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COUPLING REACTIONS OF ORGANOALUMINATES WITH ACID CHLORIDES OR ANHYDRIDES CATALYZED BY COPPER COMPOUNDS. A CONVENIENT ROUTE TO KETONES FROM 1-OLEFINS VIA HYDROALUMINATION

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Hydroalumination of 1-olefins with lithium aluminum hydride followed by treatment with acid chlorides or anhydrides in the presence of a catalytic amount of copper(I) chloride resulted in coupling. This new development provides a simple and general method for the synthesis of ketones.

Many reports on the synthesis of ketones from organometallic compounds and carboxylic acid derivatives have appeared.1) In the case of organoaluminum compound reagents, the following facts have been revealed:2),3) 1) trialkyl aluminum compounds cannot afford a smooth ketone synthesis because the initial aluminum-carbon bond reacts too vigorously, leading to additional reaction between the ketone and the aluminum trialkyls, 2) in ketone syntheses via dialkyl aluminum chloride only one of the alkyl groups on the aluminum is utilized, and 3) the monoalkyl aluminum dichlorides can be smoothly converted into ketones by reaction with acid chlorides. Taking these facts into consideration, it is recommended that for ketone syntheses, AlR_3 or AlR_2Cl should be converted into $AlRCl_2$ prior to treatment with acid chloride.3) Ketone synthesis using $AlRCl_2$ seems to be highly attractive because the reaction proceeds smoothly under mild conditions giving ketones in excellent yields, and, moreover, the reaction proceeds satisfactorily even when the acyl halide contains functional groups that are sensitive to nucleophilic attack. However, hitherto, impracticability of preparing various organoaluminum compounds by simple methods appears to have limited the availability of this reaction, and the reaction was only carried out using readily obtained compounds such as CH_3AlCl_2 and $C_2H_5AlCl_2$.2)

The recently developed hydroalumination reaction catalyzed by titanium complexes4) makes many organoaluminum compounds readily available for organic syntheses, and therefore renews interest in ketone synthesis via organoaluminum compounds. Thus, we commenced a study on the synthesis of ketones via hydroalumination of olefins. In preliminary studies, acetyl chloride was treated with $Al(C_6H_{13})Cl_2$, obtained by the $TiCl_4$-catalyzed reaction of $AlHCl_2$ and 1-hexene in tetrahydrofuran.5) Contrary to expectation, the reaction did not proceed. This unreactivity is thought to be due to coordination of the organoaluminum compounds with THF. In this light, it was actually found that even $Al(C_2H_5)_3$ did not react with acetyl chloride in THF at room temperature.

Fortunately, however, in part of our study on the carbon-carbon bond forming reaction using organoaluminum compounds,[6)] we discovered that various organoaluminates prepared by hydroalumination of 1-olefins with $LiAlH_4$ react rapidly with acyl halides or acid anhydrides in the presence of transition metal complexes to give ketones in fair to excellent yields.
The results of the coupling reaction of $LiAl(C_6H_{13})_4$ with acetic anhydride in the presence of catalytic amounts of transition metal complexes, which are shown in Table 1, demonstrate that various transition metal complexes are effective catalysts for this reaction, copper compounds being especially effective.

Table 1. YIELDS OF 2-OCTANONE BY THE REACTION OF $LiAl(C_6H_{13})_4$ WITH ACETIC ANHYDRIDE IN THE PRESENCE OF VARIOUS CATALYSTS

Catalyst	Yields of 2-octanone[a] %
without catalyst	trace
CuCl	40
CuBr	38
CuI	30
$CuCl_2$	40
$Cu(OAc)_2$	35
$FeCl_2$	30
$CoCl_2$	30
$[Rh(CO)_2Cl]_2$	25

[a] Yield by GLC analysis and based on 1-hexene.

Table 2 summarizes the results of the reaction of various organoaluminates and acid halides or anhydrides in the presence of CuCl. Reactions proceeded satisfactorily giving the coupling products in fair to excellent yields. Though products isolated by distillation were more than 99% pure when acid anhydrides were used as reagent, products of reactions with non-aromatic acyl chlorides contained unidentified products up to a few per cent. Thus it is recommended that acid anhydrides are used instead of acid chlorides in these reactions.

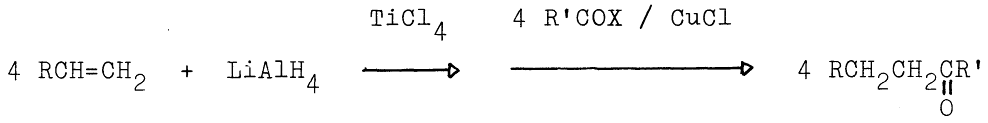
The characteristics of the present ketone syntheses are as follows.

1) As the starting materials are olefins, the present procedure is clearly a general method for the synthesis of ketones.[7)]
2) The present reaction is an operationally-simple one-pot reaction.
3) Introduction of the acyl group selectively to one of the double bonds of a diolefin is possible as shown in entrys 9-13 in Table 2.

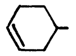
4) The reaction proceeds similarly with acyl halides containing functional group such as Cl or $CH_3OC(O)-$ as shown in entrys 6 and 8.

It was found only traces of ketone were obtained when an equimolar amount of radical scavenger (diphenylpicrylhydrazyl) versus CuCl was added to the system. This finding strongly suggests a free radical mechanism for these coupling reactions, as was proposed for the transition metal compound promoted coupling reactions of Grignard reagents with acyl halides.[8)]

Table 2



$$4\ RCH{=}CH_2 + LiAlH_4 \xrightarrow{TiCl_4} \xrightarrow{4\ R'COX\ /\ CuCl} 4\ RCH_2CH_2\underset{\overset{\|}{O}}{C}R'$$

Entry	R in olefin $RCH{=}CH_2$	R' in acid derivative R'COX	Isolated yield[a] X = Cl %	Isolated yield[a] X = OCOR' %
1	H	Ph	65	
2	$n\text{-}C_4H_9$	CH_3	$(39)^b$	$(40)^b$
3		C_2H_5	57^c	65
4		$i\text{-}C_3H_7$	66^c	76
5		$n\text{-}C_4H_9$	70^c	63
6		$CH_3O\underset{\overset{\|}{O}}{C}CH_2CH_2$	36	
7		Ph	71	
8		p-ClPh	52	
9	$CH_3CH{=}CHCH_2$	CH_3		$(39)^{b,d}$
10	$CH_2{=}C(CH_3)CH_2CH_2$	CH_3		$(42)^{b,e}$
11		CH_3		$(43)^{b,f}$
12		C_2H_5		59^g
13		$n\text{-}C_3H_7$		62^h

[a] All products gave satisfactory spectral data. Characteristic NMR signals and b.p. of several compounds are shown in notes d-h. [b] GLC analysis. [c] Product contains a few per cent unidentified by-products. [d] b.p. 87 °C/35 mmHg, NMR (C_6D_6) δ 5.37(m,2H,olefinic), 2.10(t,2H,$CH_2C{=}O$). [e] b.p 87°C/20 mmHg, NMR (C_6D_6) δ 4.72(s,2H,olefinic), 2.13(t,2H,$CH_2C{=}O$), 1.81(s,3H,$CH_3C{=}O$), 1.65 (s,3H,$CH_3\text{-}C{=}$). [f] b.p. 75 °C/6 mmHg, NMR (C_6D_6) δ 5.63(s,2H,olefinic).
[g] b.p. 76 °C/5 mmHg, NMR (CCl_4) δ 5.58(s,2H,olefinic), 2.35(m,4H,$CH_2\underset{\overset{\|}{O}}{C}CH_2$), 1.0 (t,3H,$CH_3$).
[h] b.p. 77 °C/4 mmHg, NMR (CCl_4) δ 5.57(s,2H,olefinic), 2.30(m,4H,$CH_2\underset{\overset{\|}{O}}{C}CH_2$), 0.9 (t,3H,$CH_3$).

A typical procedure is illustrated by the reaction of valeric anhydride with lithium tetrahexyl aluminate. $TiCl_4$ (0.08 g, 0.45 mmol) was added to a mixture of $LiAlH_4$ (30 ml of 0.28 M solution in THF, 8.4 mmol) and 1-hexene (2.5 g, 30 mmol). After 2h reaction at 30°C valeric anhydride (7.1 g, 38 mmol) and CuCl (0.4 g, 4 mmol) were added. The exothermic reaction occured instantaneously. The reaction mixture was stirred at 30°C for 2h, during which time metallic copper appeared. After hydrolysis by dilute hydrochloric acid, the THF layer was separated and the aqueous solution was extracted with 10 ml of ether. The combined THF and ether layers were washed with 1N NaOH and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled to give 4.1 g of 5-undecanone.

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