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Alkynylations of Oxiranes with Lithium Acetylides by the Catalysis of Trimethylgallium

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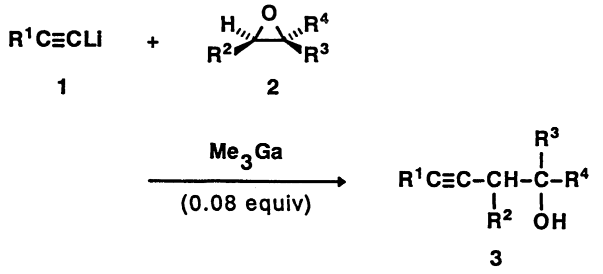
The reaction of 1-lithio-1-alkynes with oxiranes under the catalytic action of trimethylgallium afforded the corresponding β-hydroxy acetylenic compounds in good yields with excellent regioselectivities. No isomerization of oxiranes was observed during the reactions because of low Lewis acidity of trimethylgallium. The mechanism including activation of an oxirane by the coordination to trimethylgallium was proposed.

The ring-opening reactions of oxiranes with metal acetylides have been used as the most important tool for preparation of β-hydroxy acetylenic compounds,[1–5] which are versatile intermediates in organic syntheses.[6–8] Although several methods have appeared for the reaction, they usually require severe reaction conditions and/or resulted in low yields of the expected products. Recently Yamaguchi et al. reported alkynylation of oxiranes with lithium acetylides by the action of $BF_3 \cdot OEt_2$, and prepared varieties of β-hydroxy acetylenic compounds in good yields.[9] Although the utilities of the BF_3-catalyzed reaction has been proved by several successful applications,[10,11] this reaction requires stoichiometric amount of $BF_3 \cdot OEt_2$. On the other hand, lithium acetylides attack oxiranes under the action of catalytic amount of trimethylgallium to give β-hydroxy acetylenic compounds in good to excellent yields.[12] This paper describes in detail the regioselective reaction of lithium acetylides and oxiranes under trimethylgallium catalysis.

Ring-Opening Reaction of Oxirane with Lithium Acetylides. The reaction of lithium acetylides with oxiranes was tried in the presence of catalytic amount of trimethylgallium; treatment of a THF (tetrahydrofuran) solution of a 1-lithio-1-alkyne with catalytic amount of Me_3Ga and an oxirane was examined. The expected β-hydroxy acetylenic product was obtained in good yield by regioselective attack of acetylide to the less substituted carbon (Scheme 1). In the absence of trimethyl-



Scheme 1.

Table 1. The Reaction of Oxiranes with Lithium Acetylides in the Presence of Trimethylgallium

R^1	R^2	R^3	R^4	Conditions		Product	Yield[a)]/%
C_6H_{13}	H	H	H	R.T.	1 h	**3a**[e)]	92 (10)
	H	CH_3	H	R.T.	1.5 h	**3b**	87 (3)
	H	C_2H_5	H	R.T.	5 h	**3c**	74
	H	CH_3	CH_3	R.T.	5 h	**3d**	70
	$-(CH_2)_4-$		H	Reflux	6 h	**3e**	71
	$-(CH_2)_3-$		H	Reflux	6 h[b)]	**3f**	82
	H	CH_2Cl	H	0 °C	6 h[b)]	**3g**	64
	H	CH_2Cl	H	R.T.	6 h[b)]	**3h**	85[c)]
C_5H_{11}	H	CH_3	H	R.T.	5 h	**3i**	77
	H	CH_3	CH_3	R.T.	5 h	**3j**	79
	H	Ph	H	50 °C	4 h	**3k**, **3l**[f)]	78[d)]
C_2H_5	$-(CH_2)_4-$		H	Reflux	5 h	**3m**	80
Ph	H	H	H	R.T.	2 h	**3n**[g)]	99 (4)
	H	CH_3	H	R.T.	2 h	**3o**[h)]	88 (3)
Me_3Si	H	C_4H_9	H	Reflux	40 min	**3p**	79 (18)

a) Yields in parentheses indicate those obtained by the reaction without Me_3Ga. b) 0.16 equiv of Me_3Ga was used. c) The product was 1,2-epoxy-4-undecyne. d) The product was a mixture of 1-phenyl-3-nonyn-1-ol (**3k**) and 2-phenyl-3-nonyn-1-ol (**3l**) in the ratio of 7 : 3. e) Ref. 14. f) Ref. 9. g) Ref. 15. h) Ref. 16.

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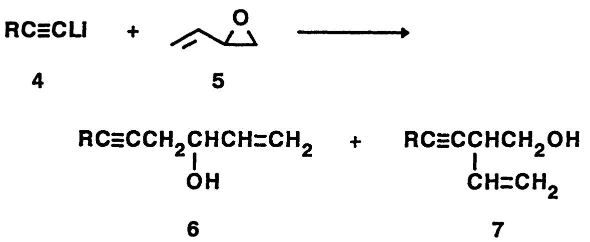
gallium, the reaction proceeded sluggishly. Reaction conditions and results are summarized in Table 1.

As shown in Table 1, alkynylation of cyclohexene oxide or cyclopentene oxide gave *trans*-2-alkynylcyclohexanol or -cyclopentanol in good yield under THF reflux. This result is in contrast to that of the reaction with alkynylmagnesium bromide; the reaction of cyclohexene oxide with 1-octynylmagnesium bromide did not gave 2-(1-octynyl)cyclohexanol but afforded a mixture of 2-bromocyclohexanol (58%) and 1-cyclopentyl-2-nonyn-1-ol (31%), indicating the isomerization of cyclohexene oxide into cyclopentanecarbaldehyde under the reaction conditions. It should be noted that no isomerization of oxiranes was observed in the case of trimethylgallium-catalyzed alkynylation of oxiranes. The reaction of epichlorohydrin at 0 °C gave corresponding chlorohydrin **3g**; The reaction at room temperature afforded 1,2-epoxy-4-undecyne **3h**, which was derived from initially produced lithium alkoxide by intramolecular reaction. Among various oxiranes shown in Table 1, reaction with styrene oxide showed relatively good regioselectivity by predominant attack of lithium acetylides on less substituted carbons, whereas BF_3-catalyzed reaction of styrene oxide with 1-lithio-1-heptyne showed non-regioselectivity to give a 1 : 1 mixture of possible two products. These results are shown in Table 1.

In the case of butadiene monoepoxide, Me_3Ga-catalyzed reaction with lithium acetylides showed considerable regioselectivity; the reaction of 1-lithio-1-octyne (**4a**) with butadiene monoepoxide (**5**) gave 1-dodecen-5-yn-3-ol (**6a**) and 2-vinyl-3-decyn-1-ol (**7a**) in the ratio of 71 : 29 without other by-products. The reaction with 1-lithio-2-trimethylsilylethyne (**4b**) gave 6-trimethylsilyl-1-hexen-5-yn-3-ol (**6b**) with high regioselectivity. Above two examples show that alkynyl group was introduced mainly from less substituted carbon of oxirane in the case of trimethylgallium catalyzed alkynylation. On the contrary, in the case of $BF_3 \cdot OEt_2$ mediated alkynylation of butadiene monoepoxide (**5**), the regioselectivity to give **6** is low and several by-products were formed besides regioisomer **7**. Results are summarized in Table 2.



Scheme 2.

Table 2. Alkynylation of Butadiene Monoepoxide

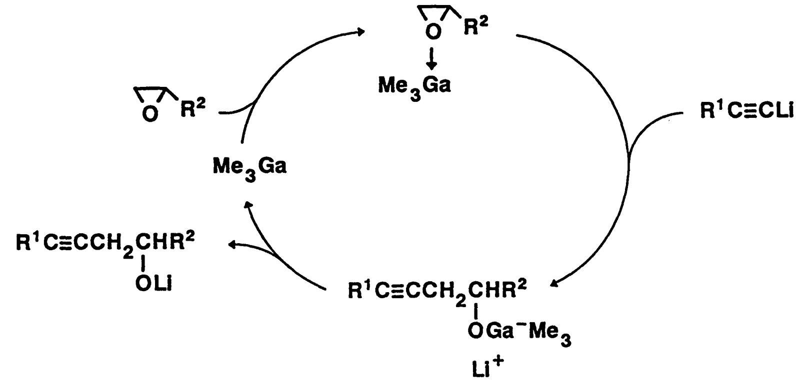
Entry	R	Method[a]	Yield/%	Ratio (**6**:**7**)
1	C_6H_{13}	A	76	71:29
2		B	44[b]	43:57
3	Me_3Si	A	78	92: 8
4		B	35[b]	54:46

a) A: in th presence of Me_3Ga (0.2 equiv), 50 °C, 4 h. B: in the presence of $BF_3 \cdot OEt_2$ (1.0 equiv), −78 °C, 30 min. b) Isolated yield after column chromatography.

These results as well as relatively regioselective reaction of styrene oxide indicated that Lewis acidity of trimethylgallium is not so strong to induce the isomerization of oxirane or to produce allylic or benzylic cation species but sufficient to catalyze regioselective reaction of oxirane with lithium acetylides.

Mechanistic Considerations

NMR analyses of the mixtures of oxirane, lithium acetylides, and Me_3Ga were informative to the mechanistic considerations. The peak of oxirane protons of cyclohexene oxide was observed at δ=3.12 in $CDCl_3$–hexane. When slightly excess Me_3Ga (hexane solution) was added to a $CDCl_3$ solution of cyclohexene oxide, that of oxirane protons moved to δ=3.33 with broadening. This result indicates that Me_3Ga affected as a Lewis acid by coordinating to the oxygen of cyclohexene oxide and thus activated for the alkynylation. Lewis acidic activation of oxiranes by trimethylgallium



Scheme 3. Catalytic cycle for trimethylgallium-catalyzed alkynylation of oxirane with 1-lithio-1-alkyne.

was also reported in the isonitrile formation by the reaction with cyanotrimethylsilane.[13]

Although exothermic interaction was observed when hexane solution of trimethylgallium was added to THF solution of 1-lithio-1-octyne (1 : 1), any positive evidence could not be obtained for the formation of an ate complex from trimethylgallium and 1-lithio-1-alkyne at this moment.

On the basis of the above discussion, the trimethylgallium catalyzed alkynylation of oxiranes is explained as shown in Scheme 3.

Conclusion

The above described trimethylgallium catalyzed reaction of oxiranes with lithium acetylides to give β-hydroxy acetylenic compounds possesses the following respects: (1) acetylides attacked regioselectively on less substituted carbon with respect to the applied oxiranes, even with styrene oxide and butadiene monoepoxide, (2) relative low Lewis acidity of Me_3Ga did not induce any isomerization of oxiranes before the coupling reaction, (3) catalytic amount of Me_3Ga was sufficient in contrast to the stoichiometric use of $BF_3 \cdot OEt_2$ in reported case, and (4) the expected β-hydroxy acetylenic compounds were obtained in high yields under mild reaction conditions.

Experimental

IR spectra were obtained on a JASCO IR-810 spectrometer. ^{1}H NMR (200 MHz) were measured on a Varian XL-200. Elemental analyses were performed at Elemental Analysis Center of Kyoto University.

Alkynylation of Oxirane (2) with Lithium Acetylide (1) under the Catalysis of Trimethylgallium (General Procedure): To a THF solution of 1-lithio-1-alkyne (**1**) prepared from 1-alkyne (10 mmol) and butyllithium (1.86 M in hexane, 5.6 ml, 10 mmol, 1 M=1 mol dm^{-3}) 10 ml of THF, trimethylgallium (0.8 M in hexane, 1.0 ml, 0.8 mmol) was added at 0 °C. To the reaction mixture, an oxirane (**2**, 12 mmol, 1.2 eguiv) was added and the whole was stirred for 40 min to 6 h at 0—50 °C or at reflux. The reaction mixture was worked up with brine and extracted with ether. The ethereal solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Chromatographical purification (Silica gel) of the residue gave the product.

4-Undecyn-2-ol (3b): ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=6.7 Hz), 1.24 (3H, d, J=6.2 Hz), 1.20—1.60 (8H, m), 2.15 (2H, dt, J=6.7, 2.4 Hz), 2.20 (1H, br-s), 2.32 (2H, tt, J=2.4, 6.6 Hz), 3.90 (1H, tq, J=5.8, 6.2 Hz); IR (neat) 3600—3000, 1150, 1080, 940 cm^{-1}. Found: C, 78.41; H, 12.22%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

5-Dodecyn-3-ol (3c): ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.8 Hz), 0.98 (3H, t, J=7.8 Hz), 1.19—1.70 (10H, m), 1.96 (1H, d, J=5.0 Hz), 2.17 (2H, tt, J=2.4, 7.0 Hz), 2.28 (1H, ddt, J=7.0, 16.4, 2.4 Hz), 2.42 (1H, ddt, J=5.2, 16.4, 2.4 Hz), 3.63 (1H, m); IR (neat) 3600—3050, 1265, 1115, 1070, 1012, 976 cm^{-1}. Found: C, 78.92; H, 12.22%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

2-Methyl-4-undecyn-2-ol (3d): ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.8 Hz), 1.21—1.56 (8H, m), 1.28 (6H, s), 1.99 (1H, s), 2.20 (2H, tt, J=2.2, 7.0 Hz), 2.34 (2H, t, J=2.2 Hz); IR (neat) 3700—3100, 1264, 1249, 1210, 1145, 981, 906 cm^{-1}. Found: C, 78.91; H, 12.07%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

2-(1-Octynyl)cyclohexanol (3e): ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=6.5 Hz), 1.08—1.85 (15H, m), 1.99 (2H, m), 2.17 (2H, br-t, J=6.2 Hz), 2.36 (1H, d, J=2.0 Hz), 3.37 (1H, ddt, J=2.0, 3.0, 9.5 Hz); IR (neat) 3600—3100, 1285, 1085 cm^{-1}. Found: C, 80.54; H, 11.84%. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61%.

2-(1-Octynyl)cyclopentanol (3f): ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.5 Hz), 1.12—2.03 (14H, m), 1.92 (1H, s), 2.13 (2H, dt, J=2.0, 7.0 Hz), 2.50 (1H, ddt, J=2.0, 6.0, 6.0 Hz), 4.09 (1H, dt, J=6.0, 6.0 Hz); IR (neat) 3600—3100, 1292, 1122, 1073, 1029, 992, 721 cm^{-1}. Found: C, 80.43; H, 11.68%. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

1-Chloro-4-undecyn-2-ol (3g): ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.0 Hz), 1.20—1.65 (8H, m), 2.27 (2H, tt, J=2.1, 6.9 Hz), 2.35 (1H, d, J=6.0 Hz), 2.48 (1H, tt, J=2.1, 7.0 Hz), 2.60 (1H, dq, J=7.0, 2.1 Hz), 3.62 (1H, dd, J=6.1, 11.0 Hz), 3.74 (1H, dd, J=4.6, 11.0 Hz), 3.95 (1H, m); IR (neat) 3600—3050, 1090, 1050, 710, 700 cm^{-1}. Found: C, 65.26; H, 9.72%. Calcd for $C_{11}H_{19}OCl$: C, 65.17; H, 9.45%.

1,2-Epoxy-4-undecyne (3h): ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=6.0 Hz), 1.15—1.62 (9H, m), 2.15 (2H, tt, J=2.3, 7.2 Hz), 2.43 (1H, ddt, J=5.0, 17.7, 2.3 Hz), 2.60 (1H, ddt, J=4.6, 17.7, 2.3 Hz), 2.65 (1H, dd, J=2.5, 4.8 Hz), 2.79 (1H, dd, J=3.6, 4.8 Hz), 3.08 (1H, ddd, J=2.5, 3.6, 5.0 Hz); IR (neat) 960, 930, 840, 830 cm^{-1}. Found: C, 79.36; H, 11.02%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

4-Decyn-2-ol (3i): ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, J=6.9 Hz), 1.25 (3H, d, J=6.4 Hz), 1.20—4.58 (6H, m), 2.06 (1H, d, J=4.9 Hz), 2.19 (2H, tt, J= 2.3, 7.0 Hz), 2.28 (1H, ddt, J=6.8, 16.0, 2.3 Hz), 2.40 (1H, ddt, J=5.0, 16.0, 2.3 Hz), 3.90 (1H, dddq, J=4.9, 5.0, 6.8, 6.9 Hz); IR (neat) 3650—3100, 1116, 1085, 940 cm^{-1}. Found: C, 77.56; H, 11.95%. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%.

2-Methyl-4-decyn-2-ol (3j): ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=6.9 Hz), 1.21—1.59 (6H, m), 1.30 (6H, s), 2.01 (1H, s), 2.19 (2H, tt, J=2.5, 7.0 Hz), 2.34 (2H, t, J=2.5 Hz); IR (neat) 3600—3100, 1266, 1210, 1146, 975, 906, 762 cm^{-1}. Found: C, 78.49; H, 12.12%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

2-(1-Butynyl)cyclohexanol (3m): ^{1}H NMR ($CDCl_3$) δ=1.16 (3H, t, J=7.5 Hz), 1.20—2.10 (9H, m), 2.20 (1H, m), 2.21 (2H, dq, J=2.0, 7.5 Hz), 3.41 (1H, ddd, J=2.5, 9.5, 9.5 Hz); IR (neat) 3650—3100, 1310, 1275, 1075 cm^{-1}. Found: C, 78.60; H, 10.85%. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%.

1-Trimethylsilyl-1-octyn-4-ol (3p): ^{1}H NMR ($CDCl_3$) δ=0.16 (9H, s), 0.88 (3H, t, J=6.9 Hz), 1.17—1.57 (6H, m), 1.95 (1H, d, J=5.0 Hz), 2.29 (1H, dd, J=7.0, 16.7 Hz), 2.45 (1H, dd, J=5.0, 16.7 Hz), 3.67 (1H, m); IR (neat) 3600—3100, 2174, 1250, 1125, 1082, 1045, 1017, 841, 758, 697 cm^{-1}. Found: C, 66.55; H, 11.36%. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18%.

1-Dodecen-5-yn-3-ol (6a): ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.5 Hz), 1.19—1.69 (8H, m), 2.07 (1H, d, J=6.0 Hz), 2.18 (2H, tt, J=2.5, 6.0 Hz), 2.40 (1H, ddt, J=6.5, 16.1, 2.3 Hz), 2.50 (1H, ddt, J=6.5, 16.1, 2.7 Hz), 4.17 (1H, m), 5.18 (1H, ddd, J=1.1, 1.1, 10.5 Hz), 5.31 (1H, ddd, J=1.1, 1.1, 17.0 Hz), 5.91 (1H, ddd, J=6.0, 10.5, 17.0 Hz); IR (neat) 3630—3100, 3080, 1379, 1330, 1122, 1034, 992, 923 cm^{-1}. Found: C, 79.69; H, 11.31%. Calcd for $C_{11}H_{20}O$: C, 79.94; H, 11.18%.

2-Vinyl-3-decyn-1-ol (7a): ^{1}H NMR (CDCl$_3$) δ=0.91 (3H, t, J=6.3 Hz), 1.20—1.64 (8H, m), 1.83 (1H, dd, J=6.1, 6.5 Hz), 2.23 (2H, dt, J=2.1, 7.1 Hz), 3.29 (1H, m), 3.55 (1H, ddd, J=6.1, 6.9, 16.0 Hz), 3.69 (1H, ddd, J=6.5, 6.9, 16.0 Hz), 5.21 (1H, ddd, J=1.6, 1.6, 10.0 Hz), 5.40 (1H, ddd, J=1.6, 1.6, 17.0 Hz), 5.75 (1H, ddd, J=6.9, 10.0, 17.0 Hz); IR (neat) 3650—3100, 3082, 1632, 1379, 1331, 1053, 991, 920, 721 cm^{-1}. Found: C, 79.98; H, 11.31%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

6-Trimethylsilyl-1-hexen-5-yn-3-ol (6b): ^{1}H NMR (CDCl$_3$) δ=0.18 (9H, s), 2.07 (1H, d, J=5.7 Hz), 2.46 (1H, dd, J=6.7, 17.0 Hz), 2.56 (1H, dd, J=5.9, 17.0 Hz), 4.27 (1H, ddddt, J=5.7, 5.9, 6.0, 6.7, 1.5 Hz), 5.17 (1H, ddd, J=1.5, 1.5, 10.0 Hz), 5.29 (1H, ddd, J=1.5, 1.5, 17.5 Hz), 5.89 (1H, ddd, J=6.0, 10.0, 17.5 Hz); IR (neat) 3700—3100, 3082, 3005, 2176, 1250, 1123, 1044, 1001, 926, 842, 759, 697 cm^{-1}. Found: C, 64.21; H, 9.70%. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58%.

4-Trimethylsilyl-2-vinyl-3-butyn-1-ol (7b): ^{1}H NMR (CDCl$_3$) δ=0.15 (9H, s), 1.81 (1H, t, J=6.6 Hz), 3.34 (1H, dtt, J=6.6, 1.2, 6.6 Hz), 3.61 (1H, ddd, J=3.4, 6.6, 6.6 Hz), 3.65 (1H, ddd, J=3.4, 6.6, 6.6 Hz), 5.25 (1H, ddd, J=1.2, 1.2, 10.5 Hz), 5.42 (1H, ddd, J=1.2, 1.2, 17.0 Hz), 5.81 (1H, ddd, J=6.6, 10.5, 17.0 Hz); IR (neat) 3700—3100, 3084, 3010, 2170, 1642, 1299, 1250, 1049, 991, 925, 883, 842, 759, 697, 635 cm^{-1}. Found: 64.23; H, 9.76%. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58%.

Alkynylation of Butadiene Monoepoxide: The alkynylations of butadiene monoepoxide catalyzed by trimethylgallium were carried out along the procedure described above using 0.2 equiv of trimethylgallium. The $BF_3 \cdot OEt_2$ mediated alkynylations were accomplished by the procedure reported in the literature. Thus, $BF_3 \cdot OEt_2$ (2 mmol) was added at −78 °C to THF–hexane solution of 1-lithio-1-alkyne (2 mmol), which was prepared from the reaction of 1-alkyne (2 mmol) with hexane solution of butyllithium (2 mmol). After the whole was stirred at −78 °C for 10 min, butadiene monoepoxide (2 mmol) was added to the solution and the whole was stirred at −78 °C for additional 30 min. The reaction mixture was worked up with sat NH_4Cl and extracted with ether. The ethereal solution was dried (Na_2SO_4) and concentrated to give the crude product, which was purified by column chromatography (silica gel).

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