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# A CONVENIENT ROUTE FROM 1-ALKENES TO TERMINAL ACETYLENES VIA HYDROALUMINATION REACTIONS

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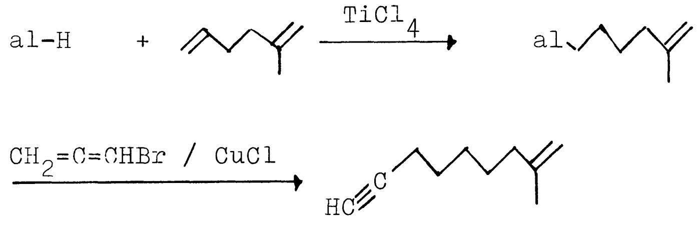
Hydroalumination of 1-alkenes with lithium aluminum hydride by catalysis of titanium tetrachloride followed by treatment with bromopropadiene was found to be a convenient route to add the acetylene moiety to the terminal double bond.

Recently it was found that hydroalumination of 1-alkenes with $LiAlH_4$ by catalysis of $TiCl_4$[1] followed by reaction with 3-halo-1-propene or 3-halo-1-propyne in presence of a catalytic amount of CuCl results in coupling by an $S_N2'$ pathway giving good yields of terminal olefins[2] or terminal allenes[3], respectively. These results suggested that terminal acetylenes might be obtained by hydroalumination of 1-alkenes followed by treatment with bromopropadiene readily prepared from commercial 3-bromo-1-propyne.[4]
This procedure, as represented by the specific example shown below, has in fact proved quite satisfactory.



(al = 1/4 Al)

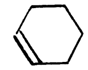
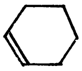
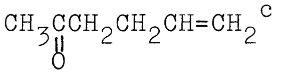
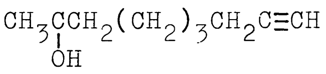
After hydroalumination of 2-methyl-1,5-hexadiene (1.84 g, 18.6 mmol) with $LiAlH_4$ (20 ml of 0.26 molar solution in THF, 5.20 mmol) by catalysis of $TiCl_4$ (0.05 g, 0.27 mmol), bromopropadiene (2.54 g, 21.4 mmol) and CuCl (0.3 g, 3.0 mmol) were added at 0°C. The reaction mixture was allowed to warm up to room temperature, stirred for 5 hours and then hydrolyzed by dilute hydrochloric acid. GLC analysis indicated the presence of 2-methyl-1-nonen-8-yne, free from 8-methyl-1,2,8-nonatriene, in 54% yield based on olefin.
A summary of the experimental results obtained for the synthesis of various terminal acetylenes is given in Table 1.
The characteristics of the present procedure are summarized as follows.

(1) As the starting materials are readily available olefins, this procedure is a general method for synthesis of terminal acetylenes.
(2) The present procedure is an operationally simple one-pot reaction.

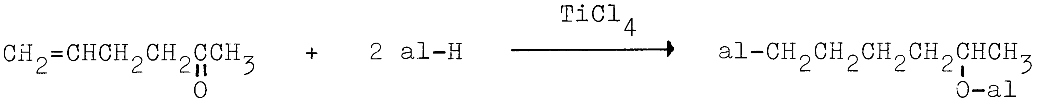
(3) Introduction of the acetylene moiety selectively to one of the double bonds of a diolefin is possible.

It has been observed that though the reaction of LiAlR$_4$ with 3-halo-1-propene uses all of the four alkyl groups of LiAlR$_4$,$^{2)}$ only two of the alkyl groups of LiAlR$_4$ participate in the reaction with 3-halo-1-propyne.$^{3)}$ Since, in the reaction under discussion, yields of acetylenes based on olefins were better than 50% in many cases, it is likely that more than two alkyl groups of LiAlR$_4$ participate in the reaction.

Table 1 Addition of the acetylene moiety to 1-olefins via reaction of the corresponding LiAlR$_4$ with bromopropadiene in presence of copper(I) chloride

| Olefin | Product acetylene[a] | Yield[b]<br>% |
|---|---|---|
| $CH_2=CH_2$ | $CH_3CH_2CH_2C\equiv CH$ | 43 |
| $CH_3CH_2CH_2CH=CH_2$ | $CH_3(CH_2)_4CH_2C\equiv CH$ | 49 |
| $CH_3CH_2CH_2CH_2CH=CH_2$ | $CH_3(CH_2)_5CH_2C\equiv CH$ | 50 |
| $CH_3CH=CHCH_2CH=CH_2$ | $CH_3CH=CH(CH_2)_3CH_2C\equiv CH$ | 52 |
| $CH_2=C(CH_3)CH_2CH_2CH=CH_2$ | $CH_2=C(CH_3)CH_2(CH_2)_3CH_2C\equiv CH$ | 55 |
|  -CH=CH$_2$ |  -CH$_2$CH$_2$CH$_2$C≡CH | 54 |
|  $CH_3\underset{\| \atop O}{C}CH_2CH_2CH=CH_2$[c] |  $CH_3\underset{\mid \atop OH}{C}CH_2(CH_2)_3CH_2C\equiv CH$ | 52 |

[a]Identified by IR, GLC, $^1$H NMR and mass spectra. [b]Yields determined by GLC analysis and based on olefin. [c] Hydroalumination of 5-hexen-2-one proceeded readily according to the following equation.



$$CH_2=CHCH_2CH_2\underset{\| \atop O}{C}CH_3 \quad + \quad 2\ \text{al-H} \xrightarrow{TiCl_4} \text{al-}CH_2CH_2CH_2CH_2\underset{\mid \atop O\text{-al}}{C}HCH_3$$

This new method could provide a convenient route to many complex acetylene derivatives difficult to prepare by other methods, and a study to find the scope and limitations of these reactions is now under way.

## References

1) F. Sato, S. Sato and M. Sato, J. Organometal. Chem., 131, C26 (1977).
F. Sato, S. Sato, H. Kodama and M. Sato, J. Organometal. Chem., 142, 71 (1977)
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) F. Sato, K. Oguro and M. Sato, Chem. Lett., in press.
4) T.L. Jacobs and W.F. Brill, J. Amer. Chem. Soc., 75, 1314 (1953).

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