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APPLICATION OF HYDROALUMINATION REACTIONS IN ORGANIC SYNTHESES. A CONVENIENT ROUTE TO TERMINAL ALLENES FROM 1-OLEFINS

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Hydroalumination of 1-olefins with lithium aluminum hydride followed by treatment with 3-bromo-1-propyne in the presence of a catalytic amount of copper(I) chloride resulted in coupling. This new development provides a general method for the synthesis of terminal allenes.

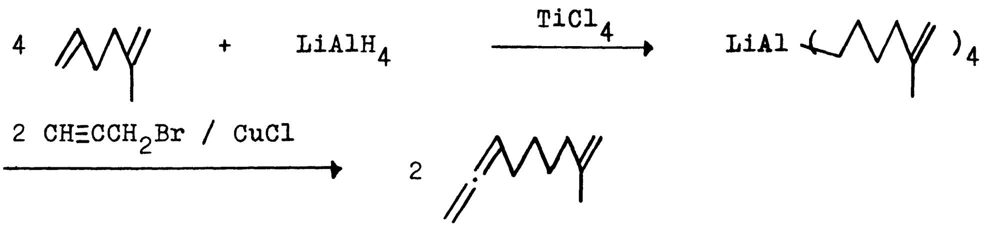
Recently it was shown that hydroalumination of olefins with $LiAlH_4$[1] followed by reaction with 3-halo-1-propene in the presence of a catalytic amount of CuCl provides a very useful method of lengthning the carbon chain by three atoms and that this coupling reaction proceeds via an S_N2' pathway.[2]

Replacing 3-halo-1-propene by 3-bromo-1-propyne in the above reactions, we have now developed a simple and general method for addition of the allene moiety to olefinic double bonds.

The following description of the preparation of 1,2-nonadiene is representative. To a clear solution of $LiAlH_4$ in THF (25 ml of 0.342 molar, 8.56 mmol) was added 1-hexene (2.6 g, 30.8 mmol) and $TiCl_4$ (86 mg, 0.45 mmol). After 3 hours under nitrogen at 25°C, the temperature was lowered to 0°C and 3-bromo-1-propyne (4.4 g, 36.9 mmol) and CuCl (0.4 g, 4.04 mmol) were added. The mixture was stirred for 10 minutes at 0°C and then 5 hours at room temperature. After hydrolysis, gas chromatographic analysis indicated the formation of 1,2-nonadiene in a 42% yield from 1-hexene, containing less than 1% of 1-nonyne if any.

As shown in Table 1, various 1-olefins, including those with a sterically hindered double bond or 1,3-dioxolan group, reacted satisfactorily to give the corresponding coupling products.[3]

It was observed that when using equimolar amounts of olefin and 3-halo-1-propyne, yields of allenes based on olefins were lower than 50%, while in the cases where a half molar amount of 3-bromo-1-propyne was used, yields based on the halide were 70 to 88%. These results strongly suggest that two of the alkyl groups of $LiAlR_4$ participate in the reaction as represented in the specific example shown below.



As the starting materials are olefins, the present procedure is clearly a general method for the synthesis of terminal allenes.

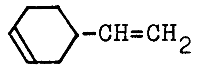
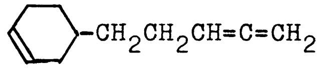
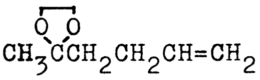
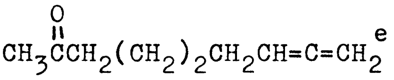
Two other useful methods for the preparation of allenes from olefins are known: dehalogenation of gem-dihalocyclopropanes obtained from olefins,4) or hydroboration followed by treatment with the lithium salt of 3-chloro-1-propyne.5)

The present procedure is an attractive alternative to these methods.

Noteworthy, here is the fact that introduction of the allenic moiety to one of the double bonds in the diolefin selectively is only possible by the present method.

Yields of allenes from olefins for these reactions, though around 40%, are not inferior to the other methods.

Table 1. Addition of the allene moiety to 1-olefins via the reaction of corresponding $LiAlR_4$ with 3-bromo-1-propyne in the presence of CuCl.

Olefin	Reactant[a] ratios	Product allene[b,c]	Yield[d] %
$CH_2{=}CH_2$	A	$CH_3CH_2CH{=}C{=}CH_2$	88
$CH_3(CH_2)_2CH{=}CH_2$	A	$CH_3(CH_2)_3CH_2CH{=}C{=}CH_2$	76
	B		39
$CH_3(CH_2)_3CH{=}CH_2$	A	$CH_3(CH_2)_4CH_2CH{=}C{=}CH_2$	80
	B		42
$CH_3CH{=}CHCH_2CH{=}CH_2$	A	$CH_3CH{=}CH(CH_2)_2CH_2CH{=}C{=}CH_2$	70
$CH_2{=}C(CH_3)CH_2CH_2CH{=}CH_2$	A	$CH_2{=}C(CH_3)CH_2(CH_2)_2CH_2CH{=}C{=}CH_2$	76
	B		36
	A		80
	B		41
	B	 $CH_3\overset{O}{\overset{\parallel}{C}}CH_2(CH_2)_2CH_2CH{=}C{=}CH_2$[e]	39

[a]A: A half molar amount of 3-bromo-1-propyne was used and yield is based on the halide. B: Equimolar amounts of olefin and 3-bromo-1-propyne were used and yield is based on olefin. [b]Identified by IR, GLC, ^1H NMR and mass spectra. [c]The allene products were more than 99% pure. [d]By GLC analysis. [e]After hydrolysis of ketal by dil. H_2SO_4.

References and Notes

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2) F. Sato, H. Kodama and M. Sato, The 37th Spring Annual Meeting of The Chemical Society of Japan, April, 1978 ; Abstr. No 2L19.

3) The $TiCl_4$-catalyzed olefin-$LiAlH_4$ reaction permitted the selective addition of $LiAlH_4$ to the less hindered C=C bond of nonconjugated dienes: see ref.1.

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