Regiochemical Control of the Ring-Opening of 1,2-Epoxides by Means of Chelating Processes. 3.[1] Aminolysis and Azidolysis of the *cis*- and *trans*-Oxides Derived from 4-(Benzyloxy)cyclohexene

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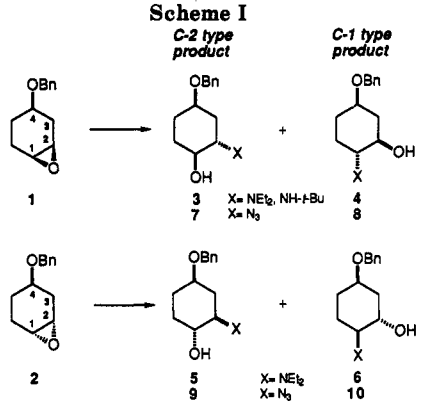
The previously observed regiocontrol of the ring-opening of epoxides bearing a remote polar group such as the title compounds (1 and 2) can also be achieved by metal-assisted methods for the direct aminolysis and azidolysis of epoxides. The appropriate use of the metal-assisted chelating or nonchelating procedures in the ring-opening of *cis*-epoxide 1 effects practically complete regiocontrol of these reactions, thus leading to regioalternating processes for the aminolysis and the azidolysis of 1.

β-Amino alcohols[2] and β-azido alcohols[3,4] are important classes of organic compounds. The former are common in natural products[2] and in medicinal chemistry,[2] and the latter serve as precursors in synthesis of β-amino alcohols and amino sugars[3] and carbocyclic nucleosides.[3,5] The usual synthetic routes to these two classes of compounds involve ring-opening of 1,2-epoxides with ammonia or amines, or their synthetic equivalents,[2] and with azides,[3-5] respectively. However, the aforementioned methodologies are not without problems in organic synthesis.[2-4] These types of reactions are usually *anti*-stereoselective,[2-5] and therefore the main goal when they are applied to the synthesis of complex organic molecules by the use of unsymmetrical epoxides is regiochemical control.[6,7]

We have demonstrated the possibility of obtaining an alternating regiocontrol in some ring-opening reactions of epoxides bearing remote polar heterofunctionalities, such as the *cis*- (1) and the *trans*-oxides (2) derived from 4-(benzyloxy)cyclohexene, through metal-assisted chelating or nonchelating processes.[6,7] Recently, we found some efficient, completely *anti*-stereoselective methods for the direct aminolysis[8] and azidolysis[9] of epoxides with amines and NaN_3 in aprotic solvents by means of common metal ion salt catalysis. It was hypothesized that the role of the metal ion salt in these reactions is to coordinate the oxirane oxygen, thus favoring the ring-opening process.[8,9] Therefore, we wanted to explore the possibility of gaining control of the regioselectivity of the aminolysis and azidolysis of oxiranes bearing a remote polar functionality, such as epoxides 1 and 2 (Scheme I),[6,7] through the use of the new metal ion catalyzed reactions.[8,9] These reactions could lead to regioalternating processes[6,7] and should be useful in the synthesis of multifunctionalized β-amino and β-azido alcohols with a well-defined structure and configuration.

Scheme I



Results

The previous study[8] on the metal salt catalyzed aminolysis of oxiranes showed that practically all amines can react in these conditions, although the reactivity depends on the structure of the epoxide, on the metal salt, and on the nucleophilicity of the amine. Diethylamine was chosen as a model for the aminolysis study of epoxides 1 and 2. The reaction of the *cis*-epoxide 1 with diethylamine under the usual conditions (reflux temperature in a protic solvent such as EtOH) afforded after 5 days in about 50% yield a mixture of the two regioisomeric amino alcohols 3 and 4 (X = NEt_2, Scheme I) in which the former predominated (95%, entry 7, Table I). When the reaction of the same

Table I. Regioselectivity of the Aminolysis of *cis*-Epoxide 1 (See Scheme I)

entry	reagents	solvent	reactn condns[a] (°C)	reactn time	yield[b]	3	4
1	$Et_2NH/LiClO_4$	CH_3CN	A (55)	1.5 h	95	8[c]	92[c]
2	$Et_2NH/LiClO_4$	CH_3CN	A (25)	8 h	95	10[c]	90[c]
3	$Et_2NH/LiClO_4$	CH_3CN	B (25)	16 h	96	18[c]	82[c]
4	$Et_2NH/LiClO_4$	CH_3CN	C (25)	18 h	94	49[c]	51[c]
5	$Et_2NH/LiClO_4$	MeOH	A (25)	3 days	80	40[c]	60[c]
6	$Et_2NH/LiClO_4$	MeOH	D (25)	18 h	93	9[c]	91[c]
7	Et_2NH	EtOH	E (55)	5 days	50	95[c]	5[c]
8	Et_2NMgBr	THF	F (25)	3 h	50	98[c]	2[c]
9	Et_2NSnMe_3	CH_2Cl_2	G (40)	4 days	70	96[c]	4[c]
10	$Et_2NSiMe_3/AlCl_3$	CH_2Cl_2	G (40)	20 h	no reaction		
11	t-$BuNH_2/LiClO_4$	CH_3CN	A (25)	18 h	94	2[d]	98[d]
12	t-$BuNH_2$	EtOH	E (55)	5 days	50	97[d]	3[d]

[a] Conditions: epoxide/amine = 1:5. A, 2 M $LiClO_4$; B, 0.5 M $LiClO_4$; C, 0.2 M $LiClO_4$; D, 17 M $LiClO_4$; E, epoxide/amine = 1:10, no metal salt ($LiClO_4$) added; F, see ref 10; G, see ref 11. [b] Yields based on weight, GLC analysis, and ^1H NMR examination of the isolated crude reaction product. [c] X = NEt_2. [d] X = NH-t-Bu.

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(1) Preceding paper in this series: Chini, M.; Crotti, P.; Flippin, L. A.; Macchia, F.; Pineschi, M. *J. Org. Chem.* Submitted for publication.
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Table II. Regioselectivity of the Aminolysis and Azidolysis of *trans*-Epoxide 2 (See Scheme I)

entry	reagents	solvent	reactn condns[a] (°C)	reactn time	yield[b]	5/9	6/10
1	Et_2NH/$LiClO_4$	CH_3CN	A (55)	18 h	95	40[c]	60[d]
2	Et_2NH	EtOH	E (55)	3 days	52	27[c]	73[d]
3	NaN_3/$LiClO_4$	CH_3CN	A (80)	18 h	93	7[e]	93[f]
4	NaN_3/NH_4Cl	MeOH/H_2O 8:1	I (80)	16 h	95	5[e]	95[f]

[a] Conditions: see footnote *a*, Table I, and Table III. [b] See footnote *b*, Table I. [c] Amino alcohol **5**. [d] Amino alcohol **6**. [e] Azido alcohol **9**. [f] Azido alcohol **10**.

epoxide was carried out using acetonitrile as the solvent and $LiClO_4$ as a catalyst,[8] the reaction was much faster, affording in good yield (95%) mixtures of the two amino alcohols **3** and **4** (X = NEt_2) in ratios that changed significantly with the amount of the lithium salt and ranged up to 92:8 in favor of the regioisomer **4** (X = NEt_2) when a 2 M solution of the salt was used (entry 1, Table I). Quite similar results were obtained when *tert*-butylamine was used (entries 11 and 12, Table I). For the sake of completeness, Table I also shows the results obtained in the amination of **1** with Et_2NMgBr[10] (entry 8) and with Et_2NSnMe_3[11] (entry 9, Table I), which afford mixtures of **3** and **4** (X = NEt_2) in which the former largely predominates as in the reaction of **1** under the classic aminolysis conditions (entry 7, Table I). The ring-opening reaction of **1** with Et_2NSiMe_3 in the presence of $AlCl_3$[11] did not afford any opening products (entry 10, Table I).

In reactions of the *trans*-epoxide **2** with diethylamine, the Li^+-catalyzed opening reaction is faster, as expected,[8] than the uncatalyzed reaction carried out in a protic solvent (EtOH) (entries 1 and 2, Table II). However, in this case similar ratios of the regioisomeric amino alcohols **5** and **6** (Scheme I) are obtained in the two different reaction conditions.

The ring-opening reaction of the *cis*-epoxide **1** with azide in a protic solvent under acidic conditions[12,13] (entries 13 and 14, Table III) afforded mixtures of regioisomers **7** and **8** in which the former largely predominated (>95%). When epoxide **1** was subjected to the new metal salt ($LiClO_4$) catalyzed reaction with NaN_3 in CH_3CN,[9] the regioisomeric ratio was practically reversed (entries 1–3, Table III). The percentage of compound **8** was always more than 90%, reaching a value of 97% when a 2 M solution of $LiClO_4$ was used (entry 1, Table III). In accord with previous results[9] metal ions other than lithium can be used as catalysts in the azidolysis of **1**, the order of effectiveness being $Zn^{2+} > Mg^{2+} > Li^+ \gg Na^+$ (see reaction times of entries 2 and 4–6, Table III). Furthermore, the different metal ions are also able to modulate the regiochemical outcome of the azidolysis of **1** markedly, leading to a reversal of the regiochemistry. In fact, when the same metal salt molar concentration (0.5 M, Table III, reaction condition B) is used, the **7**/**8** ratio changes from 5:95 for the lithium salt (entry 2) to 90:10 for the sodium salt (entry 6). The order of the ability to force the regioselectivity toward regioisomer **8** turns out to be $Li^+ > Mg^{2+} > Zn^{2+} > Na^+$. When the metal salt (2 M $LiClO_4$) catalyzed aminolysis and azidolysis is carried out in MeOH, the reaction is less regioselective than it is in CH_3CN (entries 1 and 5, Table I, and entries 1 and 11, Table III). Only when a large amount of $LiClO_4$[7] in MeOH is used is the regioselectivity similar to that observed in CH_3CN (entries 1 and 6, Table I, and entries 1 and 12, Table III). While a suspension of NaN_3 is not effective (entry 7, Table III), a suspension of LiN_3 in CH_3CN reacts directly with epoxide **1**, with a lower regioselectivity than with NaN_3 and $LiClO_4$ (entries 1–3 and 9, Table III). However, the regioselectivity of the azidolysis of **1** was practically equivalent either with 2 M LiN_3 in MeOH or with 2 M $LiClO_4$ in MeOH in the presence of NaN_3 (entries 10 and 11, Table III). For comparison, the previously reported results of the azidolysis of epoxide **1** carried out under different conditions are also given in Table III (entries 15–19).[14-16]

Table III. Regioselectivity of the Azidolysis of *cis*-Epoxide 1 (See Scheme I)

entry	reagents	solvent	reactn condns[a] (°C)	reactn time	yield[b]	7	8
1	$NaN_3/LiClO_4$	CH_3CN	A (80)	8 h	95	3	97
2	$NaN_3/LiClO_4$	CH_3CN	B (80)	8 h	95	5	95
3	$NaN_3/LiClO_4$	CH_3CN	C (80)	16 h	94	8	92
4	NaN_3/$Mg(ClO_4)_2$	CH_3CN	B (80)	6 h	96	20	80
5	$NaN_3/Zn(OTf)_2$[c]	CH_3CN	B (80)	4 h	95	75	25
6	$NaN_3/NaClO_4$	CH_3CN	B (80)	36 h	94	90	10
7	NaN_3	CH_3CN	D (80)	3 days	no reaction		
8	NaN_3	MeOH	E (80)	3 days	60	95	5
9	LiN_3	CH_3CN	F (80)	18 h	93	21	79
10	LiN_3	MeOH	G (25)	3 days	94	18	82
11	$NaN_3/LiClO_4$	MeOH	A (25)	3 days	93	16	84
12	$NaN_3/LiClO_4$	MeOH	H (25)	18 h	96	2	98
13	NaN_3/NH_4Cl	MeOH/H_2O 8:1	I (80)	20 h	97	96	4
14	NaN_3/H_2SO_4	acetone/H_2O 1:1	J (25)	18 h	94	95	5
15	Me_3SiN_3/$Ti(O\text{-}i\text{-}Pr)_4$	CH_2Cl_2	K (25)	72 h	65	92	8
16	Me_3SiN_3/$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	K (25)	3 days	60	96	4
17	$Ti(O\text{-}i\text{-}Pr)_2(N_3)_2$	benzene	L (25)	18 h	80	91	9
18	$Ti(O\text{-}i\text{-}Pr)_2(N_3)_2$	benzene	L (80)	1 h	70	92	8
19	$(Bu)_3SnN_3$	no solvent	M (60)	8 h	85	97	3

[a] Conditions: epoxide:NaN_3 = 1:5, A, C, see footnote *a*, Table I; B, 0.5 M metal salt catalyst; D, epoxide:NaN_3 = 1:10 (suspension); E, epoxide:NaN_3 = 1:10 (solution); F, epoxide:LiN_3 = 1:10 (suspension); G, epoxide:LiN_3 = 1:10 (solution); H, epoxide:NaN_3 = 1:5, 17 M $LiClO_4$; I, see ref 12; J, see ref 13; K, see ref 14; L, see ref 15; M, see ref 16. [b] See footnote *b*, Table I. [c] OTf = O_2SCF_3.

The reaction of the *trans*-epoxide **2** with NaN_3 carried out either in a protic solvent in the presence of NH_4Cl[12] (entry 4, Table II) or in an aprotic solvent by metal salt ($LiClO_4$) catalysis (entry 3, Table II) yields the same regiochemical outcome, affording mixtures of **9** and **10** in which the latter is the main product (>90%).

Discussion

When aminolysis and azidolysis reactions of the *cis*-epoxide **1** were carried out under the classic conditions (en-

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(14) Sutowardoyo, K.; Emziane, M.; Sinou, D. *Tetrahedron Lett.* **1989**, *30*, 4673.
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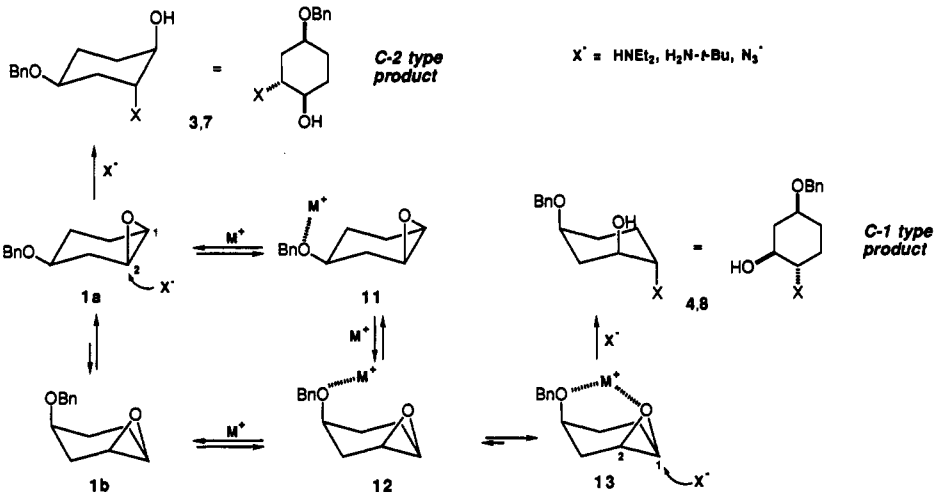
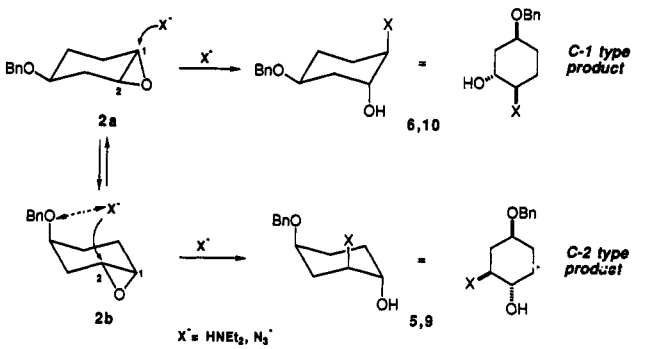
(16) Saito, S.; Yamashita, S.; Nishikawa, T.; Yokoyama, Y.; Inaba, M.; Moriwake, T. *Tetrahedron Lett.* **1989**, *30*, 4153.

Scheme II



tries 7 and 12, Table I, and entries 13 and 14, Table III, respectively), the regioselectivity observed (almost exclusive formation of *C-2-type products*)[17] is in agreement with previous results obtained with this epoxide[6,7] and can easily be rationalized on the basis of a preferential diaxial attack of the nucleophile on the most stable conformation **1a** of 1 (attack on C-2), in accordance with the Fürst–Plattner rule[18] (Scheme II). For the opposite regioselection observed in the metal salt catalyzed aminolysis and azidolysis of epoxide 1 to be rationalized, a mechanistic scheme involving metal chelation may be invoked.[6,7] According to this scheme, the initial complexation of the metal ion with the benzyloxy oxygen of 1 in either conformation **1a** or **1b** to give 11 and 12, respectively, followed by an entropically favored further coordination of the metal with the oxirane oxygen, yields the chelate structure **13** in which epoxide 1 is forced to adopt the less stable conformation **1b**. Axial attack of a nucleophile on C-1 of **13**, in accordance with the Fürst–Plattner rule[18] and the stereoelectronic factors implicated in the chelation-controlled ring-opening of 3,4-epoxy-1-alkanol derivatives,[7,19] should yield mainly *C-1-type products*,[17] as found both in the aminolysis and in the azidolysis reactions under metal ion catalysis (Scheme II). In accordance with previous results,[8,9] the rates of the metal salt catalyzed aminolysis and azidolysis reactions of 1 depend to a large extent on the type of the metal ion. The effectiveness of the metal catalysis is linked to the ability of the Lewis acid (the metal ion) to coordinate the oxirane oxygen, thus giving the above-indicated order of reactivity (entries 2 and 4–6, Table III). However, as mentioned above, the regioselectivity of these reactions depends both on the metal ion and on the reaction conditions, thus indicating the possibility of a competition between the metal-assisted chelating process and the usual nonchelating one. A decrease in the amount of the metal ion (entries 2–4, Table I, and entries 1–3, Table III) and the use of a polar protic solvent (MeOH) (entry 5, Table I, and entry 11, Table III) in the place of acetonitrile (entry 1, Tables I and III) favors the *C-2-type product* arising

Scheme III



from the nonchelating process. The order of the ability of the metal ion ($Li^+ > Mg^{2+} > Zn^{2+} > Na^+$) to force the regioselectivity of the reactions of 1 by the chelating process is different from the order of effectiveness of the same metal ions ($Zn^{2+} > Mg^{2+} > Li^+ \gg Na^+$) in catalyzing the nucleophilic oxirane ring-opening process. It would seem that the size of the metal ion affects the stability of the bidentate structure **13** since the smaller ions are the most effective in promoting the chelation-assisted addition pathway of epoxide 1.

The azidolysis reaction of 1 carried out with a suspension of LiN_3 in acetonitrile (entry 9, Table III) is less regioselective than the comparable reaction with NaN_3–$LiClO_4$ (entry 2, Table III). However, when the two reactions are carried out in MeOH (homogeneous reaction conditions), the regioselectivity is practically the same (entries 10 and 11, Table III). These results confirm the role of the metal ion as catalyst in these reactions.[8,9]

When no possibility exists for chelating processes, it is not surprising that almost the same regioisomeric mixtures (compounds **5** and **6** in the aminolysis and compounds **9** and **10** in the azidolysis of *trans*-epoxide **2**) are obtained both in the metal ion catalyzed and in the non-metal ion catalyzed reactions (Table II). Formation of nearly equivalent amounts of both the regioisomeric amino alcohols **5** and **6** undoubtedly occurs by diaxial ring-opening[18] of epoxide **2**, which reacts in the two almost equivalent conformations **2a** and **2b**, respectively (Scheme III). The much higher regioselectivity observed for the azidolysis of **2**, which in this case appears to proceed almost exclusively through conformation **2a**, could be rationalized[6,7] on the basis of the unfavorable interaction between the negatively charged nucleophile (N_3^-) and the benzyloxy oxygen in the diaxial ring-opening of **2** through conformation **2b**.[6,7]

(17) The *C-1-type* and the *C-2-type product* nomenclature refers to the attacking region of the nucleophile, that is on the C-1 or on the C-2 oxirane carbon, respectively, of both 1 and **2**, in accordance with the numbering scheme shown in Scheme I.

(18) (a) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; p 102. (b) Fürst, A.; Plattner, P. A. *Abstract of Papers*, 12th International Congress of Pure and Applied Chemistry; 1951, p 409.

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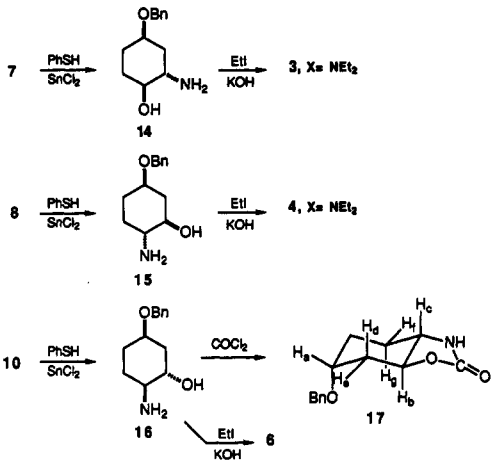
Table IV. Spectroscopic Data for Amino Alcohols 3–6 and 14–16, Azido Alcohols 7, 8, and 10, and Compound 17

compd	^{1}H NMR[a] δ (bandwidth, Hz)			IR (CCl_4) (OH stretching), cm^{-1}		
	H_a	H_b	H_c	1,2 OH···N	1,3 OH···O	OH_{free}
3 (X = NEt_2)	3.81 (8.0)	3.37 (27.0)	2.87 (27.0)[b]	3454[j]		
4 (X = NEt_2)	3.34[c]	c	2.60[b,d]	3462[j]		
3 (X = NH-t-Bu)	3.70 (8.0)	3.02 (27.0)	2.77 (27.0)[e]	3494[j]		
4 (X = NH-t-Bu)	3.43 (31.0)	2.93 (25.0)	2.27 (25.0)[e]	3502[j]		
5	3.35[c]	c	2.28[b,d]	3470[j]		
6	3.76[c]	c	2.39[b,d]	3454[j]		
7	3.75 (7.7)	3.62 (27.0)	3.42 (27.0)[f]	3598[k]		3626
8	3.46[c]	c	f, g	3594	3510[k]	
10	3.80[c]	c	3.24 (26.8)[f]	3598[k]		
14	3.72 (7.7)	3.19 (27.5)	2.89 (27.5)[h]	3514[j]		
15	3.49[c]	c	3.13 (28.0)[h]	3526[j]		
16	3.56[c]	c	3.09 (27.0)[h]	3518[j]		
17	3.93 (6.7)[i]	4.39 (28.0)[i]	3.35 (28.0)[i]			

[a] All the signals are multiplets: H_a = C*H*OBn, H_b = C*H*OH, H_c = C*H*X (see Scheme I). [b] X = NEt_2. [c] The signal of proton H_a is overlapped with the signal of proton H_b. [d] The signal of proton H_c is overlapped with the signals of the methylene protons of the $N(CH_2CH_3)_2$ group. [e] X = NH-t-Bu. [f] X = N_3. [g] The signal of proton H_c is overlapped with the signal of protons H_a and H_b. [h] X = NH_2. [i] See Scheme IV. [j] Broad band. [k] Strong band.

Scheme IV



Structures and Configurations

The relative configuration of the benzyloxy and hydroxyl groups in all new compounds (3–10, Scheme I) must correspond to that of the starting epoxides 1 (compounds 3, 4, 7, and 8) and 2 (compounds 5, 6, 9,[20] and 10), respectively. The *anti* relationship between the hydroxyl group and the amino group in 3–6 and the azido group in 7–10 can be reasonably assumed on the basis of the *anti*-stereoselectivity commonly observed in the aminolysis and azidolysis reactions of epoxides carried out under classic[2-5,12,13] and under metal salt catalyzed conditions.[8,9] The structural assignment of the regioisomeric pairs 3 and –4, 5 and 6, 7 and 8, and 9[20] and 10 is based on the following considerations and transformations (Schemes I and IV). The structure of the azido alcohols 7 and 8 derived from the *cis*-epoxide 1 is demonstrated by the presence of a 1,3 OH···O interaction[7,21] in the IR spectrum of diluted CCl_4 solution of 8 (see Table IV). The reduction of 7 and 8 with $SnCl_2$ and PhSH in the presence of NEt_3[22] yields the unsubstituted amino alcohols 14 and 15, which were alkylated with ethyl iodide in the presence of KOH to give the *N,N*-diethylamino alcohols 3 and 4 (X = NEt_2), respectively, thus indicating the relative structure of the two latter compounds. The azido alcohol 10 from *trans*-epoxide 2 was reduced[22] to the amino alcohol 16, which by treatment with phosgene yields the conformationally restricted cyclic carbamate 17. The ^{1}H NMR spectrum of 17 exhibits an equatorial proton (H_a, $W_{1/2}$ = 6.7 Hz, Table III)[23] α to the benzyloxy group, in agreement with the structure shown in Scheme IV. The corresponding unsubstituted amino alcohol (16) was transformed into its *N,N*-diethyl derivative 6, defining the regiochemistry of the latter. The ^{1}H NMR and IR spectra in a diluted CCl_4 solution of all the compounds isolated are also in complete agreement with the structures assigned (see Table IV and Experimental Section).

Experimental Section

For general experimental information and for the synthesis of epoxides 1 and 2, see ref 7.

Aminolysis of Epoxides 1 and 2 in the Presence of $LiClO_4$. The following procedure is typical. A solution of epoxide 1 (0.408 g, 2.00 mmol) in anhydrous CH_3CN (5 mL) was treated with anhydrous $LiClO_4$ (1.07 g, 10.0 mmol) and stirred until complete dissolution of the salt. Diethylamine (1.0 mL, 10.0 mmol) was added and the reaction mixture was stirred at 55 °C for 1.5 h. After cooling, ether (30 mL) was added; evaporation of the washed (water) organic solution afforded a liquid residue (0.52 g), consisting only of amino alcohols 3 and 4 (X = NEt_2, entry 1, Table I), which was subjected to preparative TLC with 1:3 hexane/AcOEt as the eluant. Extraction of the most intense band afforded pure **c-5-(benzyloxy)-t-2-(*N,N*-diethylamino)-r-1-cyclohexanol** (4, X = NEt_2) (0.32 g, 57% yield), as a liquid: IR, see Table IV; ^{1}H NMR δ 7.26–7.35 (m, 5 H, aromatic protons), 4.58 and 4.51 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), 2.60 (q, 2 H, J = 7.2 Hz, CH_2CH_3), 2.36 (q, 2 H, J = 7.2 Hz, CH_2CH_3), 1.04 (t, 6 H, J = 7.2 Hz, CH_2CH_3), and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.50; H, 9.98; N, 5.15. Hydrochloride, mp 166–167 °C. Anal. Calcd for $C_{17}H_{28}ClNO_2$: C, 65.05; H, 8.99; N, 4.46. Found: C, 65.21; H, 8.73; N, 4.85.

The crude solid reaction product of 1 with *tert*-butylamine (0.54 g), consisting only of 3 and 4 (X = NH-t-Bu) (entry 11, Table I), was recrystallized from hexane to give pure **c-5-(benzyloxy)-t-2-(*N*-*tert*-butylamino)-r-1-cyclohexanol** (4, X = NH-t-Bu) (0.43 g, 80% yield), as a solid, mp 78–79 °C: IR, see Table IV; ^{1}H NMR δ 7.26–7.35 (m, 5 H, aromatic protons), 4.58 and 4.51 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), 1.10 [s, 9 H, $C(CH_3)_3$],

(20) Azido alcohol 9 was not separated in the pure state due to the insufficient amount present in the opening reaction of *trans*-epoxide 2 (Table II). However, its presence could reasonably be substantiated on the basis of the GC and ^{1}H NMR spectra analysis of the corresponding crude reaction products.

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and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.45; H, 9.56; N, 5.25.

The crude liquid reaction product of epoxide **2** with diethylamine (0.52 g) consisting only of **5** and **6** (entry 1, Table II) was subjected to preparative TLC with 1:1:1 hexane/AcOEt/diisopropyl ether as the eluant. Extraction of the two most intense bands afforded amino alcohols **5** (R_f = 0.38, 0.114 g, 54% yield) and **6** (R_f = 0.45, 0.20 g, 64% yield).

***t*-4-(Benzyloxy)-*t*-2-(*N*,*N*-diethylamino)-*r*-1-cyclohexanol (5),** liquid: IR, see Table IV; ^{1}H NMR δ 7.25–7.36 (m, 5 H, aromatic protons), 4.58 and 4.51 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), 2.58 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 2.37 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 1.04 (t, 6 H, J = 7.4 Hz, 2 CH_3), and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.64; H, 9.49; N, 5.30. Hydrochloride, mp 144–145 °C. Anal. Calcd for $C_{17}H_{28}ClNO_2$: C, 65.05; H, 8.99; N, 4.46. Found: C, 65.10; H, 9.10; N, 4.25.

***t*-5-(Benzyloxy)-*t*-2-(*N*,*N*-diethylamino)-*r*-1-cyclohexanol (6),** liquid: IR, see Table IV; ^{1}H NMR δ 7.35–7.26 (m, 5 H, aromatic protons), 4.54 and 4.48 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), 2.66 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 2.37 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 1.05 (t, 6 H, J = 7.4 Hz, 2 CH_3), and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.81; H, 9.65; N, 5.14. Hydrochloride, mp 133–134 °C. Anal. Calcd for $C_{17}H_{28}ClNO_2$: C, 65.05; H, 8.99; N, 4.46. Found: C, 65.09; H, 8.73; N, 4.40.

Aminolysis of Epoxides 1 and 2 in EtOH. The following procedure is typical. A solution of epoxide **1** (0.408 g, 2.00 mmol) in anhydrous EtOH (10 mL) was treated with diethylamine (2.0 mL, 20 mmol), and the reaction mixture was refluxed under stirring for 5 days. After cooling, ether (30 mL) was added; evaporation of the washed (water) organic solution afforded an oily residue (0.48 g) consisting of a 50:47.5:2.5 mixture of starting epoxide **1** and amino alcohols **3** and **4** (X = NEt_2) (entry 7, Table I), which was subjected to preparative TLC with 1:3 hexane/AcOEt as the eluant. Extraction of the most intense band afforded pure ***c*-4-(benzyloxy)-*t*-2-(*N*,*N*-diethylamino)-*r*-1-cyclohexanol (3,** X = NEt_2) (0.13 g, 60% yield), as a liquid: IR, see Table IV; ^{1}H NMR δ 7.25–7.36 (m, 5 H, aromatic protons), 4.53 and 4.45 (AB dd, 2 H, J = 12.2 Hz, OCH_AH_BPh), 2.62 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 2.33 (q, 2 H, J = 7.4 Hz, CH_2CH_3), 1.05 (t, 6 H, J = 7.4 Hz, 2 CH_3), and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.86; H, 9.64; N, 5.17. Hydrochloride, mp 147–148 °C. Anal. Calcd for $C_{17}H_{28}ClNO_2$: C, 65.05; H, 8.99; N, 4.46. Found: C, 65.21; H, 9.15; N, 4.37.

The crude solid reaction product of **1** with *tert*-butylamine (0.47 g), consisting of a 50:48.5:1.5 mixture of starting epoxide **1** and amino alcohols **3** and **4** (X = NH-*t*-Bu) (entry 12, Table I), was recrystallized from hexane to give pure ***c*-4-(benzyloxy)-*t*-2-(*N*-*tert*-butylamino)-*r*-1-cyclohexanol (3,** X = NH-*t*-Bu) (0.11 g, 50% yield), as a solid, mp 64–65 °C: IR, see Table IV; ^{1}H NMR δ 7.24–7.36 (m, 5 H, aromatic protons), 4.51 (s, 2 H, OCH_2Ph), 1.12 [s, 9 H, $C(CH_3)_3$], and see Table IV. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.73; N, 5.04. Found: C, 73.51; H, 9.49; N, 4.90.

The crude liquid reaction product of **2** with diethylamine (0.47 g), consisting of a 48:38:14 mixture of starting epoxide **2** and amino alcohols **5** and **6** (entry 2, Table II), was subjected to preparative TLC with 1:1:1 hexane/AcOEt/diisopropyl ether as the eluant. Extraction of the two most intense bands afforded pure amino alcohols **5** (0.035 g, 54% yield) and **6** (0.115 g, 64% yield).

Azidolysis of Epoxides 1 and 2 with NaN_3 in the Presence of Metal Salt. The following procedure is typical. A solution of epoxide **1** (0.204 g, 1.00 mmol) in anhydrous CH_3CN (5 mL) was treated with NaN_3 (0.32 g, 5.0 mmol) and anhydrous $LiClO_4$ (1.07 g, 10.0 mmol), and the reaction mixture was stirred at 80 °C for 8 h. After cooling ether (30 mL) was added; evaporation of the washed (water) organic solution afforded a solid residue (0.23 g), consisting only of azido alcohols **7** and **8** (entry 1, Table III), which was recrystallized from hexane to give pure ***t*-2-azido-*c*-5-(benzyloxy)-*r*-1-cyclohexanol (8)** (0.175 g, 71% yield), as a solid, mp 67–68 °C: IR, see Table IV; ^{1}H NMR δ 7.23–7.35 (m, 5 H, aromatic protons), 4.57 and 4.50 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), and see Table IV. Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.92; N, 16.98. Found: C, 63.28; H, 6.75; N, 17.05.

Following the above-described procedure, reactions of epoxide **1** with NaN_3 in the presence of different metal salts gave the results shown in Table III (entries 4–6).

The crude solid reaction product from *trans*-epoxide **2** (0.23 g), consisting only of **9** and **10** (entry 3, Table II), was recrystallized from pentane to give pure ***t*-2-azido-*t*-5-(benzyloxy)-*r*-1-cyclohexanol (10)** (0.18 g, 72% yield), as a solid, mp 42–43 °C: IR, see Table IV; ^{1}H NMR δ 7.25–7.35 (m, 5 H, aromatic protons), 4.49 (s, 2 H, OCH_2Ph), and see Table IV. Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.92; N, 16.98. Found: C, 63.35; H, 6.84; N, 17.14.

Reaction of Epoxide 1 with NaN_3 and LiN_3. The following procedure is general. A solution of epoxide **1** (0.204 g, 1.00 mmol) in the anhydrous solvent (5 mL) was treated with the required amount of NaN_3 (or LiN_3) (entries 7–9, Table III), and the reaction mixture was stirred at 80 °C for the time shown in Table III. Usual workup afforded crude reaction products consisting of mixtures of azido alcohols **7** and **8**, which were analyzed by GC to give the results shown in Table III.

Reaction of Epoxides 1 and 2 with NaN_3 in the Presence of NH_4Cl. Following the Sharpless procedure,[12] a solution of epoxide **1** (0.204 g, 1.00 mmol) in a 8:1 MeOH/H_2O mixture (9 mL) was treated with NaN_3 (0.325 g, 5.0 mmol) and NH_4Cl (0.117 g, 2.2 mmol), and the reaction mixture was stirred at 80 °C for 20 h. Usual workup[12] afforded a crude liquid residue (0.24 g), consisting only of azido alcohols **7** and **8** (entry 13, Table III), which was subjected to preparative TLC with 1:1 hexane/AcOEt as the eluant. Extraction of the most intense band afforded pure ***t*-2-azido-*c*-4-(benzyloxy)-*r*-1-cyclohexanol (7)** (0.17 g, 69% yield), as a liquid: IR, see Table IV; ^{1}H NMR δ 7.24–7.36 (m, 5 H, aromatic protons), 4.53 and 4.44 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), and see Table IV. Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.92; N, 16.98. Found: C, 63.08; H, 6.84; N, 16.78.

The crude solid reaction product from *trans*-epoxide **2** (0.23 g), consisting only of **9** and **10** (entry 4, Table II), was recrystallized from pentane to give pure azido alcohol **10** (0.17 g, 69% yield).

Reduction of Azido Alcohols 7, 8, and 10. Following a previously described procedure,[22] treatment of azido alcohol **7** (0.247 g, 1.00 mmol) with $SnCl_2$ (1.5 mmol), PhSH (6.0 mmol), and Et_3N (4.5 mmol) afforded a solid residue (0.21 g, 95% yield) consisting only of amino alcohol **14** (IR and ^{1}H NMR), which was recrystallized from AcOEt to give pure ***t*-2-amino-*c*-4-(benzyloxy)-*r*-1-cyclohexanol (14)** (0.15 g, 68% yield), as a solid, mp 87–88 °C: IR, see Table IV; ^{1}H NMR δ 7.24–7.35 (m, 5 H, aromatic protons), 4.53 and 4.45 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), and see Table IV. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.32. Found: C, 70.37; H, 8.59; N, 6.30.

The same treatment[22] of azido alcohol **8** (0.247 g, 1.00 mmol) afforded a crude solid product (0.21 g, 95% yield) consisting only of amino alcohol **15** (IR and ^{1}H NMR), which was recrystallized from 8:2 diisopropyl ether/benzene to give pure ***t*-2-amino-*c*-5-(benzyloxy)-*r*-1-cyclohexanol (15)** (0.135 g, 61% yield), as a solid, mp 47–48 °C: IR, see Table IV; ^{1}H NMR δ 7.24–7.35 (m, 5 H, aromatic protons), 4.53 and 4.45 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), and see Table IV. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.32. Found: C, 70.45; H, 8.50; N, 6.49.

Analogous treatment[22] of azido alcohol **10** (0.247 g, 1.00 mmol) afforded a crude solid reaction product (0.20 g, 90% yield) consisting only of amino alcohol **16** (IR and ^{1}H NMR), which was recrystallized from AcOEt to give pure ***t*-2-amino-*t*-5-(benzyloxy)-*r*-1-cyclohexanol (16)** (0.15 g, 67% yield), as a solid, mp 72–73 °C: IR, see Table IV; ^{1}H NMR δ 7.25–7.36 (m, 5 H, aromatic protons), 4.54 and 4.47 (AB dd, 2 H, J = 12.0 Hz, OCH_AH_BPh), and see Table IV. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.32. Found: C, 70.67; H, 8.49; N, 6.51.

Reaction of Amino Alcohols 14–16 and 4 with C_2H_5I. The following procedure is typical. A solution of amino alcohol **14** (0.327 g, 1.47 mmol) in EtOH (5 mL) was treated with 20% aqueous KOH (2 mL) and ethyl iodide (1.56 g, 10.0 mmol), and the resulting reaction mixture was stirred at 80 °C for 5 h. After cooling, ether (30 mL) was added; evaporation of the washed (water) organic solution afforded an oily residue consisting only of amino alcohol **3** (X = NEt_2) (0.39 g, 95% yield), practically pure (IR, ^{1}H NMR, and GC).

The same reaction carried out on amino alcohols **15** (0.277 g, 1.00 mmol) and **16** (0.277 g, 1.00 mmol) afforded crude reaction

products consisting of practically pure amino alcohols 4 (X = NEt_2) (0.39 g, 95% yield) and 6 (0.38 g, 93% yield), respectively (IR, ^1H NMR, and GC).

Reaction of Amino Alcohol 16 with $COCl_2$. A solution of amino alcohol **16** (0.050 g, 0.24 mmol) and pyridine (0.2 mL) in anhydrous benzene (6 mL) was treated at 0 °C with 5.4 M $COCl_2$ solution in benzene (0.6 mL), and the reaction mixture was left 20 min at 0 °C and then 10 min at rt. CH_2Cl_2 (20 mL) was added; evaporation of the washed (water, 10% aqueous HCl, saturated aqueous $NaHCO_3$, and water) organic solvent solution afforded a solid reaction product (0.057 g, 93% yield) consisting of **17**, which was recrystallized from hexane/CH_2Cl_2 to give pure **(1β,4β,6α)-4-(benzyloxy)-8-oxo-7-oxa-9-azabicyclo[4.3.0]nonane (17)** (0.045 g, 76% yield) as a solid, mp 156–157 °C: IR, 5.81 μm; ^1H NMR δ 7.26–7.40 (m, 5 H, aromatic protons), 5.24 (br s, 1 H, NH), 4.56 and 4.48 (AB dd, 2 H, J = 12.2 Hz, OCH_AH_BPh), 4.39 (ddd, 1 H, $J_{b,e}$ = 3.8, $J_{b,c}$ = 11.2, and $J_{b,d}$ = 12.5 Hz, $W_{1/2}$ = 28.0 Hz, H_b), 3.93 (m, five lines, J = 2.8 Hz, $W_{1/2}$ = 6.7 Hz, H_a), 3.35 (ddd, 1 H, $J_{c,f}$ = 4.4 and $J_{c,g} = J_{c,b}$ = 11.2 Hz, $W_{1/2}$ = 28.0 Hz, H_c). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.92; N, 5.66. Found: C, 67.85; H, 6.79; N, 5.44.

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Registry No. 1, 84029-18-5; 2, 84049-33-2; 3 (X = NEt_2), 136667-62-4; 3 (X = NEt_2)·HCl, 136667-63-5; 3 (X = NHBu-*t*), 136667-64-6; 4 (X = NEt_2), 136667-65-7; 4 (X = NEt_2)·HCl, 136667-66-8; 4 (X = NHBu-*t*), 136667-67-9; 5, 136667-68-0; 5·HCl, 136667-69-1; 6, 136667-70-4; 6·HCl, 136667-71-5; 7, 136667-72-6; 8, 136667-73-7; 9, 136667-74-8; 10, 136667-75-9; 14, 136667-76-0; 15, 136667-77-1; 16, 136667-78-2; 17, 136667-79-3; *t*-$BuNH_2$, 75-64-9; diethylamine, 109-89-7.

"Roofed" Polyquinanes: Synthesis and Electronic Structure

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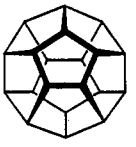
Starting from readily available norbornenobenzoquinone **7** and employing a photothermal metathesis reaction as the main strategy, novel "roofed" polyquinane bisenones **3** and **13** have been synthesized. Among these, the former is potentially serviceable for further elaboration to dodecahedrane **1**. Catalytic hydrogenation of **3** provided the dione **12**, which fully inscribes the circumference of dodecahedrane sphere. The "roofed" C_{16}-bisenone **3** has been successfully annulated to C_{19}-bisenone **24** and C_{19}-trisenone **26** by employing the Greene methodology and Pauson–Khand reaction, respectively. The molecular structures of **3** and **13** were computed using molecular mechanics and semiempirical MO methods. The nonbonded distances between the double bonds vary strongly with the method employed. The interactions between the π MO's were, therefore, probed by means of photoelectron (PE) spectroscopy. Comparison with the PE spectra of a series of model systems with increasing complexity enabled an unambiguous assignment of the observed peaks. The symmetric and antisymmetric combinations of the π MO's of the enone moieties of **3** and **13** show large splittings, characteristic of propano-bridged systems in which through-space and through-bond effects act in concert.

Introduction

Together with our travails in quest of dodecahedrane **1**, through a "molecular stitching" approach,[1] we also ventured to explore an alternate convergent strategy to this enchanting hydrocarbon.[2] The convergent approaches to polycyclic molecules of high symmetry are considered aesthetically pleasing, shorter, and more attractive in total synthesis but are always difficult to execute due to variety of factors. In the case of dodecahedrane **1**, the convergent approaches like the dimerization of triquinacene (C_{10} + C_{10}) initiated by Woodward,[3] capping of [5]peristylane (C_{15} + C_5) pursued by Eaton,[4] Paquette's bivalvane approach,[5] and Farnum's hexaene reorganization (C_8 + C_8 + C_4)[6] have all remained unattained despite their conceptual elegance. In spite of the failures of others, we considered a novel tetraquinane + diquinane (C_{12} + C_8) **2** approach to dodecahedrane **1** and sought to overcome the unfavorable steric and entropic factors, inherent in such approaches, taking recourse to a new tactic.



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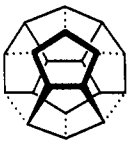

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As the major impediment in the success of earlier convergent approaches to dodecahedrane has been the singular inability to properly align the two "halves" or "fragments"

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