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ADDITION OF ORGANOALUMINATES TO ACROLEIN OR METHYL VINYL KETONE IN THE PRESENCE OF A STOICHIOMETRIC AMOUNT OF COPPER(II) ACETATE. A CONVENIENT ROUTE TO KETONES AND ALDEHYDES FROM OLEFINS VIA HYDROALUMINATION

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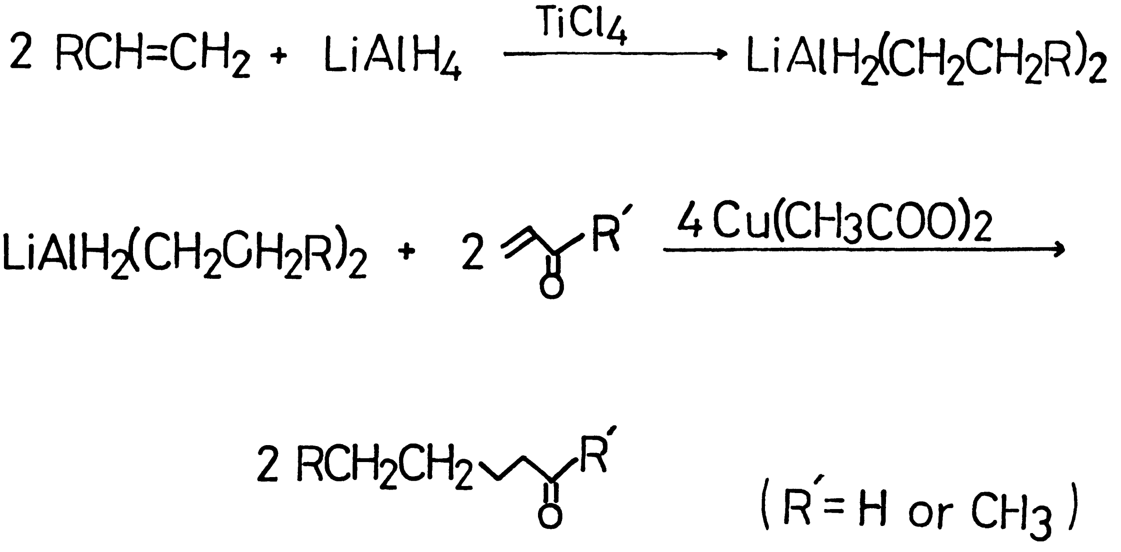
Organoaluminates, readily prepared by $TiCl_4$-catalyzed hydroalumination of olefins with $LiAlH_4$, react with acrolein or methyl vinyl ketone in the presence of a stoichiometric amount of copper(II) acetate to give the 1,4-addition product in excellent yield. The facile reactions offer a convenient method for the preparation from olefins of the corresponding aldehydes or ketones.

In our continued efforts to apply recently developed $TiCl_4$-catalyzed hydroalumination reactions in organic syntheses,[1)] we have now developed a convenient procedure for converting α-olefins to the corresponding aldehydes or ketones.

In preliminary studies, we examined the reaction of lithium tetraalkylaluminates ($LiAlR_4$) with methyl vinyl ketone in the presence of nickel acetylacetonate[2)] or a small amount of oxygen,[3)] expecting the formation of the 1,4-addition product.[4)] Disappointingly, the reaction gave only traces of the expected product. However, the recent finding that $LiAlR_4$ reacts with $Cu(OAc)_2$ producing an alkyl copper intermediates[5),6)] encouraged us to investigate the reaction of $LiAlR_4$ with methyl vinyl ketone or acrolein in the presence of $Cu(OAc)_2$, since it is well known that organocopper compounds add to α,β-unsaturated carbonyl compounds in the 1,4-position.[7)]

We now wish to report that methyl vinyl ketone or acrolein readily undergoes 1,4-addition by organoaluminum compounds in the presence of a stoichiometric amount of $Cu(OAc)_2$.

$LiAlR_4$ reacted with methyl vinyl ketone or acrolein in the presence of a stoichiometric amount of copper(II) acetate under mild conditions to give the 1,4-addition product. However, the yield of the product could not be made to exceed 50% in spite of various efforts. This led us to assume that only two of the alkyl groups of $LiAlR_4$ participate in the reaction. Fortunately, the difficulty is overcome by conducting the reaction with $LiAlR_2H_2$. Thus, hydroalumination of 2 equiv of olefin with 1 equiv of $LiAlH_4$ followed by treatment with methyl vinyl ketone or acrolein in the presence of 4 equiv of $Cu(OAc)_2$ gave the corresponding 1,4-addition product in improved yield.



As shown in Table 1, this operationally simple one-pot reaction offers an effective method for conversion of α-olefins into the corresponding ketones or aldehydes. It is noteworthy that this new ketone synthesis made it possible to prepare 2,15-hexadecanedione, known as a key intermediate for synthesis of muscone by the Stoll method,8) by a one-pot reaction from 1,7-octadiene easily obtained by the platinum catalyzed dimerization of butadiene.9),10)

It has been reported that BR_3, obtained via hydroboration of olefins, participates in a facile 1,4-addition to acrolein or methyl vinyl ketone producing the corresponding aldehydes11) and ketones,12) respectively. However, in these reactions only one of the three alkyl groups on boron are used, and, moreover, in the case of α-olefins, the product contains a considerable amount of by-product arising from a secondary boron derivative. In the present reaction, aldehydes and ketones were obtained in better yields from olefins than by hydroboration methods and in a high state of purity. Especially noteworthy here is the simple selective introduction of the carbonyl group to one of the double bonds of a nonconjugated diolefin, which appears to be impossible by hydroboration methods.

An organocopper(II) compound, formed by the reaction of copper(II) acetate and the organoaluminate, seems to play an important role in these reactions, since copper(I) compounds, such as CuCl or CuI, were ineffective.

Table 1

Conversion of Olefins into 3-Alkylpropanals or 4-Alkyl-2-butanones.

Olefin	Product[a,b]	Yield[c] %
1-Pentene[d]	Octanal	57
	2-Nonanone	64
1-Hexene[d]	Nonanal	57 (45)
	2-Decanone	67 (54)
1,4-Hexadiene[e]	7-Nonenal	63 (54)
	8-Decen-2-one	65 (58)
2-Methyl-1,5-hexadiene[e]	8-Methyl-8-nonenal	51
	9-Methyl-9-decen-2-one	61
4-Vinyl-1-cyclohexene[d]	5-(3-Cyclohexenyl)pentanal	62
	6-(3-Cyclohexenyl)hexan-2-one	71
1,7-Octadiene[d]	2,15-Hexadecanedione	(56)

[a] Identified by IR, GLC, ^{1}H NMR and mass spectra. [b] Other products are mainly the reducion products of olefin. [c] GLC yield (isolated yield) and based on olefin. [d] Hydroalumination reaction was carried out at room temperature for 8h. [e] Hydroalumination reaction was carried out at 23 °C for 1.5h (2-methyl-1,5-hexadiene) and 2h (1,4-hexadiene) ; too long reaction time resulted in formation of dihydroalumination products.

The following experiments exemplify typical procedures for conversion of α-olefins to the corresponding ketones or aldehydes.

For 8-decen-2-one : after reaction of 1,4-hexadiene (1.2 g, 14 mmol) and $LiAlH_4$ (30 ml of 0.24 molar solution in THF, 7.2 mmol) in the presence of $TiCl_4$ (0.05 g, 0.3 mmol) for two hours at 23 °C, the reaction mixture was cooled to -78 °C and then $Cu(OAc)_2$ (5.2 g, 28 mmol) and methyl vinyl ketone (4.0 g, 57 mmol) were added. The reaction mixture was stirred for 1h at that temperature, then CH_3COOH (1.7 g, 28 mmol) was added in one portion by a syringe.[13)] After bringing to room temperature over about one hour, 10 ml of 1N hydrochloric acid was added and the aqueous layer was separated and extracted with ether several times. The combined THF and ether layers were washed with dilute aqueous NaOH solution and then brine, and dried over anhydrous magnesium sulfate. Distillation under vaccum gave 1.3 g (58% yield) of 8-decen-2-one, b.p. 90-92°C/9 mmHg.

For nonanal[14)]: after hydroalumination of 1-hexene (0.8 g, 9.4 mmol) with $LiAlH_4$ (20 ml of 0.23 molar solution in THF, 4.6 mmol), the reaction mixture was cooled to -78°C and $Cu(OAc)_2$ (3.4 g, 19 mmol) was added. The reaction mixture was stirred for 1h at that temperature and a mixture of acrolein (2.1 g, 37 mmol) and acetic acid (1.1 g, 19 mmol) in 10 ml of THF was added dropwise over about 30 minutes.

After gradually bringing the reaction mixture to room temperature, the usual work-up gave 0.6 g (45 % yield) of nonanal, b.p. 86.5-88.5°C/9 mmHg.

The present procedure is so simple and so general that it should provide a convenient route to aldehydes or ketones from olefins.

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13) When the reaction mixture was not quenched with acetic acid, yield of the ketone decreased.

14) This procedure is a little different from the reaction with methyl vinyl ketone. The same procedure used in the case of methy vinyl ketone gave the aldehydes in lower yield (around 30%) presumably because of the tendency of acrolein to polymerize.

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