Alcoholysis of Epoxides Catalyzed by Tetracyanoethylene and Dicyanoketene Acetals

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A typical π-acid tetracyanoethylene and capto-dative olefin dicyanoketene acetals were found to catalyze stereospecific alcoholysis of epoxides at the ambient temperature to 50 °C in good yields. Mildness and significant chemoselectivity of the catalysts were demonstrated by intactness of tetrahydropyranyl ether and ethylene acetal groups. A novel regioselectivity associated with anchimeric assistance of the ethereal group on the side chain was observed in the ring opening reaction of the 1,2-disubstituted epoxides.

Reactions of epoxides frequently constitute crucial process in transformation of aliphatic compounds due to high regio- and stereo-selectivity and specificity.[1] Epoxide ring opening reaction to give β-substituted alcohols with carbon- and heteroatomic nucleophiles, rearrangement reaction providing carbonyl compounds, and isomerization reaction leading to allylic alcohols are useful tools in organic synthesis and most of these reactions generally proceed under basic or acidic conditions. Extensive studies have been focused on search for mild and neutral catalysts in the epoxide-ring opening reaction particularly with heteroatomic nucleophiles such as alcohols, thiols, and amines in view of chemo-, regio-, and stereoselectivities.[2—5] Among the promoters which have been developed, neutral alumina reported by Posner,[2] organotin phosphate condensate by Otera,[3] and Nafion-H by Olah[4] appear to be versatile promoters for heteroatomic nucleophilic ring opening of isolated epoxides. According to the procedures reported so far, the efficiency of those promoters is still unsatisfactory because of need of significant amounts of promoters in order to attain high yield of desired products except in the reaction at the elevated temperature.

Recently, Iranpoor and co-workers have disclosed that widely used neutral oxidants, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and ammonium cerium(IV) nitrate (CAN), catalyze ring-opening reaction of epoxides with alcohols, thiols, and acetic acid.[6] DDQ was also reported to catalyze tetrahydropyranylation of alcohols,[7] glycosidation using glycols,[8] and deprotection of acetals,[9] silyl ethers,[10] and orthoesters.[11] In this context, we have reported that a catalytic amount of tetracyanoethylene (TCNE), a representative π-acid and one-electron acceptor,[12] accelerates substrate-specific rearrangement, acetonidation,[13] and alcoholysis of epoxides,[14] and Mukaiyama aldol reaction of acetals[15] in preliminaly communications. Furthermore, during investigation of the reaction mechanism of TCNE-catalyzed alcoholysis of epoxides,[14] we have envisaged catalytic ability of dicyanoketene dimethyl acetal (**35**; $(CN)_2C{=}C(OMe)_2$), which can be formed in methanolysis of TCNE,[16] in the reactions of epoxides and acetals. Recently, we have reported that dicyanoketene acetals, a new type of π-acid which have a capto-dative olefin structure, catalyze monothioacetalization of saturated acetals,[17] tetrahydropyranylation of alcohols,[18] and alcoholysis of epoxides[19] in preliminary communications. We disclose herein a full detail of a mild, chemoselective, and stereospecific alcoholysis of epoxides catalyzed by TCNE and dicyanoketene acetals including novel regioselective ring-opening associated with remote anchimetric assistance of the ethereal oxygen function. The mechanistic aspects of these reactions are also discussed here.

Results and Discussion

A trisubstituted epoxide (**1**) reacted with MeOH under the presence of catalytic amount (0.1 molar ammount) of TCNE at room temperature to give a secondary alcohol (**2a**) as a single regioisomer in high yield (97%). In a variety of alcohols such as 2-propanol, allyl alcohol, propargyl alcohol, and benzyl alcohol, highly regioselective ring-opening reaction of the epoxide (**1**) proceeded smoothly at room temperature or 40 °C to afford only the corresponding secondary alcohols (**2b—e**) (Table 1). The corresponding regio-isomers could not be detected in the reaction mixtures.

Various kinds of epoxides including a variety of substitution modes and functional groups have been examined in view of regio- and chemo-selectivity of the reaction and the results are summarized in Table 2. Reaction of trisubstituted epoxides (**1**, **10**, **13**) involved highly regioselective introduction of alkoxy groups at the more substituted side providing secondary alcohols. 1,2-Disubstituted and terminal epoxides (**5**) underwent alcoholysis with low or without regioselectivity. The results appeared largely analogous to those observed generally in acid-catalyzed epoxide opening

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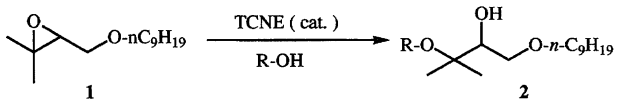
Table 1. Alcoholysis of a Trisubstituted Epoxide (**1**) Catalyzed by TCNE

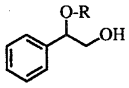
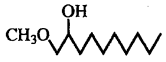
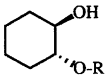
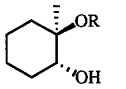
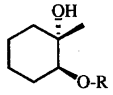
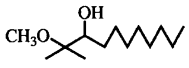
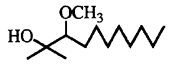
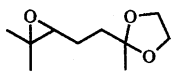
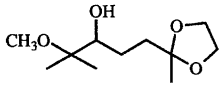
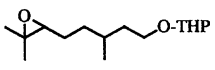
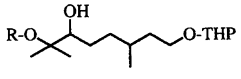
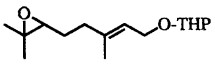
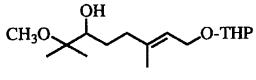


1 **2**

Alcohol (solvent)	TCNE (molar amount)	Temp	Time/h	Product	Yield
CH_3OH	0.1	R. T.	3	**2a**	97%
$H_2C{=}CHCH_2OH$	0.1	R. T.	4	**2b**	95%
$HC{\equiv}CCH_2OH$	0.1	R. T.	4	**2c**	91%
i-PrOH	0.2	40 °C	5	**2d**	69%
BnOH (3 molar amounts)[a)]	0.2	40 °C	3	**2e**	71%

a) Several molar amounts of benzyl alcohol (BnOH) were used for the sake of convenience in work-up procedure.

Table 2. Alcoholysis of Various Epoxides Catalyzed by TCNE

Entry	Epoxide	Alcohol (solvent)	TCNE (molar amount)	Temp	Time	Product/Yield	
							
1	**3**	CH_3OH	0.1	R. T.	1 h	**4a** R=CH_3	92%
2		$CH_2{=}CHCH_2OH$	0.1	R. T.	1 h	**4b** R=$CH_2CH{=}CH_2$	86%
3		BnOH	0.2	40 °C	30 min	**4c** R=Bn	63%
							
4	**5**	CH_3OH	0.2	R. T.	3 h	**6** 37%	**7** 51%
							
5	**8**	CH_3OH	0.2	R. T.	2 h	**9a** R=CH_3	81%
6		$CH_2{=}CHCH_2OH$	0.1	R. T.	1.5 h	**9b** R=$CH_2CH{=}CH_2$	91%
7		$HC{\equiv}CCH_2OH$	0.1	R. T.	4 h	**9c** R=$CH_2C{\equiv}$ CH	84%
8		*i*-PrOH	0.2	R. T.	6 h	**9d** R=*i*-Pr	55%
9		BnOH	0.2	40 °C	2 h	**9e** R=Bn	66%
							
10	**10**	CH_3OH	0.1	R. T.	15 min	R=CH_3 **11a** 76%	**12a** 4%
11		BnOH	0.2	40 °C	30 min	R=Bn **11b** 57%	**12b** 1%
							
12	**13**	CH_3OH	0.1	R. T.	30 min	**14** 91%	**15** 2%
							
13	**16**	CH_3OH	0.1	−30 °C	19 h	**17**	78%
							
14	**18**	CH_3OH	0.1	R. T.	45 min	**19a** R=CH_3	81%
15		BnOH	0.25	40 °C	1.5 h	**19b** R=Bn	66% (S.M. 13%)
							
16	**20**	CH_3OH	0.1	R. T.	30 min	**21**	75%

reactions.[1)] In methanolysis of styrene oxide (**3**), the ring-opening product (**4a**) was obtained as a sole product, although the corresponding regio-isomer was obtained in 10% yield in the methanolysis catalyzed by sulfuric acid.[20)]

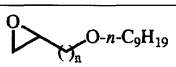
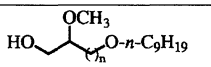
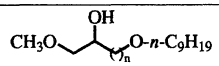
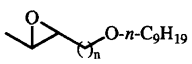
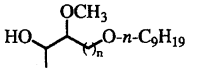
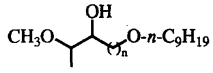
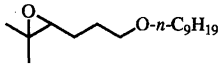
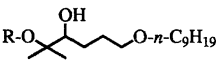
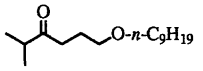
TCNE is a neutral and very mild catalyst for acid sensitive functional groups. The conditions of TCNE-catalyzed alcoholysis of epoxides left the acid-labile functions (ethylene acetal (**16**) and tetrahydropyranyl ethers (**18**, **20**)) intact, although it is neccessary to carry out the reaction at the low temperature (−30 °C) in the case of a substrate (**16**) containing the acetal portion. In contrast to TCNE-catalyst, the use of Lewis acid such as BF_3–Et_2O remove immediately the tetrahydropyranyl group under the same condition.

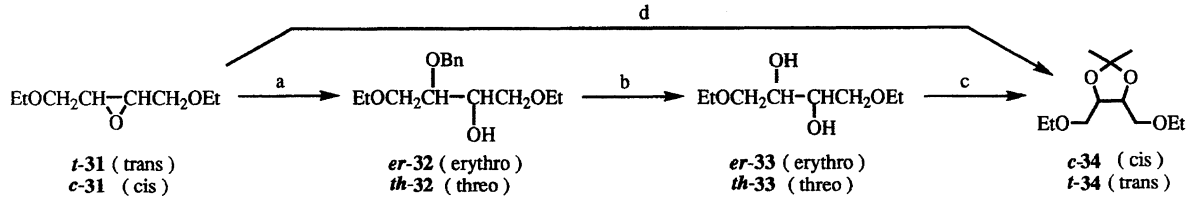
Anchimeric Assistance of Intramolecular Etheric Oxygen. As shown in Table 3, novel high regioselectivity associated with 5-exo mode[21] of anchimeric assistance[22] was observed for certain epoxides which bear an etheric oxygen function at the remote position on the side chain by three methylene units from the epoxide portion. Thus, screening of the reaction of a series of 1,2-epoxy-ethers (Entries 1—4) and 2,3-epoxy-ethers (Entries 5—8) which contain various length of carbon chain between the epoxide and ethereal function, revealed that only 5-nonyloxy-1-pentene oxide (**22c**) and *trans*-6-nonyloxy-2-hexene oxide (**25c**) underwent highly regio-selective methanolysis at the more hindered side of the oxirane ring. This results are ascribed to activation of one of the C–O bond of oxirane by 5-*exo* mode assistance of an intramolecular etheric oxygen. Other substrates examined produced non-regioselective methanolysis products (Entries 4 and 8) or provided predominantly the products which derived by methanolysis at the less hindered side particularly of epoxy-ethers with one or two methylene unit(s) length (Entries 1, 2, 5, 6). On the other hand, with trisubstituted epoxy-ethers having an ethereal oxygen function at the remote position by three methylene units from the epoxy function, rearrangement occurred competitively to give a ketone (**30**)[13] as well as alcoholysis providing a secondary alcohol (Entries 9 and 10).

Stereochemistry. As shown in Scheme 1, stereochemical investigation demonstrated that the TCNE-catalyzed alcoholysis proceeds through the stereospecific *anti*-opening mode. *trans*-1,4-Diethoxy-2-butene oxide (***t*-31**) was subjected to the TCNE-catalyzed alcoholysis in benzyl alcohol to give an alcohol (***er*-32**) as a single stereoisomer. Stereochemistry of the alcohol (***er*-32**) proved *erythro* by derivation of the alcohol to the *cis*-diol acetonide (***c*-34**)[23] by usual hydrogenolytic debenzylation[24] providing the 2, 3-glycol (***er*-33**) followed by usual acetonidation with 2,2-dimethoxypropane in the presence of *p*-TsOH.[25] The acetonide (***c*-34**) was identified with that obtained directly from the starting *trans*-epoxide (***t*-31**) by the known method for stereospecific transformation of epoxides to acetonides using BF_3–Et_2O as a catalyst in acetone.[26] From the corresponding *cis*-epoxide (***c*-31**), *trans*-acetonide (***t*-34**) was obtained as a sole product by way of the same sequence of the reactions (***c*-31**→***th*-32**→***th*-33**→***t*-34**).[23]

Alcohlysis of Epoxides Catalyzed by Dicyanoketene Acetals. A trace amount of dicyanoketene dimethyl acetal

Table 3. Anchimeric Assistance of an Intramolecular Etheric Oxygen

Entry	Epoxide	Alcohol (Solvent)	TCNE (molar amount)	Temp	Time/h	Product/Yield	
							
1	**22a** n=1	CH_3OH	0.2	R. T.	7	**23a** 15%	**24a** 74%
2	**22b** n=2	CH_3OH	0.2	R. T.	6	**23b** 19%	**24b** 72%
3	**22c** n=3	CH_3OH	0.2	R. T.	7	**23c** 84%	**24c** 8%
4	**22d** n=4	CH_3OH	0.2	R. T.	4	**23d** 34%	**24a** 56%
							
5	**25a** n=1	CH_3OH	0.2	R. T.	7	**26a** 26%	**27a** 70%
6	**25b** n=2	CH_3OH	0.1	R. T.	7	**26b** 32%	**27b** 68%
7	**25c** n=3	CH_3OH	0.1	R. T.	4	**26c** 72%	**27c** 9%
8	**25d** n=4	CH_3OH	0.1	R. T.	7	**26d** 43%	**27d** 51%
							
9	**28**	CH_3OH	0.1	R. T.	1.5	**29a** R=CH_3 62%	**30** 34%
10		BnOH	0.2	40 °C	3	**29b** R=Bn 16%	61%



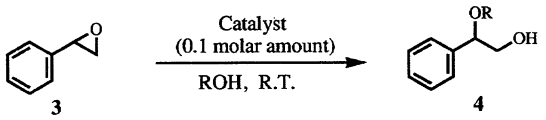
Scheme 1.

(DCKDMA; **35**)[16] was detected in the reaction mixture of methanolysis of epoxides catalyzed by TCNE. When the catalytic activity of DCKDMA (**35**) was examined, DCKDMA (**35**) was found to catalyze methanolysis of styrene oxide (**3**) to afford the corresponding ring-opening product (**4a**) in 94% yield. Therefore, attention was focused on the catalytic activity of various types of capto-dative ethylenes in methanolysis of styrene oxide as a model reaction, and the results are summarized in Table 4. The relative activity of dicyanoketene acetals as a π-acid catalyst was observed to be the following order: **35**≈**36**>**37**>**38**. **39** and **41** were a poor catalyst for alcoholysis of epoxides, and no reaction proceeded at all. Although the activity of **40** appeared nearly equal to that of dicyanoketene ethylene acetal (DCKEA) (**37**),[16] the net activity of **40** is ambiguous because **40** was found to be converted partially to reactive DCKDMA (**35**) under the reaction conditions. Therefore, we selected DCKDMA (**35**), which is the most reactive catalyst examined, and DCKEA (**37**), which is easily available and highly reactive, and have investigated their catalytic activity in the alcoholysis of typical epoxides.

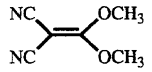
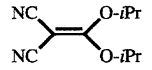
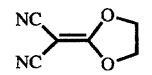
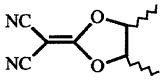
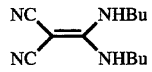
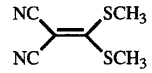
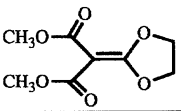
Treatment of a cyclohexene oxide (**8**) in MeOH with catalytic amount (0.2 molar amount) of DCKDMA (**35**) at room temperature for 0.5 h gave a secondary alcohol (**9a**) in good yield (87%). In several alcohols including allyl alcohol and *i*-PrOH, ring-opening reaction of the cyclohexene oxide (**8**) proceeded smoothly at room temperature or 50 °C. Typical epoxides have been examined in view of regio- and chemoselectivity of the reaction, and the results are summarized in Table 5.

Reaction of trisubstituted epoxides involved highly regioselective introduction of alkoxy groups at the more substituted side providing secondary alcohols. Terminal epoxides underwent alcoholysis with low or without regioselectivity except for styrene oxide, which gave results analogous to those observed generally in acid-catalyzed epoxide opening reactions,[1] and afforded exclusively primary alcohols. The conditions of DCKEA-catalyzed alcoholysis of epoxides left the acid-labile functions (tetrahydropyranyl ethers (**20**)) intact. Highly regioselective methanolysis was exhibited also in the case of the epoxides (**22c**) and (**25c**) to give internal methyl ethers (**23c**) and (**26c**) as the major product, respec-

Table 4. The Catalytic Activity of Capto-dative Ethylenes for Alcoholysis of Styrene Oxide

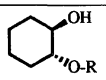
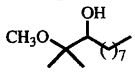
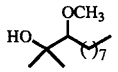
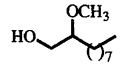
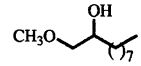
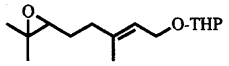
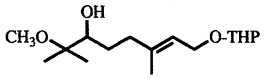
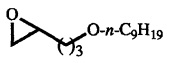
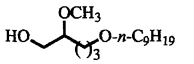
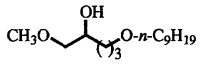
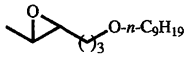
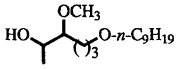
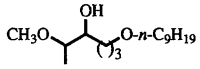
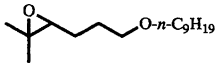
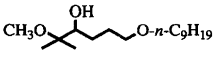
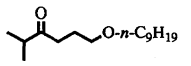


3 **4**

Entry	Catalyst		ROH	Time	Product/Yield	
1			CH_3OH	1 h	**4a**	94%
2		**35**	*i*-PrOH	20 h	**4d**	78% [a,b]
3			*t*-BuOH	45 h	**4e**	36% [a,c]
4		**36**	CH_3OH	1 h	**4a**	94%
5		**37**	CH_3OH	1 h	**4a**	Trace
6			CH_3OH	18 h	**4a**	91%
7		**38**	CH_3OH	24 h	**4a**	Trace
8		**39**	CH_3OH	24 h	**4a**	0%
9		**40**	CH_3OH	1 h	**4a**	Trace
10			CH_3OH	18 h	**4a**	97% [d]
11		**41**	CH_3OH	3d	**4a**	0%

a) Catalytic amount (0.3 molar amount) of **35** was used. b) Compound (**42**) was obtained as a by-product in 14% yield based on the catalyst (**35**) used. c) Compound (**42**) was obtained as a by-product in 50% yield based on the catalyst (**35**) used. d) A significant amount of **35** was detected.

Table 5. Alcoholysis of Epoxides Catalyzed by Dicyanoketene Acetals

Epoxide	Catalyst	Molar amount	Alcohol (Solvent)	Temp	Time/h	Product/Yield	
							
8	**35**	0.2	CH_3OH	R. T.	0.5	**9a** R=CH_3	87%
	35	0.2	Allyl–OH	R. T.	21	**9b** R=$CH_2CH{=}CH_2$	96% [a]
	35	0.2	*i*-PrOH	50 °C	23	**9d** R=*i*-Pr	59% [b]
	37	0.2	CH_3OH	R. T.	3	**9a** R=CH_3	92%
	37	0.2	Allyl–OH	40 °C	24	**9b** R=$CH_2CH{=}CH_2$	73%
							
13	**35**	0.2	CH_3OH	R. T.	1	**14** 95%	**15** 3%
	37	0.1	CH_3OH	R. T.	19	**14** 95%	**15** 3%
	**37**	0.2	CH_3OH	R. T.	25		
5						**6** 39%	**7** 54%
	**37**	0.1	CH_3OH	R. T.	4		
20						**21** 87%	
	**37**	0.1	CH_3OH	R. T.	24		
22c						**23c** 85%	**24c** 8%
	**37**	0.1	CH_3OH	R. T.	48		
25c						**26c** 87%	**27c** 7%
	**37**	0.1	CH_3OH	R. T.	48		
28						**29a** 63%	**30** 33%

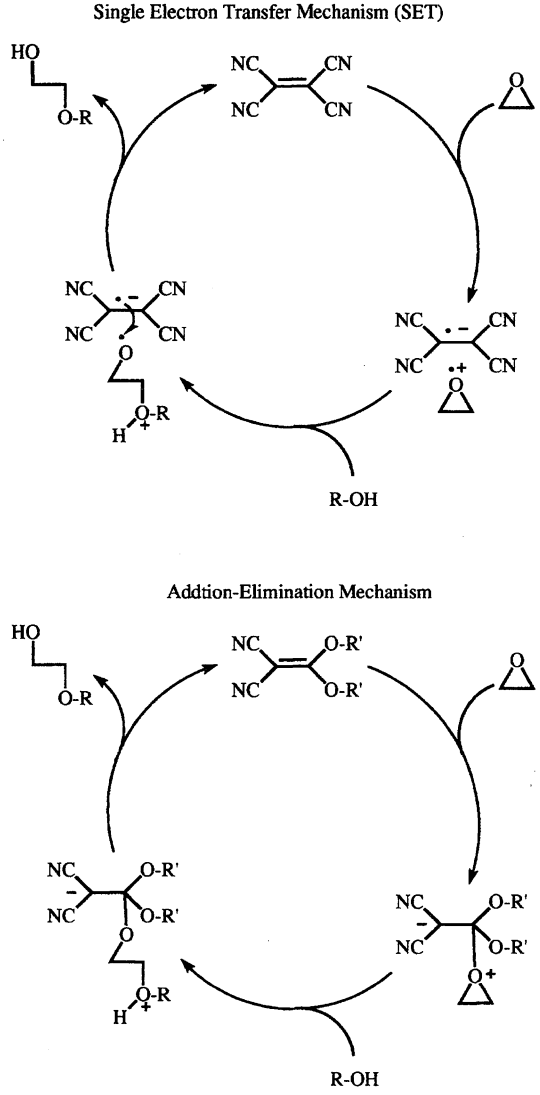
a) Compound (**43**) was obtained as a by-product in 11% yield based on the catalyst (**35**) used. b) Compound (**43**) was obtained as a by-product in 72% yield based on the catalyst (**35**) used.

tively.

Mechanism. A strong acid, tricyanovinyl alcohol[27] generated from TCNE and water if exists in the solvent (alcohols) as impurity, appears to be ruled out as the catalyst, because this alcoholysis described proceeds faster under anhydrous conditions than wet conditions. The UV spectroscopic measurement on the mixture of TCNE and cyclohexene oxide (**8**) in CH_3CN showed significant charge transfer (CT) absorption bands at 295 nm (ε 30.6 $dm^3\,mol^{-1}\,cm^{-1}$).[28] The intensity of CT absorption bands were dependent on the concentration of cyclohexene oxide (**8**). Under the oxgen bubbling condition the reaction was disturbed. Therefore, as shown in Scheme 2, the activation of C–O bond of epoxides for attack of alcohols is presumed to be intiated by the single electron transfer (SET) to the π-system of TCNE from oxygen of epoxides (Scheme 2).

As described in the preceding communication,[17,19] it is worth noting that the reduction-potential of DCKEA measured was very low ($E_p^{red} < -2.0$ V vs. SCE in MeCN) compared with those of TCNE (E_p^{red} 0.15 V vs. SCE in MeCN)[9] and DDQ (E_p^{red} 0.59 V vs. SCE in MeCN),[9] and that no charge-transfer (CT) absorption band could be detected in the UV spectroscopic measurement of the mixture of DCKEA and cyclohexene oxide (**8**) in CH_3CN, although the same mixture of TCNE exhibited a CT absorption band. The adducts (**42**, **43**) of DCKDMA and epoxides (**3**, **37**) were detected as by-products in the reaction mixture (Chart 1). These adducts (**42**, **43**) may be formed via nucleophilic attack of the oxygen of epoxides to the double bond of DCKDMA associated with epoxide ring fission accompanied by cyclization. Although mechanisms for the present reaction are still ambiguous on the basis of the above observations so far, coordination between the π-system of dicyanoketene acetals and the oxygen of epoxides is presumed to be one of the factors responsible for the activation of the C–O bond of epoxides (Scheme 2).

Conclusion. TCNE and dicyanoketene acetals are mild and neutral catalysts for the alcoholysis of epoxides. We demonstrated the stereospecific anti-opening and favorable chemoselectivity without cleavage of tetrahydropyranyl ether and ethylene acetal groups. In the reaction of terminal and 1,2-disubstituted epoxides, a novel regioselective opening reaction associated with anchimeric assistance of the intramolecular etheric oxygen.



Scheme 2.

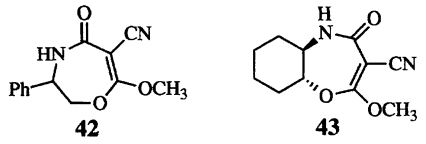


Chart 1.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and were uncorrected. IR absorption spectra were recorded on a JASCO IRA-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) and a JEOL JNM-EX-400 (400 MHz) spectrometer with $SiMe_4$ as an internal standard. Mass spectra (MS) and high-resolution MS (HRMS) were recorded on a JEOL JMS-D300 and a JEOL JMS-SX102A spectrometer and are indicated at *m/z*. UV-visible absorption spectra were recorded on a Shimadzu UV-260. Products were purified by column chromatography on silica gel (Merck, Kieselgel 60, 70—230 or 230—400 mesh). TCNE was purified by recrystallization from 1,2-dichloroethane. The reaction solvents (alcohols) were distilled from sodium and stored over molecular sieves.

3-Methyl-1-nonyloxy-2-butene Oxide (1): 3-Methyl-2-buten-1-ol (5.00 g, 58.1 mmol) was added to a suspension of NaH (2.09 g, 87.1 mmol) in DMF (60 ml) under argon atmosphere, and the mixture was stirred at room temperature for 2 h. Nonyl bromide (14.4 g, 69.7 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 24 h. Water was added, and the reaction mixture was extracted with ether. The crude product thus obtained was purified by distillation to give 3-methyl-1-nonyloxy-2-butene (9.08 g, 74%) as a colorless oil (103 °C/2 mmHg). *m*-Chloroperbenzoic acid (MCPBA) (1.45 g, 8.41 mmol) was added to a solution 3-methyl-1-nonyloxy-2-butene (1.70 g, 8.01 mmol) in CH_2Cl_2 (32 ml) at 0 °C, and the mixture was stirred at the same temperature for 1 h. After addition of aq 2% NaOH, and the reaction mixture was extracted with CH_2Cl_2. The crude product thus obtained was purified by silica-gel chromatography (ether–hexane, 1 : 30) to give **1** (1.46 g, 80%) as a colorless oil. IR (neat) 1455, 1375, 1105 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2-C<u>H</u>$_3$), 1.27 (12H, m), 1.29 (3H, s, C–CH_3), 1.34 (3H, s, C–CH_3), 1.59 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.95 (1H, t, J = 5.9 Hz, CH), 3.42—3.65 (4H, m, O–CH_2×2). HRMS (FAB) Calcd for $C_{14}H_{29}O_2$: (M+H$^+$), 229.2168. Found: *m/z* 229.2178.

2-Methyl-2-undecene Oxide (13): Compound **13** was prepared by MCPBA oxidation of 2-methyl-2-undecene which was obtained by the reported method.[29] Colorless oil; IR ($CHCl_3$) 1460, 1390, 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2-C<u>H</u>$_3$), 1.26 (3H, s, C–CH_3), 1.27 (12H, m), 1.31 (3H, s, C–CH_3), 1.51 (2H, m, CH–C<u>H</u>$_2$), 2.71 (1H, t, J = 6.4 Hz, CH). HRMS (FAB) Calcd for $C_{12}H_{25}O$: (M+H$^+$), 185.1906. Found: *m/z* 185.1917.

3-Nonyloxy-1-propene Oxide (22a): Compound **22a** was prepared from allyl alcohol by the similar synthetic method of **1**. Colorless oil; IR (neat) 1470, 1105, 910, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.27 (12H, m), 1.58 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.61 (1H, m, CH–C<u>H</u>$_2$), 2.80 (1H, m, CH–C<u>H</u>$_2$), 3.15 (1H, m, CH), 3.35—3.56 (3H, m, O–CH_2), 3.71 (1H, m, O–CH_2). Found: C, 71.87; H, 12.15%. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

4-Nonyloxy-1-butene Oxide (22b): Compound **22b** was prepared from 3-buten-1-ol by the similar synthetic method of **1**. Colorless oil; IR (neat) 1465, 1110 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.27 (12H, m), 1.57 (2H, m, O–CH_2–C<u>H</u>$_2$), 1.68—1.93 (2H, m, CH–C<u>H</u>$_2$), 2.52 (1H, dd, J = 4.9, 2.9 Hz, O–C<u>H</u>$_2$–CH), 2.78 (1H, m, O–C<u>H</u>$_2$–CH), 3.05 (1H, m, CH), 3.42 (2H, t, J = 6.8 Hz, O–CH_2), 3.55 (2H, t, J = 6.8 Hz, O–CH_2). HRMS (FAB) Calcd for $C_{13}H_{27}O_2$: (M+H$^+$), 215.2011. Found: *m/z* 215.2016.

5-Nonyloxy-1-pentene Oxide (22c): Compound **22c** was prepared from 4-penten-1-ol by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1460, 1370, 1100, 840, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.27 (12H, m), 1.52—1.82 (6H, m), 2.48 (1H, dd, J = 4.9, 2.9 Hz, CH–C<u>H</u>$_2$–O), 2.75 (1H, m, CH–C<u>H</u>$_2$–O), 2.95 (1H, m, CH), 3.37—3.52 (4H, m, O–CH_2×2). HRMS (FAB) Calcd for $C_{14}H_{29}O_2$: (M+H$^+$), 229.2168. Found: *m/z* 229.2181.

6-Nonyloxy-1-hexene Oxide (22d): Compound **22d** was prepared from 5-hexen-1-ol by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1465, 1100, 830 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.27 (14H, m), 1.48—1.69 (6H, m), 2.47 (1H, dd, J = 5.4, 2.9 Hz, CH–C<u>H</u>$_2$–O), 2.75 (1H, dd, J = 4.9, 3.9 Hz, CH–C<u>H</u>$_2$–O), 2.91 (1H, m, CH), 3.37—3.44 (4H, m, O–CH_2×2). HRMS (FAB) Calcd for $C_{15}H_{31}O_2$: (M+H$^+$), 243.2324. Found: *m/z* 243.2318.

(*E*)-4-Nonyloxy-2-butene Oxide (25a): Compound **25a** was

prepared from *trans*-2-buten-1-ol by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1470, 1460, 1125, 1100, 860 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.27 (12H, m), 1.33 (3H, d, J=5.4 Hz, CH–$C\underline{H_3}$), 1.57 (2H, m, O–CH_2–$C\underline{H_2}$), 2.88 (2H, m, CH×2), 3.39—3.50 (3H, m, O–CH_2), 3.63 (1H, dd, J=11.7, 3.4 Hz, O–CH_2). Found: C, 72.51; H, 12.23%. Calcd for $C_{13}H_{26}O_2$: C, 72.85; H, 12.23%.

(*E*)-5-Nonyloxy-2-pentene Oxide (25b): *trans*-3-Penten-1-ol was synthesized by $LiAlH_4$ reduction of *trans*-3-pentenoic acid which was obtained by the hydrolysis of *trans*-3-pentenenitrile.[30] **25b** was prepared from *trans*-3-penten-1-ol by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1470, 1370, 1100 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.27 (12H, m), 1.30 (3H, d, J=4.9 Hz, CH–$C\underline{H_3}$), 1.57 (2H, m, O–CH_2–$C\underline{H_2}$), 1.65—1.93 (2H, m, CH–$C\underline{H_2}$), 2.79 (2H, m, CH×2), 3.42 (2H, t, J=6.8 Hz, O–CH_2), 3.53 (2H, m, O–CH_2). Found: C, 73.22; H, 12.38%. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36%.

(*E*)-6-Nonyloxy-2-hexene Oxide (25c): Compound **25c** was prepared from *trans*-4-hexen-1-ol[31] by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1470, 1450, 1100 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.26 (12H, m), 1.30 (3H, d, J=5.4 Hz, CH–$C\underline{H_3}$), 1.51—1.81 (6H, m), 2.67 (1H, m, CH), 2.76 (1H, m, CH), 3.37—3.48 (4H, m, O–CH_2×2). Found: C, 74.02; H, 12.52%. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.47%.

(*E*)-7-Nonyloxy-2-heptene Oxide (25d): Compound **25d** was prepared from *trans*-5-hepten-1-ol[32] by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1460, 1090 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.28 (14H, m), 1.29 (3H, d, J=6.8 Hz, CH–$C\underline{H_3}$), 1.53—1.66 (6H, m), 2.63 (1H, m, CH), 2.75 (1H, m, CH), 2.75 (1H, m, CH), 3.39 (4H, m, O–CH_2×2). Found: C, 74.54; H, 12.68%. Calcd for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58%.

2-Methyl-6-nonyloxy-2-hexene Oxide (28): Compound **28** was prepared from 5-methyl-4-hexen-1-ol[33] by the similar synthetic method of **1**. Colorless oil; IR ($CHCl_3$) 1460, 1380, 1105, 895 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.27 (15H, m), 1.31 (3H, s, C–CH_3), 1.51—1.86 (6H, m), 2.75 (1H, t, J=5.9 Hz, CH), 3.37—3.52 (4H, m, O–CH_2×2). HRMS (EI) Calcd for $C_{16}H_{32}O_2$: (M^+), 256.2402. Found: *m/z* 256.2381.

(*E*)-1,4-Diethoxy-2-butene Oxide (*t*-31):[34] *trans*-2-Butene-1,4-diol[35] (5.00 g, 56.8 mmol) was added to a suspension of NaH (4.09 g, 170.2 mmol) in DMF (130 ml) under argon atmosphere, and the mixture was stirred at room temperature for 4 h. Ethyl iodide (25.0 g, 160.3 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 18 h. Water was added, and the reaction mixture was extracted with ether. The crude product thus obtained was purified by distillation to give 1,4-diethoxy-2-butene (7.29 g, 89%) as a colorless oil (74—77 °C/18 mmHg, 1 mmHg=133.322 Pa). *m*-Chloroperbenzoic acid (MCPBA) (2.15 g, 12.5 mmol) was added to a solution 1,4-diethoxy-2-butene (1.50 g, 10.4 mmol) in CH_2Cl_2 (40 ml), and the mixture was stirred at room temperature for 18 h. 2% NaOH aq was added, and the reaction mixture was extract with CH_2Cl_2. The crude product thus obtained was purified by silica-gel chromatography to give ***t*-31** (1.48 g, 89%) as colorless oil. IR (neat) 1375, 1220, 1100, 870 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.21 (6H, t, J=7.3 Hz, CH_3×2), 3.07 (2H, m, CH×2), 3.45 (2H, dd, J=11.7, 5.4 Hz), 3.49—3.63 (4H, m), 3.72 (2H, dd, J=11.7, 2.9 Hz).

(*Z*)-1,4-Diethoxy-2-butene Oxide (*c*-31):[34] Similarly to the preparation of ***t*-31**, ***c*-31** was obtained from *cis*-2-butene-1,4-diol. white crystals; Mp 38 °C. IR ($CHCl_3$) 1380, 1220, 1100, 1020, 890, 850 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.23 (6H, t, J=7.3 Hz, CH_3×2), 3.22 (2H, m, CH×2), 3.47—3.71 (4H, m).

General Procedure for Alcoholysis of Epoxides Catalyzed by TCNE: A catalytic amount (0.1—0.25 molar amount) of TCNE was added to a solution of epoxides in alcohols, and the mixture was stirred at room temperature or 40 °C for 15 min—6 h. The reaction solvent was evaporated off and the residue was chromatographed on silica gel to give the ring opening product. Some of the alcoholic products were derived to the corresponding acetates for isolation and identification. The yields and conditions were shown in Tables 1 and 2.

Existence of a trace amount of dicyanoketene dimethyl acetal (DCKDMA) was detected by a sharp singlet at δ=4.21 in ^1H NMR spectrum of the reaction mixture whenever methanol was used as a nucleophile. Compounds **9b**[2] and **9d**[36] were identified by comparison of their spectroscopic properties with those described in the literature. Products **19a**, **19b**, and **21** were obtained as an inseparable mixture of diastereomers.

2- Methoxy- 2- methyl- 1- (nonyloxymethyl)propyl Acetate (Acetate of 2a): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1240, 1065 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.16 (3H, s, C–CH_3), 1.19 (3H, s, C–CH_3), 1.26 (12H, m), 1.53 (2H, m, O–CH_2–$C\underline{H_2}$), 2.11 (3H, s, Ac), 3.23 (3H, s, O–CH_3), 3.33 (1H, dt, J=8.8, 6.8 Hz, O–CH_2), 3.43—3.55 (2H, m, O–CH_2), 3.68 (1H, dd, J=11.2, 2.9 Hz, CH–$C\underline{H_2}$), 5.15 (1H, dd, J=8.3, 2.9 Hz, CH). HRMS (FAB) Calcd for $C_{17}H_{35}O_4$: ($M+H^+$), 303.2535. Found: *m/z* 303.2514

2- Allyloxy- 2- methyl- 1- (nonyloxymethyl)propyl Acetate (Acetate of 2b): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1240, 1050 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.19 (3H, s, C–CH_3), 1.22 (3H, s, C–CH_3), 1.26 (12H, m), 1.52 (2H, m, O–CH_2–$C\underline{H_2}$), 2.10 (3H, s, Ac), 3.33 (1H, dt, J=8.8, 6.8 Hz, O–$C\underline{H_2}$–CH_2), 3.44—3.57 (2H, m), 3.71 (1H, dd, J=11.2, 2.9 Hz, AcO–CH–$C\underline{H_2}$), 3.96 (2H, m, O–$C\underline{H_2}$CH=), 5.08—5.30 (3H, m), 5.81—5.95 (1H, m, $C\underline{H}$=CH_2). HRMS (FAB) Calcd for $C_{19}H_{37}O_4$: ($M+H^+$), 329.2962. Found: *m/z* 329.2677.

3- Methyl- 1- nonyloxy- 3- (2- propynyloxy)- 2- butanol (2c): Colorless oil; IR ($CHCl_3$) 3520 (OH), 3300 (C≡C), 1450, 1360, 1150, 1080 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.23 (3H, s, C–CH_3), 1.24 (12H, m), 1.27 (3H, s, C–CH_3), 1.58 (2H, m, O–CH_2–$C\underline{H_2}$), 2.39 (1H, t, J=2.4 Hz, C≡CH), 2.63 (1H, d, J=2.9 Hz, OH), 3.39—3.49 (3H, m, O–CH_2), 3.59 (1H, dd, J=9.8, 3.4 Hz, HO–CH–$C\underline{H_2}$), 3.72 (1H, m, HO–$C\underline{H}$), 4.17 (2H, d, J=2.4 Hz, $C\underline{H_2}$–C≡C). Found: C, 71.58; H, 11.46%. Calcd for $C_{17}H_{32}O_3$: C, 71.79; H, 11.34%.

2- Isopropoxy- 2- methyl- 1- (nonyloxymethyl)propyl Acetate (Acetate of 2d): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1240, 1110 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.11 (6H, d, J=6.4 Hz, CH–$C\underline{H_3}$×2), 1.15 (3H, s, C–CH_3), 1.18 (3H, s, C–CH_3), 1.26 (12H, m), 1.51 (2H, m, O–CH_2–$C\underline{H_2}$), 2.09 (3H, s, Ac), 3.29—3.54 (3H, m), 3.74 (1H, dd, J=11.2, 2.9 Hz, AcO–CH–$C\underline{H_2}$), 3.88 (1H, m, O–CH), 5.07 (1H, dd, J=8.3, 2.9 Hz, AcO–$C\underline{H}$). HRMS (FAB) Calcd for $C_{19}H_{39}O_4$: ($M+H^+$), 331.2848. Found: *m/z* 331.2837.

3-Benzyloxy-3-methyl-1-nonyloxy-2-butanol (2e): Colorless oil; IR ($CHCl_3$) 3520 (OH), 1470, 1380, 1150, 1110, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.8 Hz, CH_2–$C\underline{H_3}$), 1.27 (3H, s, C–CH_3), 1.28 (12H, m), 1.29 (3H, s, C–CH_3), 1.59 (2H, m, O–CH_2–$C\underline{H_2}$), 2.54 (1H, brs, OH), 3.47 (3H, m, O–CH_2), 3.63 (1H, dd, J=9.8, 3.4 Hz, HO–CH–$C\underline{H_2}$), 3.79 (1H, dd, J=7.8, 3.4 Hz, HO–$C\underline{H}$), 4.50 (2H, s, Ph–$C\underline{H_2}$), 7.32 (5H, m, ArH). HRMS (FAB) Calcd for $C_{21}H_{37}O_3$: ($M+H^+$), 337.2742. Found: *m/z* 337.2714.

2-Methoxy-2-phenylethyl Acetate (Acetate of 4a): Colorless

oil; IR ($CHCl_3$) 1735 (C=O), 1450, 1365, 1120, 1035, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 2.08 (3H, s, Ac), 3.29 (3H, s, O–CH_3), 4.19 (2H, m, CH_2), 4.43 (1H, dd, J = 7.3, 4.4 Hz, CH), 7.35 (5H, m, ArH). HRMS (FAB) Calcd for $C_{11}H_{15}O_3$: ($M+H^+$), 195.1021. Found: *m/z* 195.1023.

2-Allyloxy-2-phenylethyl Acetate (Acetate of 4b): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1450, 1360, 1220, 1030, 925, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 2.07 (3H, s, Ac), 3.85 (1H, dd, J = 13.2, 6.3 Hz, O–CH_2), 4.02 (1H, dd, J = 13.2, 5.4 Hz, O–CH_2), 4.21 (2H, d, J = 5.9 Hz, AcO–CH_2), 4.60 (1H, t, J = 5.9 Hz, Ph–CH), 5.18 (1H, dd, J = 10.3, 1.5 Hz, CH=CH_2), 5.26 (1H, dd, J = 17.6, 1.5 Hz, CH=CH_2), 5.83—5.97 (1H, m, CH=CH_2), 7.35 (5H, m, ArH). Found: C, 70.74; H, 7.31%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

2-Benzyloxy-2-phenylethyl Acetate (Acetate of 4c): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1445, 1360, 1085, 1020 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 2.05 (3H, s, Ac), 4.20 (1H, dd, J = 11.7, 4.4 Hz, AcO–CH_2), 4.26 (1H, dd, J = 11.7, 7.3 Hz, AcO–CH_2), 4.34, 4.58 (2H, each d, J = 11.7 Hz, Ph–CH_2), 4.61 (1H, dd, J = 7.3, 4.4 Hz, Ph–CH), 7.25—7.40 (10H, m, ArH). HRMS (FAB) Calcd for $C_{17}H_{19}O_3$: ($M+H^+$), 271.1334. Found: *m/z* 271.1321.

2-Methoxydecyl Acetate (Acetate of 6): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1460, 1365, 1235, 1095, 1035 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 7.3 Hz, CH_2–CH_3), 1.28 (12H, m), 1.51 (2H, m, O–CH_2–CH_2), 2.09 (3H, s, Ac), 3.36 (1H, m, O–CH), 3.41 (3H, s, O–CH_3), 4.02 (1H, dd, J = 11.7, 5.9 Hz, AcO–CH_2), 4.17 (1H, dd, J = 11.7, 3.4 Hz, AcO–CH_2). HRMS (FAB) Calcd for $C_{13}H_{27}O_3$: ($M+H^+$), 231.1961. Found: *m/z* 231.1968.

1-Methoxymethylnonyl Acetate (Acetate of 7): Colorless oil; IR ($CHCl_3$) 1725 (C=O), 1460, 1370, 1240, 1110, 1015 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–CH_3), 1.26 (12H, m), 1.58 (2H, m, AcO–CH–CH_2), 2.07 (3H, s, Ac), 3.36 (3H, s, O–CH_3), 3.44 (2H, m, O–CH_2), 5.01 (1H, m, AcO–CH). HRMS (FAB) Calcd for $C_{13}H_{27}O_3$: ($M+H^+$), 231.1960. Found: *m/z* 231.1969.

***trans*-2-Methoxy-1-cyclohexanol (9a):** Colorless oil; IR (neat) 3410 (OH), 1450, 1185, 1095, 990, 910, 840 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.01—1.37 (4H, m), 1.71 (2H, m), 1.96—2.15 (2H, m), 2.77 (1H, brs, OH), 2.94 (1H, m, O–CH), 3.37—3.46 (1H, m, O–CH), 3.40 (3H, s, O–CH_3). HRMS (EI) Calcd for $C_7H_{14}O_2$: (M^+), 130.0993. Found: *m/z* 130.0986.

***trans*-2-(2-Propynyloxy)-1-cyclohexanol (9c):** Colorless oil; IR ($CHCl_3$) 3540 (OH), 3310 (C≡C), 1450, 1080, 1010 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.22 (4H, m), 1.72 (2H, m), 2.05 (2H, m), 2.45 (1H, m, ≡CH), 2.68 (1H, brs, OH), 3.26 (1H, m, O–CH), 3.45 (1H, m, O–CH), 4.19, 4.30 (2H, each dd, J = 16.1, 2.4 Hz, ≡C–CH_2). HRMS (EI) Calcd for $C_9H_{14}O_2$: (M^+), 154.0994. Found: *m/z* 154.1009.

***trans*-2-Benzyloxy-1-cyclohexanol (9e):** Colorless oil; IR (neat) 3420 (OH), 1450, 1080, 730, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.24 (4H, m), 1.70 (2H, m), 2.01 (1H, m), 2.14 (1H, m), 2.69 (1H, s, OH), 3.19 (1H, m, O–CH), 3.48 (1H, m, O–CH), 4.47, 4.70 (2H, each d, J = 11.7 Hz, Ph–CH_2), 7.34 (5H, m, ArH). HRMS (EI) Calcd for $C_{13}H_{18}O_2$: (M^+), 206.1307. Found: *m/z* 206.1318.

***trans*-2-Methoxy-2-methyl-1-cyclohexanol (11a):** Colorless oil; IR ($CHCl_3$) 3540 (OH), 1465, 1425, 1375, 1110, 1070, 1030 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.15 (3H, s, CH_3), 1.30 (4H, m), 1.64—1.89 (4H, m), 2.22 (1H, brs, OH), 3.23 (3H, s, O–CH_3), 3.57 (1H, m, HO–CH). HRMS (EI) Calcd for $C_8H_{16}O_2$: (M^+), 144.1151. Found: *m/z* 144.1164.

***trans*-2-Methoxy-1-methyl-1-cyclohexanol (12a):** Colorless oil; IR (neat) 3420 (OH), 1460, 1380, 1175, 1150, 1100, 980, 930, 890 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.19 (3H, s, C–CH_3), 1.21—1.47 (4H, m), 1.59—1.72 (3H, m), 1.96 (1H, m), 2.27 (1H, brs, OH), 3.02 (1H, dd, J = 5.9, 4.4 Hz, O–CH), 3.39 (3H, s, O–CH_3). HRMS (EI) Calcd for $C_8H_{16}O_2$: (M^+), 144.1151. Found: *m/z* 144.1141.

***trans*-2-Benzyloxy-2-methyl-1-cyclohexanol (11b):** Colorless oil; IR ($CHCl_3$) 3540 (OH), 3420, 1450, 1380, 1110, 1075, 1060, 1020, 690 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.23—1.53 (4H, m), 1.27 (3H, s, CH_3), 1.65 (2H, m), 1.91 (2H, m), 2.26 (1H, d, J = 2.0 Hz, OH), 3.66 (1H, m, HO–CH), 4.45, 4.50 (2H, each d, J = 11.2 Hz, Ph–CH_2), 7.33 (5H, m, ArH). HRMS (EI) Calcd for $C_{14}H_{20}O_2$: (M^+), 220.1463. Found: *m/z* 220.1479.

***trans*-2-Benzyloxy-1-methyl-1-cyclohexanol (12b):** Colorless oil; IR ($CHCl_3$) 3330 (OH), 1450, 1365, 1140, 1080, 975 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.23 (3H, s, CH_3), 1.29—1.42 (4H, m), 1.57—1.72 (3H, m), 1.95 (1H, m), 2.19 (1H, brs, OH), 3.28 (1H, m, O–CH), 4.48, 4.69 (2H, each d, J = 12.2 Hz, Ph–CH_2), 7.34 (5H, m, ArH). HRMS (EI) Calcd for $C_{14}H_{20}O_2$: (M^+), 220.1463. Found: *m/z* 220.1475.

2-Methoxy-2-methyl-3-undecanol (14): Colorless oil; IR ($CHCl_3$) 3520 (OH), 1470, 1380, 1370, 1150, 1060 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–CH_3), 1.08 (3H, s, C–CH_3), 1.12 (3H, s, C–CH_3), 1.27 (13H, m), 1.62—1.68 (1H, m, HO–CH–CH_2), 2.50 (1H, d, J = 1.5 Hz, OH), 3.23 (3H, s, O–CH_3), 3.45 (1H, m, HO–CH). Found: C, 71.93; H, 13.24%. Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.04%.

3-Methoxy-2-methyl-2-undecanol (15): Colorless oil; IR (neat) 3430 (OH), 1470, 1375, 1100 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.89 (3H, t, J = 6.8 Hz, CH_2–CH_3), 1.13 (3H, s, C–CH_3), 1.18 (3H, s, C–CH_3), 1.28 (12H, m), 1.47 (2H, m, CH–CH_2), 2.28 (1H, brs, OH), 2.91 (1H, dd, J = 7.8, 3.2 Hz, O–CH), 3.51 (3H, s, O–CH_3). HRMS (FAB) Calcd for $C_{13}H_{27}O$: ($M+H-H_2O^+$), 199.2062. Found: *m/z* 199.2052.

2-Methoxy-2-methyl-1-[2-(2-methyl-1,3-dioxolan-2-yl)ethyl]-propyl Acetate (Acetate of 17): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1070 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.15 (6H, s, C–CH_3×2), 1.31 (3H, s, CH_3), 1.59—1.81 (4H, m, CH–CH_2–CH_2), 2.09 (3H, s, Ac), 3.22 (3H, s, O–CH_3), 3.93 (4H, m, O–CH_2–CH_2–O), 4.95 (1H, m, CH). HRMS (FAB) Calcd for $C_{13}H_{25}O_5$: ($M+H^+$), 261.1702. Found: *m/z* 261.1695.

1-(1-Methoxy-1-methylethyl)-4-methyl-6-(2-tetrahydropyranyloxy)hexyl Acetate (Acetate of 19a): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1070, 1020 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.90 (3H, d, J = 6.4 Hz, CH–CH_3), 1.14 (6H, s, C–CH_3×2), 1.29—1.85 (13H, m), 2.09 (3H, s, Ac), 3.22 (3H, s, O–CH_3), 3.36—3.52 (2H, m, O–CH_2), 3.71—3.91 (2H, m, O–CH_2), 4.57 (1H, m, O–CH–O), 4.93 (1H, dd, J = 10.7, 2.9 Hz, AcO–CH). HRMS (FAB) Calcd for $C_{18}H_{35}O_5$: ($M+H^+$), 331.2484. Found: *m/z* 331.2460.

1-(1-Benzyloxy-1-methylethyl)-4-methyl-6-(2-tetrahydropyranyloxy)hexyl Acetate (Acetate of 19b): Colorless oil; IR ($CHCl_3$) 1725 (C=O), 1450, 1365, 1060, 1020 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.90 (3H, m, CH–CH_3), 1.24 (6H, s, C–CH_3×2), 1.17—1.83 (13H, m), 2.09 (3H, s, Ac), 3.45 (2H, m, O–CH_2), 3.81 (2H, m, O–CH_2), 4.49 (2H, m, Ph–CH_2), 4.55 (1H, m, O–CH–O), 5.04 (1H, dd, J = 10.7, 2.4 Hz, AcO–CH), 7.31 (5H, m, ArH). HRMS (FAB) Calcd for $C_{24}H_{39}O_5$: ($M+H^+$), 407.2798. Found: *m/z* 407.2785.

***(E)*-1-(1-Methoxy-1-methylethyl)-4-methyl-6-(2-tetrahydropyranyloxy)-4-hexenyl Acetate (Acetate of 21):** Colorless oil; IR ($CHCl_3$) 1720 (C=O), 1370, 1070, 1015 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.14 (6H, s, C–CH_3×2), 1.54—2.05 (10H, m), 1.68 (3H, s, =CCH_3), 2.09 (3H, s, Ac), 3.22 (3H, s, O–CH_3), 3.52, 3.89 (2H,

each m, O–CH_2), 4.01 (1H, dd, J = 11.7, 7.3 Hz, O–C<u>H</u>$_2$CH=), 4.24 (1H, dd, J = 12.2, 6.8 Hz, O–C<u>H</u>$_2$CH=), 4.63 (1H, t, J = 3.9 Hz, O–CH–O), 4.95 (1H, m, AcO–C<u>H</u>), 5.37 (1H, t, J = 5.9 Hz, =CH). Found: C, 65.60; H, 9.81%. Calcd for $C_{18}H_{32}O_5$: C, 65.82; H, 9.82%.

General Procedure for the Alcoholysis of Epoxides 22a—d (Table 3): TCNE (9.0 mg, 0.07 mmol) was added to a solution of epoxide **22a** (70 mg, 0.35 mmol) in CH_3OH (2 ml), and the reaction mixture was stirred at room temperature for 7 h. The reaction solvent was evaporated off and the residue was chromatographed on silica gel to give 2-methoxy-3-nonyloxy-1-propanol (**23a**) (60.0 mg, 74%) and 1-methoxy-3-nonyloxy-2-propanol (**24a**) (12.2 mg, 15%).

(23a): Colorless oil; IR ($CHCl_3$) 3550, 3460 (OH), 1465, 1110 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.27 (12H, m), 1.57 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.20 (1H, brs, OH), 3.37—3.79 (7H, m), 3.47 (3H, s, O–CH_3). HRMS (FAB) Calcd for $C_{13}H_{29}O_3$: ($M+H^+$), 233.2117. Found: m/z 233.2110.

(24a): Colorless oil; IR (neat) 3430 (OH), 1470, 1190, 1110, 965 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 7.1 Hz, CH_2–C<u>H</u>$_3$), 1.27 (12H, m), 1.57 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.56 (1H, d, J = 4.2 Hz, OH), 3.39 (3H, s, O–CH_3), 3.46 (6H, m, O–CH_2 × 3), 3.96 (1H, m, HO–C<u>H</u>). HRMS (FAB) Calcd for $C_{13}H_{29}O_3$: ($M+H^+$), 233.2116. Found: m/z 233.2118.

The mixtures (Entries 2—4 in Table 3) were derived to the acetate of alcohols for determining the ratio between **23b—d** and **24b—d**. Because **23b—d** and **24b—d** cannot be isolated, the ratio between **23b—d** and **24b—d** were determined by the chemical shifts and integral in ^1H NMR. The yields and conditions were shown in Table 3.

^1H NMR ($CDCl_3$) δ = 4.04 (1H, dd, J = 11.7, 5.4 Hz, AcO–C<u>H</u>$_2$), 4.23 (1H, dd, J = 11.7, 3.4 Hz, AcO–C<u>H</u>$_2$) for acetate of **23b** and 5.14 (1H, m, AcO–C<u>H</u>) for acetate of **24b** (Entry 2).

^1H NMR ($CDCl_3$) δ = 4.01—4.21 (2H, m, AcO–C<u>H</u>$_2$) for acetate of **23c** and 5.04 (1H, m, AcO–C<u>H</u>) for acetate of **24c** (Entry 3).

^1H NMR ($CDCl_3$) δ = 4.03 (1H, dd, J = 11.7, 5.4 Hz, AcO–C<u>H</u>$_2$), 4.17 (1H, dd, J = 11.7, 3.9 Hz, AcO–C<u>H</u>$_2$) for acetate of **23d** and 5.01 (1H, m, AcO–C<u>H</u>) for acetate of **24d** (Entry 3).

General Procedure for the Alcoholysis of Epoxides 25a—d (Table 3): TCNE (7.2 mg, 0.06 mmol) was added to a solution of epoxide **25a** (60 mg, 0.28 mmol) in CH_3OH (2 ml), and the reaction mixture was stirred at room temperature for 7 h. The reaction solvent was evaporated off and the residue was chromatographed on silica gel to give 3-methoxy-4-nonyloxy-2-butanol (**26a**) (48.3 mg, 70%) and 3-methoxy-1-nonyloxy-2-butanol (**27a**) (17.9 mg, 26%).

(26a): Colorless oil; IR (neat) 3420 (OH), 1465, 1375, 1110 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.20 (3H, d, J = 6.6 Hz, CH–C<u>H</u>$_3$), 1.26 (12H, m), 1.58 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.66 (1H, d, J = 5.1 Hz, OH), 3.20 (1H, m), 3.45 (2H, m), 3.47 (3H, s, O–CH_3), 3.59 (2H, m), 3.94 (1H, m). HRMS (FAB) Calcd for $C_{14}H_{31}O_3$: ($M+H^+$), 247.2274. Found: m/z 247.2280.

(27a): Colorless oil; IR (neat) 3440 (OH), 1460, 1105 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.17 (3H, d, J = 6.4 Hz, CH–C<u>H</u>$_3$), 1.27 (12H, m), 1.58 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.41 (1H, d, J = 3.9 Hz, OH), 3.31—3.55 (5H, m), 3.36 (3H, s, O–CH_3), 3.76 (1H, m). HRMS (FAB) Calcd for $C_{14}H_{31}O_3$: ($M+H^+$), 247.2273. Found: m/z 247.2287.

The mixtures (Entries 6,7 in Table 3) were oxidized to the ketones by Jones' oxidation for determining the ratio between **26b—d** and **27b—d**. Because **26b—d** and **27b—d** cannot be isolated, the ratio between **26b—d** and **27b—d** were determined by the chemical shifts and integral in ^1H NMR. The yields and conditions were shown in Table 3.

^1H NMR ($CDCl_3$) δ = 2.18 (3H, s, CO–CH_3) for ketone of **26b** and 2.77 (2H, t, J = 6.3 Hz, CO–C<u>H</u>$_2$) for ketone of **27b** (Entry 6).

^1H NMR ($CDCl_3$) δ = 2.16 (3H, s, CO–CH_3) for ketone of **26c** and 2.62 (2H, t, J = 7.3 Hz, CO–C<u>H</u>$_2$) for ketone of **27c** (Entry 7).

^1H NMR ($CDCl_3$) δ = 2.16 (3H, s, CO–CH_3) for ketone of **26d** and 2.56 (2H, t, J = 7.8 Hz, CO–C<u>H</u>$_2$) for ketone of **27d** (Entry 8).

1- (1- Methoxy- 1- methylethyl)- 4- nonyloxybutyl Acetate (Acetate of 29a): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1100, 1065 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2–C<u>H</u>$_3$), 1.14 (6H, s, C–CH_3 × 2), 1.27 (12H, m), 1.54—1.74 (6H, m), 2.09 (3H, s, Ac), 3.22 (3H, s, O–CH_3), 3.38 (4H, m, O–CH_2 × 2), 4.98 (1H, m, AcO–C<u>H</u>). HRMS (FAB) Calcd for $C_{19}H_{39}O_4$: ($M+H^+$), 331.2848. Found: m/z 331.2858.

2-Benzyloxy-2-methyl-6-nonyloxy-3-hexanol (29b): Colorless oil; IR ($CHCl_3$) 3530 (OH), 1150, 1095, 1050 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 7.1 Hz, CH_2–C<u>H</u>$_3$), 1.23 (3H, s, C–CH_3), 1.25 (12H, m), 1.26 (3H, s, C–CH_3), 1.52—1.92 (6H, m), 2.87 (1H, d, J = 2.7 Hz, OH), 3.39—3.57 (5H, m), 4.48 (2H, s, Ph–C<u>H</u>$_2$), 7.32 (5H, m, ArH). HRMS (FAB) Calcd for $C_{23}H_{41}O_3$: ($M+H^+$), 365.3056. Found: m/z 365.3073.

2-Methyl-6-nonyloxy-3-hexanone (30): Colorless oil; IR ($CHCl_3$) 1700 (C=O), 1470, 1100 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.88 (3H, t, J = 7.3 Hz, CH_2–C<u>H</u>$_3$), 1.09 (6H, d, J = 6.8 Hz, CH–C<u>H</u>$_3$ × 2), 1.27 (12H, m), 1.55 (2H, m, O–CH_2–C<u>H</u>$_2$), 1.84 (2H, m, O–CH_2–C<u>H</u>$_2$), 2.52—2.64 (3H, m, CH_2–CO–CH), 3.38 (4H, m, O–CH_2 × 2). HRMS (EI) Calcd for $C_{16}H_{32}O_2$: (M^+), 256.2403. Found: m/z 256.2414.

Reaction of *trans*-1,4-Diethoxy-2-butene Oxide (*t*-31) with Benzyl Alcohol (Scheme 1): TCNE (12.0 mg, 0.098 mmol) was added to a solution of ***t*-31** (50 mg, 0.31 mmol) in BnOH (101 mg, 0.94 mmol), and the reaction mixture was stirred at 40 °C for 11 h. The reaction mixture was chromatographed on silica gel to give *erythro*-3-benzyloxy-1,4-diethoxy-2-butanol (***er*-32**) in 47% yield. Compound ***er*-32** was deprotected by H_2/Pd–C[24] to afford *erythro*-1,4-diethoxy-2,3-diol (***er*-33**). Compound ***er*-33** was protected by *p*-TsOH/2,2-dimethoxypropane[25] to give *cis*-4,5-bis(ethoxymethyl)-2,2-dimethyl-1,3-dioxolane (***c*-34**). Colorless oil; IR ($CHCl_3$) 1380, 1100, 860 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.21 (6H, t, J = 7.3 Hz, CH_2–C<u>H</u>$_3$ × 2), 1.37, 1.47 (6H, each s, C–CH_3 × 2), 3.53 (8H, m, O–C<u>H</u>$_2$ × 4), 4.33 (2H, m, CH × 2). HRMS (EI) Calcd for $C_{10}H_{19}O_4$: ($M-CH_3^+$), 203.1283. Found: m/z 203.1280.

Similarly to the preparation of ***c*-34**, *trans*-4,5-diethoxymethyl-2,2-dimethyl-1,3-dioxolane (***t*-34**) was obtained from *cis*-1,4-dimethoxy-2-butene oxide (***c*-31**). The yields and conditions were shown in Scheme 1.

***trans*-4,5-Bis(ethoxymethyl)-2,2-dimethyl-1,3-dioxolane (*t*-34):** Colorless oil; IR ($CHCl_3$) 1380, 1070, 990, 850 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.21 (6H, t, J = 7.3 Hz, CH_2–C<u>H</u>$_3$ × 2), 1.42 (6H, s, C–CH_3 × 2), 3.56 (8H, m, O–C<u>H</u>$_2$ × 4), 3.96 (2H, m, CH × 2). HRMS (EI) Calcd for $C_{10}H_{19}O_4$: ($M-CH_3^+$), 203.1283. Found: m/z 203.1281.

Preparation of Capto-Dative Olefins: Compounds (**35**,[16] **37**,[16] **40**,[37] **41**[38]) were prepared according to the reported methods.

Dicyanoketene Diisopropyl Acetal (36): Et_3N (0.3 ml, 2.23 mmol) was added to a solution of TCNE (300 mg, 2.23 mmol) in *i*-PrOH (10 ml) under argon atmosphere, and the mixture was stirred at room temperature for 6 h. The reaction solvent was evaporated off and residue was chromatographed on silica gel to give **36** (176.5 mg, 41%) as a yellow prism. Mp 59 °C. IR ($CHCl_3$) 2220 (CN), 1540, 1415, 1310, 1090 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.44 (12H,

d, J = 6.4 Hz, Me×4), 5.26 (2H, m, CH×2). Found: C, 61.78; H, 7.29; N, 14.46%. Calcd for $C_{10}H_{14}O_2N_2$: C, 61.84; H, 7.27; N, 14.42%.

(38): 2,3-Butanediol (0.71 ml, 7.807 mmol) and Et_2NH (40 μl, 0.39 mmol) were addeed to a solution of TCNE (500 mg, 3.903 mmol) in THF (6 ml) under argon atmosphere, and the mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with AcOEt. The crude product thus obtained was purified by recrystallization (AcOEt–ether–hexane) to give **38** (75 mg, 12%) as a yellow prism. Mp 99 °C. IR ($CHCl_3$) 2240 (CN), 1610 (C=C), 1415, 1145, 1130, 1035, 850 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.70 (6H, d, J = 5.4 Hz, Me×2), 4.77 (2H, m, CH×2). Found: C, 58.69; H, 4.85; N, 17.12%. Calcd for $C_8H_8O_2N_2$: C, 58.53; H, 4.91; N, 17.06%.

(39): *n*-$BuNH_2$ (7.7 ml, 78.06 mmol) was added to TCNE (500 mg, 3.90 mmol) slowly at 0 °C, and the mixture was stirred at room temperature for 13 h. *n*-$BuNH_2$ was evaporated off and residue was purified by recrystallization (ether) to give **39** (537 mg, 63%) as a pale brown prism. Mp 72 °C. IR ($CHCl_3$) 3440, 3310 (NH), 2200, 2180 (CN), 1575 (C=C), 1465 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 0.96 (6H, t, J = 7.3 Hz, CH_3×2), 1.40 (4H, m, CH_3–CH_2×2), 1.62 (4H, m, N–CH_2–CH_2×2), 3.32 (4H, m, N–CH_2×2), 5.17 (2H, m, NH×2). ^{13}C NMR ($CDCl_3$) δ = 13.5 (q), 19.6 (t), 31.4 (t), 32.8 (s), 43.6 (t), 118.8 (s), 163.5 (s). Found: C, 65.35; H, 9.21; N, 25.38%. Calcd for $C_{12}H_{20}N_4$: C, 65.42; H, 9.15; N, 25.43%.

General Procedure for Alcoholysis of Epoxides Catalyzed by Dicyanoketene Acetals: A catalytic amount (0.1—0.2 molar amount) of dicyanoketene acetal (dicyanoketene dimethyl acetal (DCKDMA) or dicyanoketene ethylene acetal (DCKEA)) was added to a solution of epoxides in alcohols, and the mixture was stirred at room temperature to 50 °C for 0.5 h—3 day. The reaction solvent was evaporated off and the residue was chromatographed on silica gel to give the ring-opening products. The yields and conditions were shown in Tables 4 and 5.

2-Phenyl-2-isopropoxyethyl Acetate (Acetate of 4d): Colorless oil; IR ($CHCl_3$) 1730 (C=O), 1370, 1210, 1030 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.13, 1.17 (6H, each d, J = 6.4 Hz, CH_3×2), 2.07 (3H, s, Ac), 3.56 (1H, m, Me_2–C<u>H</u>), 4.14 (2H, m, C<u>H_2</u>), 4.63 (1H, m, Ph–C<u>H</u>), 7.35 (5H, m, ArH). Found: C, 70.01; H, 8.30%. Calcd for $C_{13}H_{18}O_3$: 70.24; H, 8.16%.

2-*t*-Butoxy-2-phenylethanol (4e): Colorless prism, Mp 75 °C. IR ($CHCl_3$) 3350 (OH), 1390, 1370, 1190, 1080, 1060, 1030 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.17 (9H, s, *t*-Bu), 2.27 (1H, m, OH), 3.50 (2H, m, CH_2), 4.61 (1H, dd, J = 8.1, 4.6 Hz, CH), 7.36 (5H, m, ArH). Found: C, 73.99; H, 9.41%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

Adduct 42 Formed from DCKDMA and Styrene Oxide: Colorless prism, Mp 175 °C. IR ($CHCl_3$) 3340 (NH), 2220 (CN), 1675 (C=O), 1600, 1480, 1460, 1450, 1320, 1095 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 3.75 (3H, s, O–CH_3), 4.47 (1H, dd, J = 9.0, 6.8 Hz), 5.00 (1H, t, J = 9.0 Hz), 5.22 (1H, dd, J = 9.0, 7.1 Hz), 7.30 (2H, m, ArH), 7.41 (3H, m, ArH), 8.88 (1H, brs, NH). Found: C, 63.98; H, 5.04; N, 11.39%. Calcd for $C_{13}H_{12}O_3N_2$: C, 63.93; H, 4.95; N, 11.47%.

Adduct 43 Formed from DCKDMA and Cyclohexene Oxide: Colorless prism, Mp 208 °C. IR ($CHCl_3$) 3350 (NH), 2220 (CN), 1670 (C=O), 1590, 1440, 1360, 1315, 1150, 1070 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.25—2.02 (6H, m), 2.26 (1H, m), 2.38 (1H, m), 3.35 (1H, td, J = 11.7, 3.7 Hz, O–CH), 3.76 (3H, s, O–CH_3), 3.96 (1H, td, J = 11.7, 3.7 Hz, N–CH), 8.58 (1H, brs, NH). ^{13}C NMR ($CDCl_3$) δ = 23.2 (t), 23.5 (t), 28.2 (t), 28.6 (t), 51.5 (q), 58.0 (s), 61.7 (d), 87.5 (d), 116.1 (s), 168.3 (s), 173.5 (s). Found: C, 59.53; H, 6.42; N, 12.64%. Calcd for $C_{11}H_{14}O_3N_2$: C, 59.45; H, 6.35; N, 12.60%.

Charge-Transfer Interaction between TCNE and Cylohexene Oxide (8): The CT complex formation between TCNE and cyclohexene oxide (**8**) was evidenced in the difference UV-visible absorption spectra of a mixture of TCNE (4.8×10^{-3} mol dm^{-3}) and cyclohexene oxide (**8**) (103×10^{-3} mol dm^{-3}) vs. TCNE (4.8×10^{-3} mol dm^{-3}) in dry acetonitrile. The observed CT-bands were 295 (ε 30.6 dm^3 mol^{-1} cm^{-1}) nm.

References

1) a) A. S. Rao, S. K. Paknikar, and J. G. Kirtane, *Tetrahedron*, **39**, 2323 (1983); b) J. G. Smith, *Synthesis*, **1984**, 629.

2) G. H. Posner and D. Z. Rogers, *J. Am. Chem. Soc.*, **99**, 8208 and 8214 (1977).

3) J. Otera, Y. Niibo, N. Tatsumi, and H. Nozaki, *J. Org. Chem.*, **53**, 275 (1988); Y. Niibo, T. Nakata, J. Otera, and H. Nozaki, *Synlett*, **1991**, 97.

4) G. A. Olah, A. P. Fung, and D. Meidar, *Synthesis*, **1981**, 280.

5) J. Riego, A. Costa, and J. M. Saa, *Chem. Lett.*, **1986**, 1565; M. Caron and K. B. Sharpless, *J. Org. Chem.*, **50**, 1557 (1985); J. M. Chong and K. B. Sharpless, *J. Org. Chem.*, **50**, 1560 (1985).

6) N. Iranpoor and I. M. Baltork, *Tetrahedron Lett.*, **31**, 735 (1990); N. Iranpoor and I. M. Baltork, *Synth. Commun.*, **20**, 2789 (1990); N. Iranpoor and J. Owji, *Tetrahedron*, **47**, 149 (1991); N. Iranpoor, I. M. Baltork, and F. S. Zardaloo, *Tetrahedron*, **47**, 9861 (1991).

7) K. Tanemura, T. Horaguchi, and T. Suzuki, *Bull. Chem. Soc. Jpn.*, **65**, 304 (1992).

8) K. Toshima, T. Ishizuka, G. Matsuo, M. Nakata, and M. Kinoshita, *J. Chem. Soc., Chem. Commun.*, **1993**, 704; K. Toshima, T. Ishizuka, G. Matsuo, and M. Nakata, *Chem. Lett.*, **1993**, 2013.

9) K. Tanemura, T. Suzuki, and T. Horaguchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 979; A. Oku, M. Kinugasa, and T. Kamada, *Chem. Lett.*, **1993**, 165; K. Tanemura, T. Suzuki, and T. Horaguchi, *Bull. Chem. Soc. Jpn.*, **67**, 290 (1994).

10) K. Tanemura, T. Suzuki, and T. Horaguchi, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 2997.

11) S. Vasudevan and D. S. Watt, *J. Org. Chem.*, **59**, 361 (1994).

12) A. J. Fatiadi, *Synthesis*, **1986**, 249; **1987**, 959.

13) Y. Masaki, T. Miura, and M. Ochiai, *Chem. Lett.*, **1993**, 17.

14) Y. Masaki, T. Miura, and M. Ochiai, *Synlett*, **1993**, 847.

15) T. Miura and Y. Masaki, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 1659.

16) W. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958); C. L. Dickinson and L. R. Melby, *Org. Synth.*, Coll. Vol. IV, 276 (1963).

17) T. Miura and Y. Masaki, *Tetrahedron Lett.*, **35**, 7961 (1994).

18) T. Miura and Y. Masaki, *Synth. Commun.*, **25**, 1981 (1995).

19) T. Miura and Y. Masaki, *Chem. Pharm. Bull.*, **43**, 523 (1995).

20) W. Reeve and I. Christoffel, *J. Am. Chem. Soc.*, **72**, 1480 (1950).

21) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, **1976**, 734.

22) G. A. Molander and J. P. Haar, Jr., *J. Am. Chem. Soc.*, **113**, 3608 (1991); **115**, 40 (1993); P. -C. Boldt, M. H. M. G. Schumacher, and M. G. Peter, *Tetrahedron Lett.*, **32**, 1413 (1991); B. Capon, *Quart. Rev.*, **18**, 45 (1964).

23) Structures for the *cis*- (***c*-34**) and *trans*-acetonide (***t*-34**) were fully characterized by ^1H NMR ($CDCl_3$) spectra which show two singlets at δ = 1.37 and 1.47 assignable to the two methyl groups on the acetal carbon for ***c*-34** and a singlet of six protons at δ = 1.42 to the two equivalent methyl groups on the acetal carbon for ***t*-34**,

respectively.
24) C. H. Heathcock and R. Ratcliffe, *J. Am. Chem. Soc.*, **93**, 1746 (1971).
25) M. E. Evans, F. W. Parrish, and L. Long, Jr., *Carbohydr. Res.*, **3**, 453 (1967).
26) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, A. J. Lewis, G. R. Little, and G. J. Wright, *Tetrahedron*, **26**, 1311 (1970).
27) W. J. Middleton, U. S. Patent 2766135 (1956); A. Oku, et al. suggested that DDQ can act as a relatively strong acid in water ($pK_a = 3.42$), although any structure derived from DDQ with water was not described: Ref. 9.
28) Recently, J. E. Frey, et al. reported charge-transfer complex formation between TCNE and cyclohexene oxide (**8**) in CH_2Cl_2: J. E. Frey, T. Aiello, D. N. Beaman, S. D. Combs, S. Fu, and J. J. Puckett, *J. Org. Chem.*, **59**, 1817 (1994).
29) J. Závada, M. Pánková, and M. Svoboda, *Collect. Czech. Chem. Commun.*, **38**, 2102 (1973).
30) H. Hirai and M. Matsui, *Agr. Biol. Chem.*, **40**, 169 (1976).
31) P. Kocienski and S. Wadman, *J. Am. Chem. Soc.*, **111**, 2363 (1989).
32) J. M. Coxon, M. P. Hartshorn, and W. H. Swallow, *J. Org. Chem.*, **39**, 1142 (1974).
33) W. Cocker, N. W. A. Geraghty, T. B. H. McMurry, and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 2245.
34) M. S. Malinovskii, V. I. Avramenko, V. G. Dryuk, and V. S. Tkachenko, *Zh. Org. Khim.*, **7**, 886 (1971).
35) H. Baumann and R. O. Duthaler, *Helv. Chim. Acta*, **71**, 1025 (1988).
36) H. Hönig and P. Seufer-Wasserthal, *Synthesis*, **1990**, 1137.
37) Y. Tominaga, S. Kohra, H. Honkawa, and A. Hosomi, *Heterocycles*, **29**, 1409 (1989).
38) R. Neidlein and D. Kikelj, *Synthesis*, **1988**, 981.