

REACTION OF ORGANOALUMINATES WITH LEAD(IV) ACETATE.
A CONVENIENT ROUTE FROM 1-ALKENES TO PRIMARY ALKYL
ACETATES VIA HYDROALUMINATION REACTIONS

Fumie SATO*, Yoshikuni MORI, and Masao SATO
Department of Chemical Engineering, Tokyo Institute
of Technology, Meguro, Tokyo 152, Japan

Hydroalumination of 1-alkenes with lithium aluminum hydride by catalysis of titanium tetrachloride followed by treatment with lead(IV) acetate was found to be a convenient method for the preparation of primary alkyl acetates.

There appear presently to be only a few direct methods available for preparation of primary alkyl esters from 1-olefins. Masuda and Arase have shown that hydroboration of 1-olefins followed by treatment with lead(IV) acetate affords primary alkyl acetates with a considerable amount of secondary acetate in 50 to 60% total yields.¹ On the other hand, Suzuki and his co-workers found that a mixture of alkyl acetates was formed in 50 to 70% yield based on trialkylborane by an anodic oxidation of the compound in acetic acid-sodium acetate solution.² In comparison with these two methods, the hydroboration-mercuration-iodination reaction (Larock's method) gave mainly primary alkyl acetates in high olefin-based yields,³ and this procedure seems the most favorable method available so far for the preparation of primary alkyl acetates from 1-olefins.

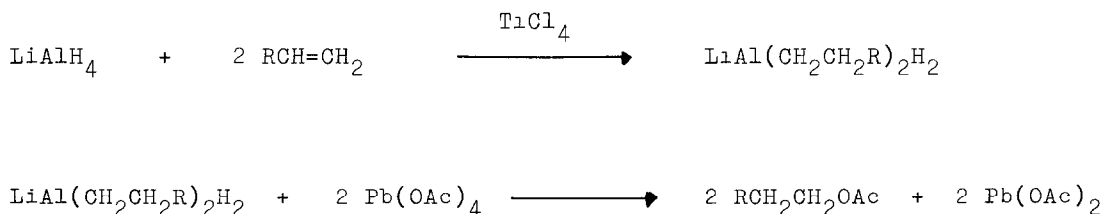
The recently developed facile addition of the aluminum-hydrogen bond to olefins by catalysis of titanium compounds makes organoaluminum complexes as readily available as the corresponding organoboranes.⁴ In our continuous efforts to apply these new hydroalumination reactions in organic syntheses,⁵

we have now developed a convenient procedure for converting 1-olefins to the corresponding primary alkyl acetates via hydroalumination followed by treatment with lead(IV) acetate.

In preliminary studies, the reaction of LiAlR_4 , obtained by TiCl_4 -catalyzed reaction of 1 equiv of LiAlH_4 with 4 equiv of olefin, with $\text{Pb}(\text{OAc})_4$ was examined. The reaction proceeded readily giving alkyl acetate, however, olefin-based yields were below 50%, in spite of considerable experimental effort. These results indicated that only two of the alkyl groups of LiAlR_4 could participate in the reaction. This difficulty was overcome by carrying out the reaction with LiAlR_2H_2 , prepared by reaction of 1 equiv of LiAlH_4 with 2 equiv of olefin.

The following procedure for the preparation of 2-(3-cyclohexenyl)ethyl acetate is representative. After reaction of 4-vinyl-1-cyclohexene (0.91g, 8.5 mmol) and LiAlH_4 (20 ml of 0.22 molar solution in THF, 4.4 mmol) in the presence of TiCl_4 (0.05 g, 0.3 mmol) for 5h at room temperature, the reaction mixture was cooled to -78°C and $\text{Pb}(\text{OAc})_4$ (5.0 g, 11 mmol) was added. The reaction mixture was brought to room temperature over about 2h and then stirred for one more hour. After the usual workup 0.9 g (64% yield based on the olefin) of 2-(3-cyclohexenyl)ethyl acetate was isolated by distillation under vacuum, b.p. $67-70^\circ\text{C}/3-4$ mmHg. In a similar manner, various primary alkyl acetates were obtained in good yields and in a high state of purity as shown in Table 1.

The results of the reaction of LiAlR_2H_2 with various amounts of $\text{Pb}(\text{OAc})_4$ revealed that high yields of acetate were realized by using greater than equimolar amounts of lead(IV) acetate versus olefin, suggesting that two electrons may take part in the formation of one molecule of alkyl acetate. Thus, the reaction would occur as follows :



Hydroalumination of 1-olefins followed by oxidation with oxygen has been shown to provide a valuable and useful synthetic procedure to terminal alcohols.⁶ However, the reaction of dihydroalumination products of α,ω -diolefins with oxygen was slow due to their insolubility in THF and did not provide a practical route to α,ω -diols. Therefore it is noteworthy that the present reaction is a convenient procedure for preparation of α,ω -diacetates from α,ω -diolefins.

TABLE 1
Anti-Markownikoff Esterification of Alkenes

Olefin	Product ^a	Yield ^b %
1-Hexene ^c	Hexyl acetate	58
1-Octene ^c	Octyl acetate	51
4-Vinyl-1-cyclohexene ^c	2-(3-Cyclohexenyl)ethyl acetate	64
2-Methyl-1,5-hexadiene ^d	5-Methyl-5-hexenyl acetate	65 ^e
1,4-Hexadiene ^d	4-Hexenyl acetate	71 ^e
1,5-Hexadiene ^c	1,6-Diacetoxylhexane	59
1,7-Octadiene ^c	1,8-Diacetoxyoctane	60

^aIdentified by IR, GLC, ¹H NMR and mass spectra. Product contains only traces of other acetates if any. ^bIsolated yield, based on olefin. ^cHydroalumination reaction was carried out at 23°C for 5h. ^dHydroalumination at 23°C for 1.5h (1,4-hexadiene) or 2h (2-methyl-1,5-hexadiene); too long reaction time resulted in formation of dihydroalumination products. ^eGLC analysis.

In summary, this work demonstrates that hydroalumination of 1-olefins followed by reaction with lead(IV) acetate is a useful one-pot synthesis for

primary alkyl acetates, and an attractive alternative to the methods via hydroboration. Moreover, the selective monohydroalumination of nonconjugated diolefins makes it possible to prepare unsaturated acetates from nonconjugated diolefins, which appears to be impossible by hydroboration methods.

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