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THE ALKYNYLATION REACTION OF OXETANES

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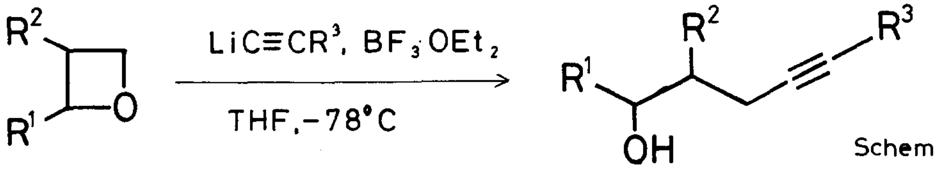
Abstract: γ-Hydroxyacetylenes were synthesized in high yields by the reaction of oxetanes with lithium acetylides in the presence of boron trifluoride etherate.

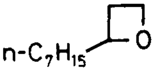
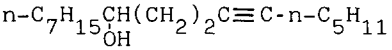
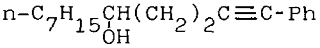
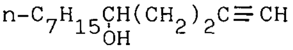
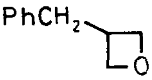
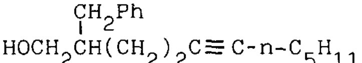
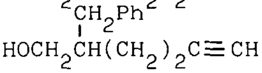
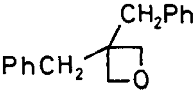
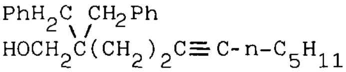
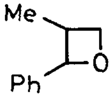
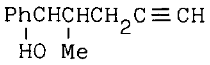
The ring opening reaction of oxetanes with various organometallic compounds is known and has been employed in organic synthesis$^{1)}$. Few reports, however, appeared for the reaction of metal acetylides$^{2)}$. Thus, the treatment of oxetanes with magnesium acetylides gave a considerable amount of halohydrins as a by-product, and no alkynylated product was detected by the use of a lithium acetylide $^{3)}$. In comparison with oxiranes, a lower homologue of oxetanes, the ring cleavage of the four membered ring is less facile. But, oxetanes, more basic than oxiranes, might be more effectively activated by a Lewis acid$^{4)}$. Previously, we have reported that, in the presence of boron trifluoride etherate, oxiranes were readily alkynylated by the lithium acetylides$^{5)}$. Then, the ring opening reaction of oxetanes by the combination of the metal acetylides and boron trifluoride etherate was tried and found to work cleanly to give γ-hydroxyacetylenes in high yields (Scheme and Table).

A typical procedure is described for the synthesis of 1-undecyn-5-ol: Under a nitrogen atomosphere, acetylene was introduced into a THF-n-hexane solution (4 ml and 1.3 ml respectively) of n-butyllithium (2 mmol) for 20 min at -78°C to generate lithium acetylide. Then, a THF solution (2 ml) of 2-heptyloxetane (78 mg, 0.5 mmol) and boron trifluoride etherate (0.3 ml) were added successively to the reaction mixture. After a 30 min's stirring at the temperature, the reaction was quenched by the addition of aqueous ammonium chloride. 1-Undecyn-5-ol (85 mg, 93 %) was isolated by a usual work-up.



Scheme

Table. The Alkynylation Reaction of Oxetanes.

oxetane	acetylene a)	product d)	yield (%) e)
	$HC\equiv C\text{-n-}C_5H_{11}$	$HO(CH_2)_3C\equiv C\text{-n-}C_5H_{11}$	quant.
	$HC\equiv C\text{-}Ph$	$HO(CH_2)_3C\equiv C\text{-}Ph$ g)	84
	$HC\equiv C\text{-}CH_2OTHP$	$HO(CH_2)_3C\equiv C\text{-}CH_2OTHP$ g)	92
	$HC\equiv C\text{-n-}C_5H_{11}$	 $\text{n-}C_7H_{15}\underset{OH}{CH}(CH_2)_2C\equiv C\text{-n-}C_5H_{11}$	85 (74) c)
	$HC\equiv C\text{-}Ph$	 $\text{n-}C_7H_{15}\underset{OH}{CH}(CH_2)_2C\equiv C\text{-}Ph$	67
	$HC\equiv CH$ b)	 $\text{n-}C_7H_{15}\underset{OH}{CH}(CH_2)_2C\equiv CH$	93
	$HC\equiv C\text{-n-}C_5H_{11}$	 $HOCH_2\overset{CH_2Ph}{CH}(CH_2)_2C\equiv C\text{-n-}C_5H_{11}$	67
	$HC\equiv CH$ b)	 $HOCH_2\overset{CH_2Ph}{CH}(CH_2)_2C\equiv CH$	91
	$HC\equiv C\text{-n-}C_5H_{11}$	 $HOCH_2\overset{PhH_2C\ \ CH_2Ph}{C}(CH_2)_2C\equiv C\text{-n-}C_5H_{11}$	79
 f)	$HC\equiv CH$ b)	 $Ph\underset{HO}{CH}\underset{Me}{CH}CH_2C\equiv CH$ f)	62

a) The molar ratio of oxetane : acetylene = 1 : 3.

b) The molar ratio of oxetane : acetylene = 1 : 4 to 1 : 5.

c) The molar ratio of oxetane : acetylene = 1 : 2.

d) All the products gave satisfactory NMR and IR spectra.

e) Isolated yield.

f) A 1.5:1 mixture of stereoisomers.

g) These products gave satisfactory elemental analysis by high resolution mass spectrometry.

References and Notes

1) For recent examples; H. J. Bestmann and O. Vostrowsky, Tetrahedron Lett., 1974, 207; J. Millon and G. Linstrumelle, ibid, 1976, 1095; C. Huynh, F. D.-Boumechal, and G. Linstrumelle, ibid, 1979, 1503; R. Rossi, A. Carpita, L. Gaudenzi, and M. G. Quirici, Gazz. Chim. Ital., 110, 237 (1980).

2) T. Cuvigny and H. Normant, C. R. Acad. Sci., 254, 316 (1962); A. S. Atavin and N. V. Egorov, Khim. Atsetilena, 1968, 17 (Chem. Abstr., 71, 70019c (1969).); Japan patent 81 73033 (Chem. Abstr. 95, 168524j (1981).).

3) The reaction of lithium phenylacetylide with oxetane in THF at r.t. gave no detectable amount of 5-phenyl-3-pentyn-1-ol.

4) P. F. Hudrlik and C.-N. Wan, J. Org. Chem., 40, 2963 (1975); S. Searles and M. Tamres, J. Am. Chem. Soc., 73, 3704 (1951).

5) M. Yamaguchi and I. Hirao, Tetrahedron Lett., 24, 391 (1983).

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