Tetrahedron Letters No. 30, pp 2615 - 2616, 1976, Pergamon Press. Printed in Great Britain.

ALLYL-NONALLYL COUPLING BY ORGANOALUMINUM REAGENTS

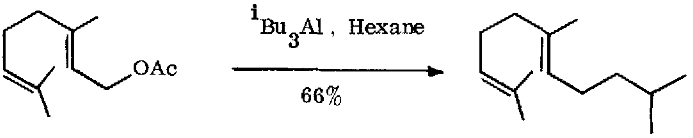
Shinsuke Hashimoto, Yoshizo Kitagawa, Satoshi Iemura, Hisashi Yamamoto,* and Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

(Received in Japan 26 April 1976; received in UK for publication 15 June 1976)

It is now well recognized that aluminum is an excellent oxygenophile, and as such, a host of useful synthetic methods have been developed which exploit this property.[1] However, a simple S_N2 reaction of organoaluminum reagent with organic halide has never been developed to any great extent, since Wurtz coupling by aluminum reagent generates a new aluminum halide bond at the expense of an aluminum-carbon bond and so produces an even stronger Lewis acid than the initial organoaluminum reactant.[2] Such autocatalytic effect may lead to the irreproducibility of the reaction. For circumventing such difficulties we developed a promising new reaction to effect allyl-nonallyl coupling.[3]

During an investigation into the chemistry of an allyl phosphate ester heterolysis by organoaluminum reagents,[4] we have developed an exceptionallyl mild procedure for carbon-carbon bond formation which proceeds without using the labile allylic halide.

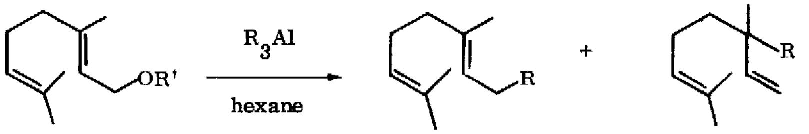
A solution of geranyl acetate (1.0 equiv) in dry hexane was cooled to -78° under an argon atomosphere, and triisobutylaluminum (4.0 equiv, *ca*. 1 *M* solution in hexane) was added slowly. The resulting clear solution was stirred for 12 hr at -78° and 1 hr at 0° to complete the alkylation.[5] The addition of 1 *N* hydrochloric acid, washing with water, and concentration under reduced pressure afforded 2,6,10-trimethyl-2-(*E*)-6-undecadiene (**1**) in 66% yield after purification by simple column chromatography (silica gel, hexane). The gas chromatographic analysis showed that the product consisted 97% of pure *E*-isomer **1** and only 3% of the regio- isomer.[6] The generality of the reaction between trialkylaluminum reagents and hydroxyl derivatives is apparent from the results summarized in Table 1. Thus, the coupling reaction proceeds smoothly with acetate, formate, carbonate esters by trialkylaluminum reagents, but it was ascertained that the alkylation was not promoted efficiently with tetrahydropyranyl ether except by trimethylaluminum reagent.



(97% pure by glpc)

1

Table 1. Alkylation of Geranyl Esters and Ether.



OR'	R_3Al	Reaction Conditions (°C, hr)	Product^a Yield (%)^b	Isomeric ratio (α/γ)^b
OAc	Me_3Al	-78,0.5; 0, 12	74	92:8
OAc	Et_3Al	0, 0.5	75	70:30
OAc	$i\text{-}Bu_3Al$	-78,12; 0,1	66	97:3
OCHO	Me_3Al	-78,0.5;0, 1	54	97:3
OCHO	Et_3Al	0, 0.5	75	80:20
OCHO	$i\text{-}Bu_3Al$	0, 1	76	96:4
OCOOEt	Me_3Al	-78, 0.5; 0, 1	86	94:6
OCOOEt	Et_3Al	0, 1	69	85:15
OCOOEt	$i\text{-}Bu_3Al$	-78, 12; 0, 1	73	97:3
OTHP	Me_3Al	-78, 0.5; 0,1; 20, 12	80	96:4
OTHP	Et_3Al	65, 12	10	94:6
OTHP	$i\text{-}Bu_3Al$	25, 12	<3	——

[a]Products have been adequately characterized by analytical and spectral data. [b]Determined by glpc analysis.

References and Notes

1. G. Bruno, Ed., "The use of Aluminum Alkyls in Organic Synthesis," Ethyl Corp., Bacon Rouge, La., 1970.
2. T. Mole and E. A. Jeffery, "Organoaluminum Compounds," Elsevier Publishing Company, New York, N. Y., 1972.
3. Similar allyl-nonallyl couplings by (a) Grignard reagents: A. Commercon, M. Bourgain, M. Delaumeny, J. F. Normant, and J. Villieras, Tetrahedron Lett., 3837 (1975), and (b) organocopper reagents: private communication from Professor S. Murahashi.
4. Y. Kitagawa, S. Iemura, S. Hashimoto, H. Yamamoto, and H. Nozaki, to be published.
5. Yields were not optimized since most of these reactions were performed only once. Longer reaction time and higher reaction temperature might increase the yields of the reaction.
6. 3,7-Dimethyl-3-isobutyl-1,6-octadiene.