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AN EFFICIENT METHOD FOR THE ALKYNYLATION OF OXIRANES USING ALKYNYL BORANES

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Abstract: Alkynyl boranes, generated in situ from lithium acetylides and boron trifluoride etherate, were found to react with oxiranes under mild reaction conditions to afford β-hydroxyacetylenes in high yields.

The oxirane ring cleavage by metal acetylides to form β-hydroxyacetylenes is one of useful synthetic tools in organic chemistry. Classical alkali acetylides, however, suffer from low yields and become unapplicable as the degree of substitution of the oxiranes is increased.[1] Several reports appeared concerning the improvement of the process; performing the reaction in an aprotic polar solvent such as dimethylsulfoxide[2] or hexamethylphosphoric triamide[3]; employing diethylalkynyl alanes in place of the alkali acetylides[4]. In spite of these efforts, however, the ring opening reaction with metal acetylides still requires a long reaction time and/or a high temperature, and often the yields of the β-hydroxyacetylenes are not very high.

We now wish to report a useful method for the alkynylation of oxiranes by the use of alkynyl boranes by which β-hydroxyacetylenes are obtained in high yields under mild reaction conditions.

The alkynyl borane reagents[5] were prepared in situ at -78°C in tetrahydrofuran (THF) by the reaction of lithium acetylides with boron trifluoride etherate and were then treated with various oxiranes at the same temperature as shown in the following Scheme. The results are summarized in Table.

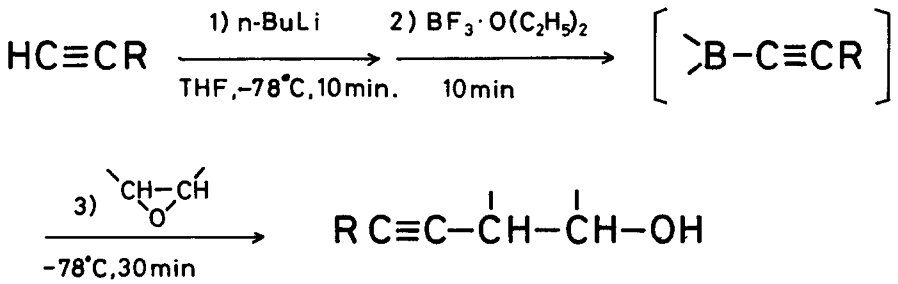
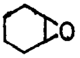
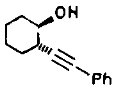
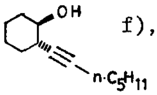
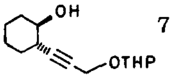
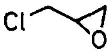
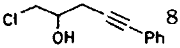
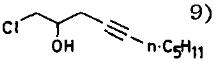
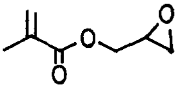
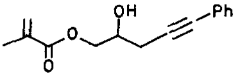
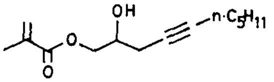
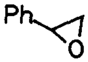
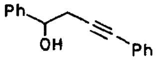
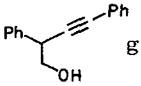
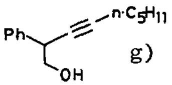


Table. The Synthesis of β-Hydroxyacetylenes

oxirane	acetylene	product a)	yield (%) c)
	$PhC\equiv CH$ d)	 f)	quant. b)
	$n\text{-}C_5H_{11}C\equiv CH$ e)	 f),6)	93 b)
	$THPOCH_2C\equiv CH$ d)	 7)	84
	$PhC\equiv CH$ d)	 8)	quant. b)
	$n\text{-}C_5H_{11}C\equiv CH$ e)	 9)	74
	$PhC\equiv CH$ d)	 10)	93
	$n\text{-}C_5H_{11}C\equiv CH$ e)	 11)	76 b)
	$PhC\equiv CH$ e)	 + 1 : 4  g)	quant.
	$n\text{-}C_5H_{11}C\equiv CH$ e)	 + 1 : 1  g)	79

a) All the products gave satisfactory spectral data (NMR,IR).

b) These compounds had satisfactory elemental composition by high-resolution mass spectrometry.

c) Isolated yields.

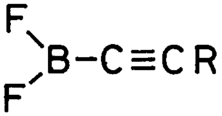
d) The molar ratio of oxirane:acetylene was 1:1.5.

e) The molar ratio of oxirane:acetylene was 1:2.

f) These compounds were identical (NMR, IR, GC) with authentic samples prepared by the lithium acetylide method2),3) which was claimed to give trans-alkynylcycloalkanols.

The present reaction is characterized by the following features. 1) The reaction was quite rapid even at -78°C, and various β-hydroxyacetylenes were obtained in high yields. 2) Alkynyl groups were introduced regioselectively at the less hindered site in the case of monoalkyl-substituted oxiranes. Styrene oxide, however, gave a mixture of products which were obtained by the substitution reaction at both more and less hindered sites, showing a cationic character at the transition state. 3) Functional groups such as halogen, ester or ketal were found to be unaffected under the present reaction conditions. 4) When cyclohexene oxide was employed, alkynylated products with trans-configuration were stereospecifically obtained.

Although the precise reaction mechanism is not fully clear, we feel that the assumption of alkynyldifluoro boranes as the intermediate may account for the above mentioned features of the reaction.



A typical procedure is described for the synthesis of 2-(2-phenylethynyl)-1-cyclohexanol: Under a nitrogen atomosphere, a solution of n-butyllithium in hexane (0.96 ml, 1.5 mmol) was added to a THF solution (2 ml) of phenylacetylene (153 mg, 1.5 mmol) at -78°C, and the mixture was stirred for 10 min. Then, boron trifluoride etherate (0.2 ml) was added to the solution and the stirring was continued for 10 min at -78°C. Finally, a THF solution of 7-oxabicyclo(4,1,0)-heptane (cyclohexene oxide, 98 mg, 1 mmol) was added, and after stirring for 30 min at -78°C, the reaction was quenched by adding aqueous ammonium chloride. The organic materials were extracted with ethyl acetate and dried over Na_2SO_4. After the removal of the solvents, 2-(2-phenylethynyl)-1-cyclohexanol (198 mg, quant.) was obtained by thin layer chromatography (silica gel).
NMR ($CDCl_3$) δ 1.2-2.2 (9H, m), 2.3-2.6 (1H, m), 3.4-3.7 (1H, m), 7.2-7.5 (5H, m). IR (neat) 3350, 2230 cm^{-1}. Found m/e 200.1241. Calcd for $C_{14}H_{16}O$, 200.1202.

Acknowledgement

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References and Notes

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3) J.R.Norton, K.E.Shenton, and J.Schwartz, Tetrahedron Lett., 1975, 51; A.B. Holmes, R.A.Raphael, and N.K.Wellard, ibid, 1976, 1539; W.Schumacher and M.Hanack, Synthesis, 1981, 490.

4) J.Fried, C.-H.Lin, and S.H.Ford, Tetrahedron Lett. 1969, 1379; G.A.Crosby and R.A.Stephenson, J. Chem. Soc., Chem. Commun., 1975, 287; T.F.Murray, V.Varma, and J.R.Norton, ibid, 1976, 907; S.Danishefsky, T.Kitahara, M.Tsai, and J.Dynak, J. Org. Chem., 41, 1669 (1976).

5) For example: G.A.Molander and H.C.Brown, ibid, 42, 3106 (1977); idem, Synthesis, 1979, 104; J.A.Sindair, G.A.Molander, and H.C.Brown, J. Am. Chem. Soc., 99, 954 (1977).

6) NMR ($CDCl_3$) δ 0.89 (3H, t, J=6Hz), 1.1-2.3 (18H, m), 3.2-3.5 (1H, m). IR (neat) 3400 cm^{-1}. Found m/e 194.1587. Calcd for $C_{13}H_{22}O$, 194.1671.

7) NMR ($CDCl_3$) δ 1.0-2.3 (15H, m), 3.1-3.9 (4H, m), 4.26 (2H, s), 4.7-4.9 (1H, m). IR (neat) 3400, 2250 cm^{-1}.

8) NMR ($CDCl_3$) δ 2.71 (2H, d, J=6Hz), 3.1-3.5 (1H, m), 3.68 (2H, d, J=4Hz), 3.8-4.2 (1H, m), 7.0-7.5 (5H, m). IR (neat) 3350 cm^{-1}. Found m/e 194.0509. Calcd for $C_{11}H_{11}OCl$, 194.0499.

9) NMR ($CDCl_3$) δ 0.6-1.1 (3H, m), 1.1-1.6 (6H, m), 1.9-2.3 (2H, m), 2.3-2.6 (2H, m), 2.9-3.1 (1H, m), 3.6-4.1 (3H, m). IR (neat) 3350 cm^{-1}.

10) NMR ($CDCl_3$) δ 1.92 (3H, s), 2.68 (3H, d, J=4.5Hz), 2.6-2.9 (1H, m), 2.9-3.4 (3H, m), 5.54 (1H, s), 6.14 (1H, s), 7.0-7.5 (5H, m). IR (neat) 3450, 1740, 1630 cm^{-1}.

11) NMR ($CDCl_3$) δ 0.89 (3H, t, J=6Hz), 1.2-1.6 (6H, m), 1.96 (3H, s), 1.9-2.3 (3H, m), 2.4-2.6 (2H, m), 3.9-4.1 (1H, m), 4.24 (2H, dd, J=1,5Hz), 5.60 (1H, s), 6.15 (1H, s). IR (neat) 3400, 1720, 1635 cm^{-1}. Found m/e 238.1565. Calcd for $C_{14}H_{22}O_3$, 238.1569.

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