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# Molybdenum Catalyzed Dehydration of Tertiary Alcohols to Olefins

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# MOLYBDENUM CATALYZED DEHYDRATION OF TERTIARY ALCOHOLS TO OLEFINS

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**Abstract :** Molybdenyl (VI) acetylacetonate is shown to be an effective catalyst for easy conversion of tertiary alcohols to the corresponding olefins in high yields.

Elimination reactions of alcohols and acetates to olefins offer a stimulating challenge for organic chemists inspite of a number of methods being available. Very few methods have been reported using transition metal catalysts[1] for this kind of olefin forming reactions. Some heterogeneous as well as homogeneous reactions using almost stoichiometric amounts of dehydrating agents such as anhydrous Cu(II) sulfate[2], ferric chloride on silica gel[3], $SOCl_2/Et_3N$[4], TsOH/PhH[5] or $BF_3/OEt_2$[6] also result in alkene formation.

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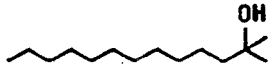
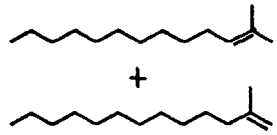
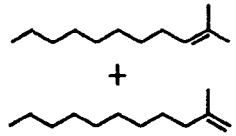
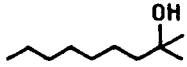
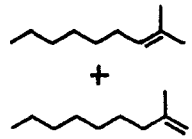
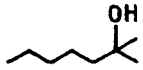
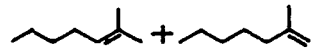
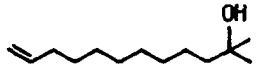
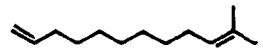
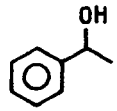
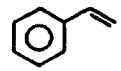
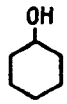
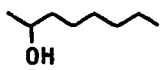
**TABLE**

**MOLYBDENUM CATALYZED DEHYDRATION OF TERTIARY ALCOHOLS TO OLEFINS**

| Entry | Substrate | Products | % Yield[a] | (Ratio of products) |
|---|---|---|---|---|
| 1 |  |  | 92 | (50:50) |
| 2 |  |  | 90 | (45:55) |
| 3 |  |  | 88 | (52:48) |
| 4 |  |  | 86 | (45:55) |
| 5 |  |  | 85 | |
| 6 |  |  | 65 | |
| 7 |  | No reaction [b] | | |
| 8 |  | No reaction [b] | | |

a) Characterized by NMR and Mass.

b) GC analysis of the product.

The low cost and ease of handling molybdenum catalysts prompted us to examine such a possibility with molybdenyl acetylacetonate complex.

We report here the molybdenyl acetylacetonate catalyzed dehydration reactions of tertiary alcohols to the corresponding olefins in high yields. Same results are obtained with molybdenum(III) acetylacetonate as well. Results of this operationally convenient procedure with different substrates are summarized in Table 1. The catalyst is effective towards tertiary and benzylic alcohols. But, the primary and secondary acyclic and cyclic alcohols were recovered as such after the reaction.

In summary, these dehydration reactions are rapid, cheap and clean.

**General procedure**

To a solution of 0.428 g (2 mmol) of tertiary alcohol (Table 1, entry 1) in 25 ml of absolute air-free dioxane, 0.065 g (0.2 mmol) of the catalyst was added. The mixture was heated under reflux and argon with stirring whereupon the orange-yellow suspension turned blue. After 6h, 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 ether, washed with saturated sodium bicarbonate solution, water, saturated sodium chloride solution and dried over $Na_2SO_4$. After evaporation, a clear colourless oil was obtained (0.360 g, 92%).

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