catalyst and Conditions[a]		Yield[%] (Conversion)[b]	Product Ratio[b] 6a:6b
1	HBF_4, 50% in H_2O (4)	dioxane, 1h, 100°C	93 (100)	100:0
2	A (0.1)	CH_2Cl_2, 24 h, 95°C	91 (100)	100:0
3	B (1)	Et_2O, 24 h, 100°C	91 (100)	100:0
4	$Pd(OAc)_2$ (2.5), $P(OPh)_3$ (30)	Et_2O, 24 h, 100°C	90 (5)	100:0
5	A (2), HOAc (50)	dioxane, 4h, 100°C	94 (100)	82:18
6	C (2)	THF, 48 h, 100°C	92 (100)	66:34
7	$Mo_2(OAc)_4$ (2), HOAc (15)	THF, 48 h, 110°C	75 (50)	33:67
8	$Mo(CO)_6$ (2), HOAc (15)	THF, 48 h, 110°C	97 (62)	30:70

[a] A = $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-toluene})]BF_4$, B = $(\eta^4\text{-pulegone})_2W(CO)_2$, C = $[Cr(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$, amounts given in brackets (mol-%); [b] obtained by GC and NMR analysis.

The mechanism of the reaction has not been examined in detail yet, it seems reasonable to postulate the initial formation of an acetate complex as intermediate so that the olefin could well be formed by proton transfer via a cyclic transition state similar to that found for pyrolytic cis-eliminations. This is illustrated in Scheme 1 for the formation of a 1,1-disubstituted olefin. The lability of acetate ligands on molybdenum towards ligand exchange reactions has already been demonstrated.[14] As the hydrogen transfer step is mechanistically different from the deprotonation of a carbocation and may well exhibit different geometric requirements, the different regioselectivity of both processes can be rationalized. The sensitivity towards the steric availability of the different β-hydrogens is very heterogeneous among the catalysts tested, as can especially be seen from the wide range of product ratios in Table 2. This is probably due to the influence of co-ligands remaining at the metal center and might be useful to achieve a further increase in selectivity.



Scheme 1. Proposed Mechanism of the Elimination Catalysis.

A second mechanistic possibility would be an oxidative addition of the substrate, subsequent β-H-elimination from one of the β-positions to form a metal-hydride and final reductive elimination of acetic acid or water. A related, photochemically induced C-O bond activation of an allylic acetate by a molybdenum hydride complex has recently been reported.[15] Further studies on intermediates and active catalysts are in progress.

In summary, the metal catalyzed elimination reaction has been found to produce olefins from tertiary alcohols or their acetates in high yield and under relatively mild conditions with smaller amounts of rearrangement products, compared to the reaction catalyzed by strong acids. The formation of β-cedrene **6b** as main product from cedryl acetate **5** in the presence of molybdenum catalysts is an example for an unusual regioselectivity of the reaction.

EXPERIMENTAL SECTION

NMR spectra were obtained on a Bruker AC 200 instrument. Chemical shifts are reported in ppm downfield from TMS. Multiplicities of ^{13}C-NMR signals are listed in brackets. Several instruments were used for GC-analyses with different capillary columns (respective starting materials listed in brackets): 40m PS240 (**1**, **2**, **4**), 30m Carbowax 20M (**3**) and 25m SE-54 (**5**). Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr.

Preparation of the starting materials:
All tertiary acetates used in this investigation were prepared from the corresponding tertiary alcohols and $CH_3COCl/C_6H_5N(C_2H_5)_2$ in Et_2O using a published method.[16] 1-Methyl-cyclohexan-1-ol was prepared from cyclohexanone and CH_3MgI. In a similar procedure, **4a** was made from (+)-camphor.

Preparation of the catalysts:
Most of the transition metal precatalysts were prepared by literature methods. Specific conditions were used for the following molybdenum complexes:

- $Mo_2(OAc)_4$ was obtained from $Mo(CO)_6$ (1.98 g, 7.5 mmol) in a boiling mixture of acetic acid, acetic anhydride and toluene (10 + 7 + 1 ml). After 24 h the product was filtered off, washed with CH_2Cl_2 and dried under high vacuum (yield: 60%; Anal. Calcd. for $C_8H_{12}Mo_2O_8$: C, 22.45; H, 2.83. Found: C, 22.31; H, 2.90).
- $Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5CH_3)BF_4$ was prepared from $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$ by heating a suspension in toluene to reflux for 96 h under argon. The green η^6-toluene complex was obtained in 96% yield. IR (KBr): 3075, 1438, 1390, 1050, 832 cm^{-1}; ^{1}H-NMR (200.1 MHz, CD_2Cl_2): δ 6.31 (d, $^3J_{HH}$ = 5.6 Hz, 2H), 6.22-6.06 (m, 3H), 5.61 (s, 7H), 2.26 (s, 3H); ^{13}C-NMR (50.1 MHz, CD_2Cl_2): δ 115.6 (1C, s), 99.7 (2C, d), 97.2 (2C, d), 96.2 (1C, d), 86.4 (7C, d), 20.6 (1C, q); Anal. Calcd. for $C_{14}H_{15}BF_4Mo$: C, 45.94; H, 4.13; Mo, 26.21. Found: C, 45.79; H, 4.14; Mo, 26.10.

Typical procedures for the elimination reaction:

- <u>in dioxane</u> (Table 2, entry 5): To a solution of 1.32 g (5 mmol) of cedryl acetate **5** and acetic acid (150 mg, 2.5 mmol) in 25 ml of absolute, air-free dioxane, 37 mg (0.1 mmol) of the catalyst $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5CH_3)]BF_4$ were added. The mixture was heated under reflux and argon with stirring, whereupon the greenish suspension turned clear yellowbrown. The reaction was monitored by TLC. When no more starting material could be detected after about 3 h, heating was continued for an additional hour. The mixture was then cooled to room temperature and most of the dioxane removed under reduced pressure. The residue was diluted with 30 ml of Et_2O, washed with sat. $NaHCO_3$ solution, water, sat. NaCl solution and dried over $MgSO_4$. After evaporation of the solvent a clear, colorless oil was obtained (960 mg, 94%). According to GC analysis it contained only α- and β-cedrene (ratio 82:18).

- in diethyl ether (Table 1, entry 1): 10 mmol (1.56 g) of the tertiary acetate **1** in 30 ml of Et_2O, the catalyst (37 mg, 0.1 mmol) and acetic acid (60 mg, 1.0 mmol) were heated to 100-110°C and magnetically stirred in a 100 ml stainless steel autoclave with a glass insert for 20 h under an inert atmosphere of argon. The reaction mixture was then extracted with sat. $NaHCO_3$ solution to remove the catalyst and acetic acid, the ether layer was dried over $MgSO_4$, the solvent removed by careful distillation using a 30 cm Vigreux column and the products distilled. The C_7-olefins were obtained in 80% yield (conversion: 96%, ratio endo-:exo-olefin = 93:7).

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