A New Route to Cyclopentene-1-carboxaldehydes by Rearrangement of 2,3-Epoxycyclohexanols

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Cyclopentene-1-carboxaldehyde and the *gem*-dimethyl substituted homologs have been synthesized in high yield by LiBr–HMPA-catalyzed rearrangement of the appropriate *cis*-2,3-epoxycyclohexanols. Extensive physical data, including ^{13}C parameters, are reported.

During structure elucidation work on sesquiterpenoids we needed *gem*-dimethyl substituted cyclopentene-1-carboxaldehydes for synthesis of expected degradation products. Cyclopentene-1-carboxaldehydes have been synthesized by various methods,[1-5] almost all of which have used adipic aldehyde derivatives as precursors or intermediates in aldol-like cyclization reactions. Since substituted adipic aldehydes are not easily accessible and because unsymmetrical aldehydes could lead to mixtures that would not be easily separated, we decided to investigate the possibility of making an acid-catalyzed ring contraction of epoxyalcohols.

When boron trifluoride, acetic acid, or sulfuric acid were used as catalysts for ring contraction only traces of the desired aldehyde were obtained. Rickborn and Gerkin[6] later published a synthesis of cyclopentanecarboxaldehydes by ring contraction of epoxycyclohexanes in anhydrous benzene with a lithium bromide–hexamethylphosphoric triamide (HMPA) complex as catalyst. In spite of formation of water in our reaction, we decided to test the equimolar LiBr–HMPA catalyst used by Rickborn and Gerkin. An exploratory study of the reaction variables showed that reaction temperature and the total amount of LiBr–HMPA had a significant effect on the yield (Table I).

TABLE I

YIELDS (VPC) IN THE REARRANGEMENT OF *cis*-5,5-DIMETHYL-2,3-EPOXYCYCLOHEXANOL (**5**) TO 4,4-DIMETHYLCYCLOPENTENE-1-CARBOXALDEHYDE (**13**) IN REFLUXING SOLVENT AS A FUNCTION OF SOLVENT BOILING POINT AND MOLAR RATIO OF CATALYST (LiBr:HMPA 1:1) TO EPOXYALCOHOL

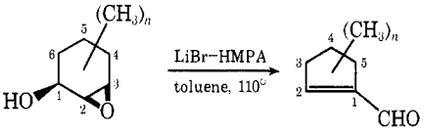
Solvent (temp, °C)	LiBr–HMPA: Epoxyalcohol	Yield, %
Benzene (80)	2.2	60
Toluene (110)	0.2	21
Toluene (110)	0.5	67
Toluene (110)	1.0	70
Toluene (110)	1.5	72
Toluene (110)	2.2	85
Xylene (139)	2.2	85

The following general procedure was found satisfactory. A toluene solution of the cis epoxyalcohol was added dropwise to a refluxing toluene solution of LiBr–HMPA under nitrogen. The reaction mixture was cooled and poured into a double volume of ether to precipitate the LiBr–HMPA complex. This gave a solution of almost pure aldehyde.

To obtain some idea of the mechanism and the limitations of the reaction, the epoxy alcohols shown in Table II were synthesized and submitted to the reaction conditions cited above.

TABLE II

PRODUCTS AND YIELDS IN THE REACTION



Epoxyalcohol Compd	Epoxyalcohol n^a	Product aldehyde(s) Compd	Product aldehyde(s) n^a	Product ratio, %	Total yield, % Vpc	Total yield, % Distn
1	0	**10**	0	100	98	43
2	1 [3]	*b*			0	
3	3 [3,5,5]	*b*			0	
4	2 [4,4]	**11**	2 [5,5]	80	92	70
		12	2 [3,3]	20		
5	2 [5,5]	**13**	2 [4,4]	100	85	76
6[d]	2 [6,6]	**11**	2 [5,5]	20	83	68
		12	2 [3,3]	80		
7	3 [1,5,5]	*b*			0	
8	1 [1]	*b*			0	
9	2,3-Epoxyhexan-4-ol	*c*			0	

[a] *n* is the number of methyl groups and position (in brackets). [b] No aldehyde formed. [c] No reaction. [d] Contains 15% of the trans isomer.

The product mixtures obtained from **4** and **6** were characterized by vpc and ^1H nmr spectroscopy. The ^1H nmr spectra of the mixtures showed a pair of unequal triplets in the vinyl region with J = 1.6 and 2.6 Hz (Figure 1). Presumably the smallest of the coupling constants is due to long-range trans coupling to the allylic methylene protons in **12**.[7] The larger coupling constant then results from vicinal coupling to the allylic methylene protons in **11**. Although the value seems to be rather small for vicinal coupling, it is well documented that olefinic protons in cyclopentene systems couple to allylic protons with coupling constants of 2–3 Hz.[7-9] To determine the product distribution unequivocally, bromine was added directly to the aldehyde mixtures in the nmr tubes. The vinyl signals at approximately 6.7 ppm disappeared completely and new signals appeared at approximately 4.5 ppm.

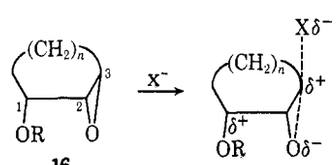
(1) J. English, Jr., and G. W. Barber, *J. Amer. Chem. Soc.*, **71**, 3310 (1949).
(2) J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950).
(3) F. Korte, K. H. Büchel, and A. Zschocke, *Ber.*, **94**, 1952 (1961).
(4) J. Chuche and J. Wiemann, *Bull. Soc. Chim. Fr.*, 1491 (1968).
(5) H. Favre and J. P. Lapointe, *Can. J. Chem.*, **49**, 3851 (1971).
(6) B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **93**, 1693 (1971).
(7) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).
(8) T. Okuda and T. Yoshida, *Tetrahedron Lett.*, 439 (1964).
(9) N. S. Bhacca and D. H. Williams in "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 87.

Obviously the singlet just upfield from 4.5 ppm belongs to **15** and the pair of doublets to **14**, thus establishing the product distribution shown in Table II (see Figure 1). These conclusions are also supported by ^{13}C nmr measurements (vinyl carbon shifts of **11** and **12**. See Table III).

For the rearrangement of alkyl-substituted cyclohexane epoxides, Rickborn and Gerkin[6] proposed a mechanism starting with a reversible epoxide ring opening by nucleophilic attack of a bromide ion. A lithium ion, solubilized by HMPA, was thought to polarize the C–O bond, thus facilitating the ring opening leading to intermediate halohydrin salts.

Several workers[10] have studied extensively epoxide ring opening in cyclic compounds such as **16** with an electron-attracting substituent in an α position to the epoxide ring. A close analogy of these systems with the present starting materials is quite obvious. Different nucleophiles (*e.g.*, OH^-, MeO^-, Br^-, Cl^-) were used under acidic and basic conditions.

In these kinetically controlled reactions, polar effects have been found to dominate steric effects[10] and appear to favor transition states like **16a**, which explain the nearly exclusive nucleophilic attack at position 3 in **16**.

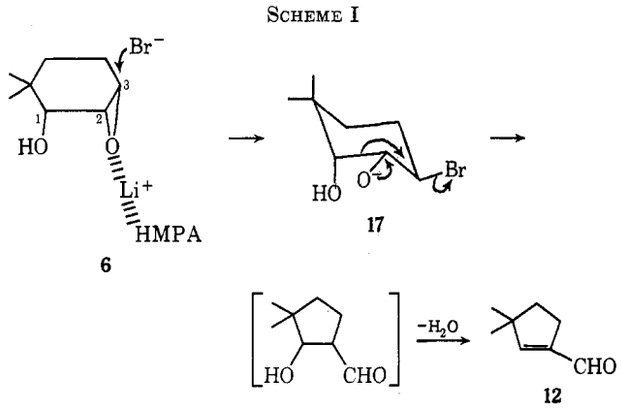


16 **16a**

R = H, CH_3
n = 1, 2

By analogy with these well-known interpretations, a mechanism for the reaction, exemplified with **6**, is suggested in Scheme I which involves epoxide ring

SCHEME I



6 **17** **12**

opening to give the intermediate **17**. In the most stable conformation of **17** the bonds between the carbons carrying oxygen and between carbon and bromine lie in a trans-coplanar arrangement suitable for ring contraction with expulsion of bromide ion.

Because significant amounts of isomeric aldehydes are formed in the rearrangements of **4** and **6** (Figure 1), other mechanisms must therefore also be involved. Expulsion of OH^- in **17** would lead to the observed by-product **11**, but OH^- is a poor leaving group, and steric

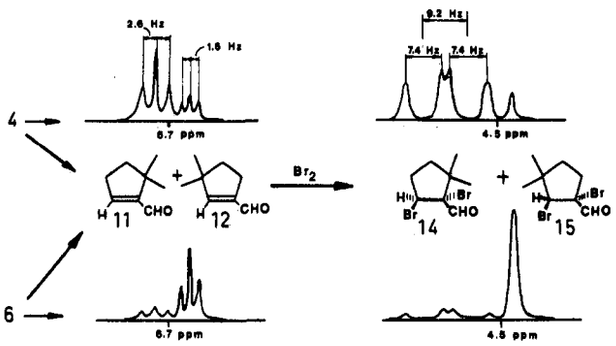
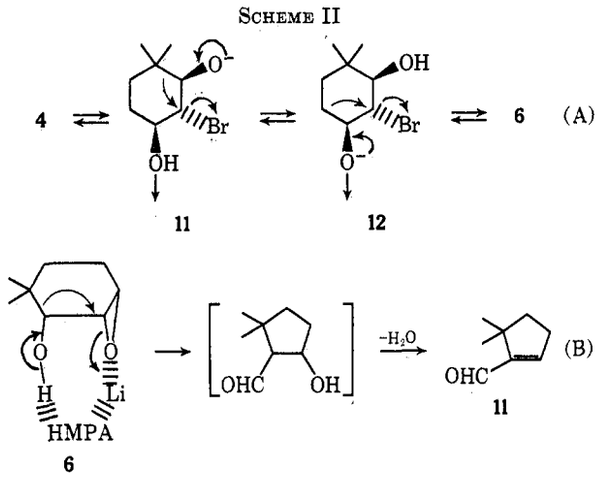


Figure 1.—Product distribution on rearrangement of epoxyalcohols **4** and **6** determined from ^1H nmr spectra.

conditions for OH^- loss are also unfavorable. A direct base-catalyzed isomerization of **6** to **4** should also lead to **11** but would require a trans arrangement of the epoxyalcohol. There remain two reasonable alternatives for the formation of the minor isomeric aldehydes: A, bromide ion attack at position 2 in **6** followed by a proton shift in the intermediate halohydrin salts[10,11] and ring contraction; or B, a concerted mechanism as depicted in Scheme II. Further mechanistic studies on these reactions are in progress.

SCHEME II



11 **12** **6**

As can be seen in Table II, cyclic epoxyalcohols with a methyl group on carbon 1 or 3 gave no aldehyde, although the starting material was consumed during the reaction. In the case of the open-chain epoxyalcohol **9**, almost all of the starting material was recovered after the reaction and no aldehyde was formed.

The epoxyalcohols were easily prepared from the corresponding allylic alcohols with *m*-chloroperbenzoic acid. Epoxidations with perbenzoic acid are known to show good selectivity for cis addition (cis:trans *ca.* 9:1),[12] but *m*-chloroperbenzoic acid proved to be even more selective, giving less than 5% trans addition except with 6,6-dimethylcyclohex-2-enol (**31**), where 15% of the trans isomer of **6** was found (quantitative vpc and ^{13}C nmr). The cyclic allylic alcohols were readily obtained from the corresponding α,β-unsaturated ketones by aluminum hydride reduction[13] or by hy-

(10) J. G. Buchanan and H. Z. Sable in "Selective Organic Transformations," Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N Y., 1972, and references cited therein.

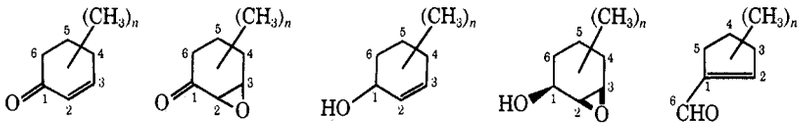
(11) G. B. Payne, *J. Org. Chem.*, **27**, 3819 (1962).

(12) P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc. B*, 1374 (1970).

(13) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

TABLE III

^{13}C NMR CHEMICAL SHIFTS[a] AND ^{13}C-^{1}H COUPLING CONSTANTS[b]



Compd (position of methyl groups)	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
			α,β-Unsaturated Ketones				
18	199.1	129.2	150.4	25.6	22.3	37.6	
19 (3)	199.4	126.1	162.7	30.7	22.3	36.7	24.3
20 (3,5,5)	198.7	124.9	159.4	44.8	33.1	50.4	23.9, 27.9
		(160)		(130)		(130)	(130) (130)
21 (4,4)	198.8	126.3	159.2	32.6	35.8*[c]	34.2*	27.5
22 (5,5)	198.6	128.2	147.6	39.2	33.0	51.1	27.6
			Epoxyketones				
23 (3)	205.8	61.6	61.2	27.4	16.2	34.7	21.2
24 (3,5,5)	207.1	61.1	64.0	42.4	35.7	47.6	30.4, 27.4, 23.5
		(180)		(135)		(132)	(130) (130) (130)
25 (4,4)	205.1	56.3*	64.4*	31.0	30.0**	33.4**	27.6, 23.0
			Allylic Alcohols				
26	65.0	129.9	129.9	24.5	18.6	31.5	
	(145)	(159)	(159)	(130)	(130)	(130)	
27 (3)	65.5	124.1	137.1	29.9*	18.8	31.3*	23.2
28 (3,5,5)	66.4	123.6	135.3	43.8*	31.0	44.8*	30.7, 25.3, 23.1
29 (4,4)	65.6	127.5	140.1	31.5	33.2	28.7	28.7
	(145)	(155)	(155)		(130)	(130)	(130)
30 (5,5)	65.8	129.3	127.6	38.8	30.5	44.8	31.1, 25.5
	(140)	(155)	(155)	(130)		(130)	(130) (130)
31 (6,6)	73.6	128.4*	128.9*	22.4	32.4	33.4	26.1, 21.3
32 (1)	67.7	133.5	128.3	25.0	19.4	37.8	29.3
33 (1,5,5)	68.6	132.3	126.5	38.7	29.3	50.2	30.9, 30.5, 27.7
34 (hex-2-en-4-ol)	17.2	133.9*	125.9*	73.9	28.7	9.3	
	(128)	(150)	(150)	(140)	(130)	(130)	
			Epoxyalcohols				
1	67.0	55.1*	55.3*	22.6	18.3	28.1	
	(140)	(175)	(175)	(130)	(130)	(130)	
2 (3)	66.5	62.2	61.0	27.9	17.6	27.9	23.2
3 (3,5,5)	66.2	62.0	60.6	42.1	30.9	39.7	30.9, 26.2, 24.4
4 (4,4)	66.4	56.3	63.2	25.7	32.4	28.6	26.3, 25.2
	(142)	(178)	(175)		(130)	(130)	(120) (120)
5 (5,5)	66.2	54.9*	54.1*	36.3	30.9	40.1	30.9, 26.4
6 (6,6)	70.7	55.3*	53.7*	20.6	25.9	32.4	24.7, 23.9
	(145)	(175)	(178)	(130)	(130)		(130) (130)
trans							
6 (6,6)	73.9	56.3*	52.9*	27.6	29.3	32.3	25.9, 18.0
7 (1)	67.5	59.0	55.5	22.9	16.2	35.3	25.3
8 (1,5,5)	68.4	58.3	56.3	36.7	30.4	48.9	30.6, 27.5
9 (2,3-epoxyhexan-4-ol)	16.6	52.3*	62.3*	72.4	26.7	9.0	
			Aldehydes				
10	147.7	152.3	27.7*	22.1	33.1*	189.0	
		(160)	(135)	(135)	(135)	(170)	
12 (3,3)	144.2	161.4	45.8	38.2	38.2	190.0	26.9
		(160)		(130)	(130)	(172)	(130)
13 (4,4)	146.1	151.2	42.8*	38.5	48.2*	189.9	29.0
11 (5,5)	153.4	152.7	30.3	40.8	43.6	189.2	25.9
		(165)	(130)	(130)		(170)	(130)

[a] Parts per million downfield from TMS. [b] Coupling constants (hertz) in parentheses. [c] Chemical shifts with * are probable but tentative.

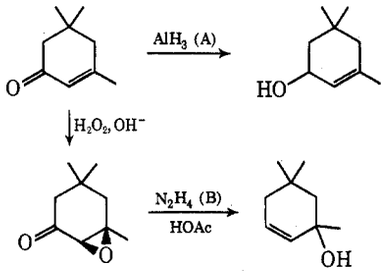
drazine reduction of the corresponding epoxyketone,[14] exemplified with isophorone in Scheme III. The epoxyketones and the α,β-unsaturated ketones were prepared by standard procedures.

^{13}C nmr data are collected in Table III. The off-resonance decoupling technique and substituent effect parameters[15] were used in making assignments of ^{13}C chemical shifts.

(14) P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).

(15) P. S. Pregosin and E. W. Randall in "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971.

SCHEME III



Experimental Section

Qualitative vpc measurements were run on a 1.5 m × 0.125 in. steel column packed with silicone XE-60 (2% on Chromosorb G, 100–120 mesh) at 180°. Quantitative vpc measurements were run on a 50 m × 0.5 mm capillary steel column (silicone GE SF 96) at 85°. Melting points are uncorrected. The ^1H nmr spectra were recorded on a Varian T-60 instrument and the ^{13}C nmr spectra on a Varian XL-100-15 instrument equipped with a Fourier transform unit. The ir spectra were run as liquid films.

Commerical cyclohex-2-enone (**18**) and 3,5,5-trimethylcyclohex-2-enone (**20**) (isophorone) were used. 3-Methylcyclohex-2-enone (**19**) was prepared according to Natelson and Gottfried,[16] 4,4-dimethylcyclohex-2-enone (**21**) according to Conia and Le Craz,[17] and 5,5-dimethylcyclohex-2-enone (**22**) according to Frank and Hall.[18]

3,5,5-Trimethyl-2,3-epoxycyclohexanone (**24**) was obtained by epoxidation of isophorone.[19]

4,4-Dimethyl-2,3-epoxycyclohexanone (**25**) was prepared by epoxidation of **21** as for the epoxidation of isophorone:[19] yield 47%; bp 82–83° (11 mm); $n^{24}D$ 1.4614; ir 1718 cm^{-1}; nmr ($CDCl_3$) δ 3.18 (s, 2), 1.22 (s, 3), 1.10 (s, 3).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.5; H, 8.7.

3-Methyl-2,3-epoxycyclohexanone (**23**) was prepared from **19** applying the same oxidation technique:[19] yield 30%; bp 85° (15 mm); $n^{22}D$ 1.4643; ir 1715 cm^{-1}; nmr ($CDCl_3$) δ 3.02 (s, 1), 1.43 (s, 3).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.7; H, 8.0. Found: C, 66.7; H, 8.0.

For ^{13}C nmr data of the ketones see Table III.

The cyclohexenols were prepared by two different procedures: by AlH_3 reduction of the appropriate α,β-unsaturated ketones (A)[13] or by N_2H_4 reduction of the α,β-epoxyketones (B)[14] as exemplified with isophorone in Scheme III.

A. Aluminum Hydride Reduction of Cyclohex-2-enones.[13]—$AlCl_3$ (16.6 g) was added to an ice-cold suspension of $LiAlH_4$ (14.4 g) in dry ether (2 l.). The resulting mixture was stirred mechanically until it had reached room temperature. Separation under nitrogen pressure through a Fiberglas plug yielded a *ca.* 0.25 *M* ethereal solution of AlH_3. Part of this solution (500 ml) was transferred under nitrogen into a 1-l., three-necked flask. The ketone (0.25 mol) dissolved in ether (50 ml) was added dropwise to the stirred AlH_3 solution over 15 min (ice cooling). The stirring was continued for another 30 min and the resulting aluminum complex was hydrolyzed with $Na_2SO_4 \cdot 10H_2O$ and finally with water. Filtration, after the addition of 2 *M* NaOH (2 ml), gave a colorless filtrate which was washed with water (2 × 50 ml) and dried over Na_2SO_4. Evaporation of the solvent and distillation through a 20-cm Vigreux column gave the allylic alcohol.

B. Hydrazine Reduction of 2,3-Epoxycyclohexanones.[14]—The epoxyketone (0.1 mol) was added to a stirred, ice-cooled solution of hydrazine hydrate (12.5 ml, *ca.* 2.5 equiv) and acetic acid (1.2 ml) in methanol (100 ml). Cooling and stirring were maintained for 30 min and the reaction mixture was then allowed to warm to room temperature. The bulk of the methanol was evaporated under reduced pressure through a 30-cm Vigreux column. Water (200 ml) was added to the residue and the water phase was extracted with ether (2 × 200 ml). The ether solution was then washed with water (100 ml), dried (Na_2SO_4), and evaporated. Distillation of the residue gave the allylic alcohol.

Cyclohex-2-enol (**26**) (by method A, yield 75%) had bp 61–62° (11 mm); $n^{23}D$ 1.4859; ir 1655, 1055, 965 cm^{-1}; nmr ($CDCl_3$) δ 5.80 (s, 2), 4.20 (m, 1).

Anal. Calcd for $C_6H_{10}O_2$: C, 73.4; H, 10.3. Found: C, 73.5; H, 10.3.

The *p*-nitrobenzoate had mp 77–78° from hexane.

3-Methylcyclohex-2-enol (**27**) (by method A, yield 80%) had bp 74–75° (11 mm); $n^{23}D$ 1.4832; ir 1675, 1038, 960 cm^{-1}; nmr ($CDCl_3$) δ 5.50 (m, 1), 4.15 (s broad, 1), 1.65 (s, 3).

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.0; H, 10.7. The *p*-nitrobenzoate had mp 69–70° from hexane.

1-Methylcyclohex-2-enol (**32**) (by method B, yield 56%) had bp 60–61° (15 mm); $n^{22}D$ 1.4757; ir 1655, 1130 cm^{-1}; nmr ($CDCl_3$) δ 5.68 (s, 2), 1.26 (s, 3).

Anal. Calcd for $C_{14}H_{15}NO_4$ (*p*-nitrobenzoate): C, 64.4; H, 5.8; N, 5.4. Found: C, 64.3; H, 5.5; N, 5.3.

The *p*-nitrobenzoate had mp 101–102° from hexane.

4,4-Dimethylcyclohex-2-enol (**29**) (by method A, yield 67%) had bp 74–77° (11 mm); $n^{23}D$ 1.4694; ir 1655, 1050 cm^{-1}; nmr ($CDCl_3$) δ 5.55 (s, 2), 4.00–4.30 (m, 1), 1.00 (s, 3), 0.95 (s, 3).

Anal. Calcd for $C_{15}H_{17}NO_4$ (*p*-nitrobenzoate): C, 65.4; H, 6.2; N, 5.1. Found: C, 65.1; H, 6.2; N, 5.0.

The *p*-nitrobenzoate had mp 40–41° from hexane.

5,5-Dimethylcyclohex-2-enol (**30**) (by method A, yield 74%) had bp 76–77° (11 mm); $n^{26}D$ 1.4677; ir 1655, 1040, 940 cm^{-1}; nmr ($CDCl_3$) δ 5.63 (s, 2), 4.00–4.50 (m, 1), 0.98 (s, 3), 0.88 (s, 3).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2; H, 11.2.

The *p*-nitrobenzoate had mp 41–42° from hexane.

6,6-Dimethylcyclohex-2-enol (**31**) (by method B, yield 55%) had bp 67–68° (11 mm); $n^{23}D$ 1.4758; ir 1655, 1060 cm^{-1}; nmr ($CDCl_3$) δ 5.72 (s, 2), 3.65–3.80 (m, 1), 0.98 (s, 3), 0.92 (s, 3).

Anal. Calcd for $C_{15}H_{17}NO_4$ (*p*-nitrobenzoate): C, 65.4; H, 6.2; N, 5.1. Found: C, 65.3; H, 6.1; N, 5.1.

The *p*-nitrobenzoate had mp 107–108° from hexane.

1,5,5-Trimethylcyclohex-2-enol (**33**) (by method B, yield 43%, *cf.* ref 14, 66%) had bp 69–72° (13 mm); $n^{22}D$ 1.4666; ir 1655, 1063, 905 cm^{-1}; nmr ($CDCl_3$) δ 5.67 (s, 1), 1.27 (s, 3), 1.05 (s, 3), 0.97 (s, 3).

Anal. Calcd for $C_{16}H_{19}NO_4$ (*p*-nitrobenzoate): C, 66.4; H, 6.6; N, 4.8. Found: C, 66.3; H, 6.6; N, 4.8.

The *p*-nitrobenzoate had mp 84–85° from hexane.

3,5,5-Trimethylcyclohex-2-enol (**28**) (by method A, yield 66%) had bp 87–88° (11 mm); $n^{23}D$ 1.4723; ir 1665, 1023 cm^{-1}; nmr ($CDCl_3$) δ 5.45 (s, 1), 4.00–4.50 (m, 1), 1.66 (s, 3), 1.02 (s, 3), 0.89 (s, 3).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.1; H, 11.4.

The *p*-nitrobenzoate had mp 71–73° from hexane.

Hex-2-en-4-ol (**34**) was prepared by standard Grignard reaction of crotonaldehyde with ethylmagnesium bromide, yield 67%. The *trans*-hexenol was contaminated with minor amounts of the cis isomer (^{13}C nmr). For ^{13}C nmr data of the allylic alcohols, see Table III.

Oxidation of the Allylic Alcohols with *m*-Chloroperbenzoic Acid.—A solution of the allylic alcohol (0.1 mol) and *m*-chloroperbenzoic acid[20] (0.1 mol) in dry methylene chloride (150 ml) was stirred under anhydrous conditions for 2 hr at 0°. The precipitated *m*-chlorobenzoic acid was filtered off and the filtrate was dried (Na_2SO_4, 5 g) for 1 hr. After anhydrous $Ca(OH)_2$ (10 g) was added to precipitate the remaining acids, the mixture was filtered, the solvent was evaporated, and the residue was distilled to obtain the cis epoxyalcohol containing less than 5% of the trans isomer (quantitative vpc) except for compound **6** where the trans isomer amounts to 15% (quantitative vpc and ^{13}C nmr).

***cis*-2,3-Epoxycyclohexanol** (**1**) (yield 84%) had bp 46° (0.3 mm); $n^{23}D$ 1.4857; ir 3000, 1070, 855 cm^{-1}; nmr ($CDCl_3$) δ 3.80–4.25 (m, 1), 3.37 (s, 2).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.2; H, 8.8.

The α-naphthylurethane had mp 173.5–174.0° (lit.[21] mp 173.5–175.0°).

1-Methyl-*cis*-2,3-epoxycyclohexanol (**7**) (yield 80%) had bp

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(18) R. L. Frank and H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **72**, 1645 (1950).

(19) R. L. Wasson and H. O. House, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 552.

(20) Large amounts of the peracid were conveniently prepared by standard synthetic reactions from inexpensive commercially available *m*-aminobenzoic acid. (AB Bofors Nobelkrut, Bofors, Sweden.)

(21) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 4608 (1957).

80–83° (11 mm); $n^{23}D$ 1.4734; ir 940, 827 cm^{-1}; nmr ($CDCl_3$) δ 3.40 (s broad, 1), 3.08 (d, 1, J = 4.0 Hz), 1.35 (s, 3).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.3.

3-Methyl-*cis*-2,3-epoxycyclohexanol (**2**) (yield 79%) had bp 39° (0.3 mm); $n^{22}D$ 1.4727; ir 1045, 848 cm^{-1}; nmr ($CDCl_3$) δ 4.00 (m, 1), 3.20 (d, 1, J = 3.0 Hz), 1.40 (s, 3).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.8; H, 9.4.

4,4-Dimethyl-*cis*-2,3-epoxycyclohexanol (**4**) (yield 89%) had bp 51° (0.4 mm); $n^{22}D$ 1.4691; ir 1068, 862 cm^{-1}; nmr ($CDCl_3$) δ 3.85–4.20 (m, 1), 3.40 (t, 1, J = 4.0 Hz), 2.92 (d, 1, J = 4.0 Hz), 1.09 (s, 3), 1.02 (s, 3).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 67.4; H, 9.9.

5,5-Dimethyl-*cis*-2,3-epoxycyclohexanol (**5**) (yield 89%) had bp 53° (0.4 mm); $n^{23}D$ 1.4706; ir 1053, 832 cm^{-1}; nmr ($CDCl_3$) δ 3.90–4.35 (m, 1), 3.36 (s, 2), 0.92 (s, 6).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 67.5; H, 9.8.

6,6-Dimethyl-*cis*-2,3-epoxycyclohexanol (**6**) (yield 86%) had bp 35° (0.3 mm); $n^{23}D$ 1.4760; ir 1068, 815 cm^{-1}; nmr ($CDCl_3$) δ 3.30–3.60 (m, 3), 1.00 (s, 3), 0.88 (s, 3). The product contained 15% of the trans isomer (^{13}C nmr, quantitative vpc).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 67.3; H, 9.9.

1,5,5-Trimethyl-*cis*-2,3-epoxycyclohexanol (**8**) (yield 78%) had bp 96–97° (12 mm); $n^{23}D$ 1.4661; ir 1020, 840 cm^{-1}; nmr ($CDCl_3$) δ 3.39 (m, 1), 3.02 (d, 1, J = 4.0 Hz), 1.38 (s, 3), 0.99 (s, 3), 0.96 (s, 3).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 69.2; H, 10.3.

3,5,5-Trimethyl-*cis*-2,3-epoxycyclohexanol (**3**) (yield 72%) had bp 46° (0.3 mm); $n^{23}D$ 1.4635; ir 1030, 823 cm^{-1}; nmr ($CDCl_3$) δ 4.10 (m, 1), 3.18 (d, 1, J = 2.0 Hz), 1.40 (s, 3), 0.94 (s, 3), 0.92 (s, 3).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 69.6; H, 10.2.

2,3-Epoxyhexan-4-ol (**9**) (yield 74%) had bp 63–66° (10 mm); $n^{24}D$ 1.4281; ir 870 cm^{-1}; nmr ($CDCl_3$) δ 1.33 (d, 3, J = 5.0 Hz), 0.98 (t, 3, J = 6.0 Hz). The product was contaminated with the epoxyalcohol originating from the cis allylic alcohol (^{13}C nmr).

Anal. Calcd for $C_6H_{12}O_2$: C, 62.0; H, 10.4. Found: C, 61.8; H, 10.4. For ^{13}C nmr data of the epoxyalcohols see Table III.

Ring Contraction of 2,3-Epoxycyclohexanols to Cyclopentene-1-carboxaldehydes.—The epoxyalcohol (0.045 mol) dissolved in dry toluene (50 ml) was added under nitrogen to a refluxing solution of LiBr (0.1 mol) and HMPA (0.1 mol) in dry toluene (50 ml) over 30 min. About 2 min after the addition was finished the reaction mixture was cooled in an ice bath and poured into ether (200 ml). The LiBr–HMPA complex that separated as a heavy oil was discarded. The ethereal solution was washed with water (3 × 15 ml) and dried (Na_2SO_4). Yields were estimated by vpc with decalin as internal standard. Solvent was removed through an efficient column at atmospheric pressure and the residue was fractionally distilled to give the pure aldehyde. The toluene solution of the aldehyde can be used directly for further reaction, thus avoiding distillation losses. Distilled yields are given in parentheses.

Cyclopentene-1-carboxaldehyde (**10**) [yield 98% (43%)] had bp 42–44° (10 mm); $n^{23}D$ 1.4874 [lit.[2] bp 52° (20 mm); $n^{17}D$ 1.4892]; uv max (99.5% EtOH) 236 nm (ε 10,800); ir 3045, 2720, 1685, 1620 cm^{-1}; nmr ($CDCl_3$) δ 9.85 (s, 1), 6.95 (m, 1).

Anal. Calcd for C_6H_8O: C, 75.0; H, 8.4. Found: C, 74.9; H, 8.4.

The dinitrophenylhydrazone had mp 216–217° from ethanol (lit.[22] mp 211–215°).

3,3-Dimethylcyclopentene-1-carboxaldehyde (**12**) [yield 83% (68%); product mixture, see Table II] had bp 58° (12 mm); $n^{23}D$ 1.4697; uv max (99.5% EtOH) 236 nm (ε 11,300); ir 3040, 2720, 1685, 1622, 1368, 1353 cm^{-1}; nmr ($CDCl_3$) δ 9.83 (s, 1), 6.62 (t, 1, J = 1.6 Hz), 1.18 (s, 6).

Anal. Calcd for $C_{14}H_{16}N_4O_4$ (dinitrophenylhydrazone): C, 55.3; H, 5.3; N, 18.4. Found: C, 55.3; H, 5.3; N, 18.3.

The dinitrophenylhydrazone had mp 213.5–214.5° from ethanol.

4,4-Dimethylcyclopentene-1-carboxaldehyde (**13**) [yield 85% (76%)] had bp 52° (10 mm); $n^{23}D$ 1.4663; uv max (99.5% EtOH) 237.5 nm (ε 12,600); ir 3050, 2720, 1685, 1620, 1370, 1360 cm^{-1}; nmr ($CDCl_3$) δ 9.76 (s, 1), 6.72 (s broad, 1), 2.25–2.52 (m, 4), 1.12 (s, 6).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.1; H, 9.8.

The dinitrophenylhydrazone had mp 227–228° from ethanol.

5,5-Dimethylcyclopentene-1-carboxaldehyde (**11**) [yield 92% (70%); product mixture, see Table II] had bp 53° (11 mm); $n^{23}D$ 1.4697; uv max (99.5% EtOH) 235 nm (ε 9700); ir 3050, 2720, 1685, 1618, 1365, 1350 cm^{-1}; nmr ($CDCl_3$) δ 9.82 (s, 1), 6.78 (t, 1, J = 2.6 Hz), 2.30–2.70 (m, 2), 1.65–2.00 (m, 2), 1.26 (s, 6).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.5; H, 9.7.

The dinitrophenylhydrazone had mp 167–170° from ethanol. For ^{13}C nmr data of the aldehydes see Table III.

Registry No.—**1,** 26828-72-8; **2,** 38309-43-2; **3,** 38309-44-3; **4,** 38309-45-4; **5,** 38309-46-5; *cis*-**6,** 38309-47-6; *trans*-**6,** 38309-48-7; **7,** 38309-49-8; **8,** 38309-50-1; **9,** 1193-06-2; **10,** 6140-65-4; **11,** 38312-90-2; **11** DNP, 38312-91-3; **12,** 38312-92-4; **12** DNP, 38312-93-5; **13,** 38312-94-6; **13** DNP, 38312-95-7; **18,** 930-68-7; **19,** 1193-18-6; **20,** 78-59-1; **21,** 1073-13-8; **22,** 4694-17-1; **23,** 21889-89-4; **24,** 10276-21-8; **25,** 1074-26-6; **26,** 822-67-3; **26** *p*-nitrobenzoate, 38313-01-8; **27,** 21378-21-2; **27** *p*-nitrobenzoate, 38313-03-0; **28,** 470-99-5; **28** *p*-nitrobenzoate, 38313-05-2; **29,** 5020-09-7; **29** *p*-nitrobenzoate, 38313-07-4; **30,** 25866-56-2; **30** *p*-nitrobenzoate, 38313-09-6; **31,** 38313-10-9; **31** *p*-nitrobenzoate, 38313-11-0; **32,** 23758-27-2; **32** *p*-nitrobenzoate, 38313-13-2; **33,** 3779-25-2; **33** *p*-nitrobenzoate, 38313-15-4.

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