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# The Addition Reaction of Acetals(Aldehydes) to Simple Olefins by the Use of a New Catalyst System

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In the coexistence of catalytic amounts of trimethylsilyl chloride and tin(II) chloride with a stoichiometric amount of lithium perchlorate, acetals react with simple 1,1-di-substituted olefins to afford the corresponding adducts in good yields. Aldehydes also react with the olefins to form the Prins-type reaction products by further addition of alkoxy trimethylsilane to the above catalyst system.

During the last few decades, acetals have been frequently employed not only for the protection of carbonyl groups but also as electrophiles in various cross-coupling reactions, especially in carbon-carbon bond forming reactions.1) Among them, the reaction of acetals with olefins is one of the most useful methods, however, the conventional methods require rather drastic conditions and yields were relatively low because of side reactions such as eliminations, isomerizations or polymerizations of the products.2)

In the previous paper,3) we have shown that in the coexistence of catalytic amounts of trimethylsilyl chloride and tin(II) chloride, activated olefins such as 3,4-dihydro-2H-pyran, vinyl ether and styrene react with acetals to afford the corresponding adducts in good yields under extremely mild conditions. In this communication, we would like to describe further extension of the above reaction by the use of a new catalyst system: The reaction of acetals with simple olefins and the Prins-type reaction of aldehydes with olefins are performed under mild conditions in the coexistence of catalytic amounts of trimethylsilyl chloride, tin(II) chloride with a stoichiometric amount of lithium perchlorate.

First, the reaction of benzaldehyde dimethylacetal($\underline{1}$) with 2-methyl-1-pentene ($\underline{2}$) was chosen as a model and several catalysts and reaction conditions were examined. It was found that the reaction proceeded at 0 °C in dichloromethane by the combined use of tin(II) chloride and trimethylsilyl chloride to afford the corresponding addition product ($\underline{3}$) and homoallyl ether($\underline{4}$), produced via the elimination of methanol from $\underline{3}$, in 15% and 35% yields, respectively. The effectiveness of the combination of two compounds, tin(II) chloride and trimethylsilyl chloride, in the above reaction is obvious since neither tin(II) chloride nor trimethylsilyl chloride promoted this reaction.4) Further, yield was remarkably improved by the addition of lithium perchlorate5) to the above catalyst system, and $\underline{3}$ and $\underline{4}$ were obtained in 10% and 72% yields, respectively (Table 1).

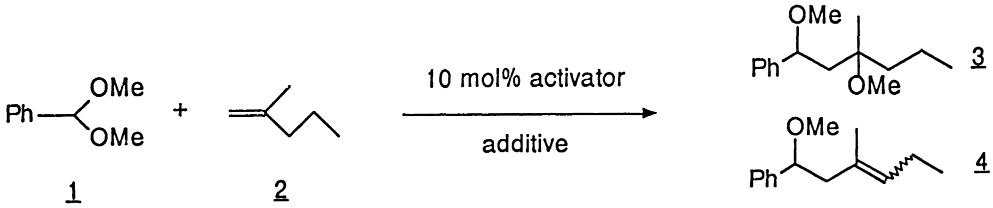
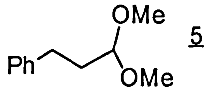
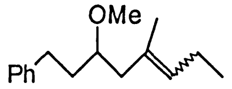
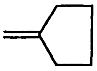
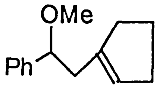
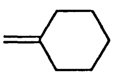
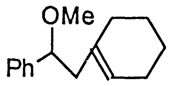
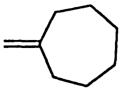
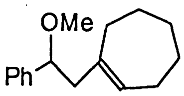
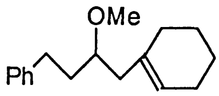
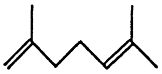
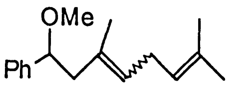


Table 1. The effect of catalysts

| Activator | Additive (eq.) | Yield ($\underline{3}$+$\underline{4}$) / % |
|---|---|---|
| $SnCl_2$ | none | 0 |
| TMSCl | none | 0 |
| TMSCl+$SnCl_2$ | none | 50 (15+35) |
| TMSCl+$SnCl_2$ | $LiClO_4$ (0.5) | 59 (57+ 2) |
| TMSCl+$SnCl_2$ | $LiClO_4$ (3.0) | 82 (72+10) |
| TMSCl+$SnCl_2$ | $LiClO_4$ (5.0) | 73 (59+14) |

Several examples of the present reaction are demonstrated in Table 2. Simple 1,1-di-substituted olefins smoothly reacted with various acetals to afford the corresponding adducts in good yields. mono-Substituted, 1,2-di-substituted or tri-substituted olefins did not react under these reaction conditions and the starting materials were recovered. In the case of diene $\underline{7}$, the acetal regio-selectively reacted at the terminal di-substituted olefin part.

Table 2. The reaction of acetals with olefins[a)]

| Acetal | Olefin | Product | Yield / % |
|---|---|---|---|
| 1 | 2 | 4 (72%, E:Z=81:19)<br>3 (10%) | 82 |
|  | 2 |  (E:Z=73:27) | 56 |
| 1 |  |  | 60 |
| 1 |  6 |  | 82 |
| 1 |  |  | 66 |
| 5 | 6 |  | 62 |
| 1 |  7 |  (E:Z=75:25) | 30 |

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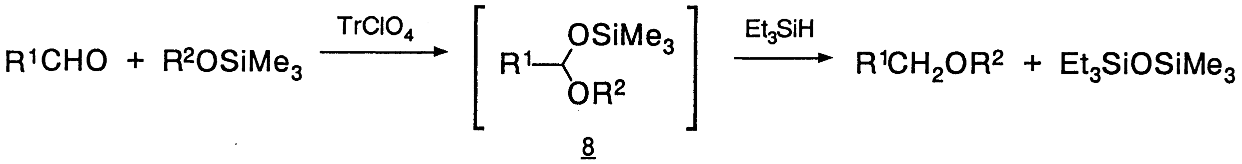
a) The reaction was carried out in the coexistence of TMSCl and $SnCl_2$ (10 mol%) with $LiClO_4$ (300 mol%).

Next, we attempted to apply this catalyst system to the reaction of aldehydes with olefins. We have already reported that in the presence of a catalytic amount of trityl perchlorate, aldehydes react with alkoxy trimethylsilane and triethylsilane to afford the corresponding unsymmetrical ethers in good yields.[6] The mechanism of this reaction is considered that hemiacetal-type compounds (8) were initially generated by the addition of alkoxy trimethylsilane to aldehydes and 8 were in turn readily reduced with triethylsilane to form unsymmetrical ethers. Therefore, it was suggested that when the intermediary hemiacetal is generated, the direct addition of aldehydes to olefins, the Prins-type reaction, would be achieved by the promotion of the above mentioned catalyst system.



Based on this consideration, the reaction of benzaldehyde with 2-methyl-1-pentene(2) was tried by further addition of methoxy trimethylsilane to catalytic amounts of trimethylsilyl chloride and tin(II) chloride with a stoichiometric amount of lithium perchlorate. As expected, the corresponding Prins-type addition product was obtained in 72% yield. Several examples of this novel Prins-type reaction are demonstrated in Table 3.

A typical procedure is described for the reaction of benzaldehyde with methylenecyclohexane(6); to a mixture of tin(II) chloride (0.049 mmol) and lithium perchlorate (1.48 mmol) in dichloromethane (2 ml) was added trimethylsilyl chloride (0.049 mmol) in dichloromethane (1 ml) at 0 °C. The mixture was stirred for 5 min, followed by addition of 6 (0.50 mmol) in dichloromethane (2 ml) at the same temperature. Stirring was continued for additional 2 h, then aqueous sodium hydrogen carbonate was added and aqueous layer was extracted with dichloromethane. The organic layer was dried and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to yield 1-(2-methoxy-2-phenylethyl)-cyclohexene (78%).

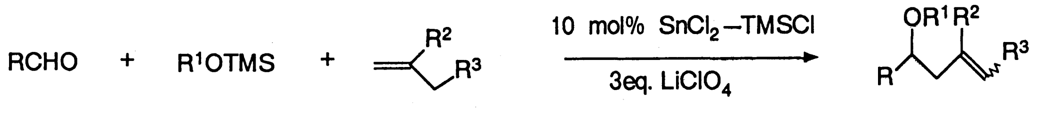


Table 3. The Prins-type reaction

| R | $R^1$ | Olefin | Yield / % |
|---|---|---|---|
| Ph | Me | 2 | 71 |
| Ph | Me | 6 | 72 |
| Ph | Bn | 6 | 77 |
| $Ph(CH_2)_2$ | Me | 2 | 58 |
| $Ph(CH_2)_2$ | Bn | 6 | 60 |

Thus, the addition reaction of acetals to simple 1,1-disubstituted olefins was performed by the use of a novel catalyst system, a catalytic amount of trimethylsilyl chloride and tin(II) chloride with a stoichiometric amount of lithium perchlorate. Further, the Prins-type reaction of aldehydes with olefins was successfully carried out by the use of the above mentioned catalyst in the coexistence of alkoxy trimethylsilane. Concerning the Prins reaction, it was reported that several side reactions frequently occurred because of strongly acidic reaction conditions and an aldehyde is generally limited to formaldehyde.7) It should be noted that, according to the present procedure, both aliphatic and aromatic aldehydes reacted with various olefins to afford the corresponding adducts under extremely mild conditions.

## References

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