Tetrahedron Letters,Vol.31,No.3,pp 323-324,1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

ORGANOALUMINUM PROMOTED CONVERSION OF ALDEHYDES TO METHYL KETONES

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Summary: The conversion of aromatic aldehydes to the corresponding methyl ketones has been accomplished with the use of the organo-aluminum aryloxide compound, $AlMe_2(BHT)(OEt_2)$.

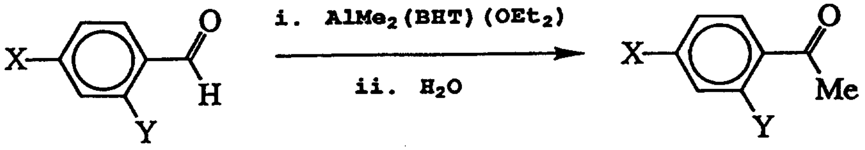
The reaction of aldehydes with organo-aluminum compounds has been little studied due to the complex mixture of products normally formed.[1] Although alkyl addition and reduction are the primary reactions observed, many minor secondary reactions have been reported,[2] none of which have been in sufficiently high yield to be synthetically useful. We report here the aluminum assisted conversion of aromatic aldehydes to their corresponding methyl ketones via a novel hydride-methyl exchange reaction.

Addition of excess Et_2O to an equimolar mixture of $AlMe_3$ and BHT-H (BHT-H = 2,6-di-tert-butyl-4-methylphenol) results in the isolation of $AlMe_2(BHT)(OEt_2)$ (**1**), as a white crystalline solid.[3]

Treatment of benzaldehyde with 1.5 equivalents of **1** in toluene at room temperature gives, after hydrolysis, acetophenone in quantitative yield.[4] Listed in Table 1 are the yields and reaction times for benzaldehyde and substituted benzaldehydes as well as the effects of varying the aldehyde to aluminum ratio. Clearly a minimum of 1.5 equivalents of **1** are required for the reaction to proceed to completion. We propose therefore that one molecule of **1** is required for the coordination of the aldehyde, while a second equivalent of **1** acts as as the methyl source for two aldehyde to ketone conversions. The initial substitution of Et_2O resulting in the formation of the aldehyde complex is indicated by the presence of an orange-red colored solution. If the reaction is carried out in pentane the aldehyde adduct is insoluble and can be isolated quantitatively. The conversion of the aldehyde adduct to the yellow-brown methyl ketone complex is supported by the stoichiometric isolation of the this complex, in addition to a mixture of aluminum hydride containing products, from the reaction mixture, prior to hydrolysis. We have previously isolated the acetophenone complex, $AlMe_2(BHT)[O{=}C(Me)Ph]$, by the direct combination of **1** with acetophenone.[5]

Work is currently underway to explore the mechanism and generality of this reaction.

Table 1. Aldehyde to methyl ketone conversion



Entry	X	Y	1:Aldehyde	Time	% Yield[a]
1	H	H	1	1.5 h	72[b]
2	H	H	1.5	1.5 h	100
3	H	H	2	1 h	100
4	Me	H	1.5	1.5 h	100
5	H	Me	1.5	12 h	57[b]
6	Cl	H	1.5	45 min	100
7	NO_2	H	1.5	≈20 min	84

[a] As determined by GC by comparison with authentic samples.

[b] Unreacted aldehyde the only other product observed.

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4. To AlMe$_2$(BHT)(OEt$_2$) (1.5 g, 4.3 mmol) in toluene (20 mL) was added the aldehyde (2.8 mmol), under a nitrogen atmosphere. An orange color formed immediately which changed to yellow-brown as the reaction proceeded. The reaction mixture was then hydrolyzed and the aqueous layer washed with Et$_2$O. The combined organic extracts were concentrated and their content determined by G.C. and ^{1}H NMR. The aldehydes may be separated from the BHT-H present in the organic phase by column chromotography.
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(Received in USA 16 October 1989)