phates on 60–80 mesh firebrick. This column separated the olefins but would not allow elution of the alcohols. The resuts are summarized in Table I.

Registry No.—III, 28252-86-0; IV, 28252-87-1; V, 28252-88-2; VI, 28252-89-3; VII, 28252-90-6; IX, 28252-91-7; X; 28252-92-8; XI, 28252-93-9; *cis*-XII, 28252-94-0; *trans*-XII, 28256-86-2; *cis*-XIII, 28252-95-1; *trans*-XIII, 28252-96-2; *cis*-5-phenylcyclooctyl *p*-toluenesulfonate, 7286-93-3; *trans*-5-phenylcyclooctyl *p*-toluenesulfonate, 7368-50-5.

Base-Induced Rearrangement of Epoxides to Allylic Alcohols. III. Alkylidenecycloalkane Oxides[1]

RANDOLPH P. THUMMEL AND BRUCE RICKBORN*

Department of Chemistry, University of California, Santa Barbara, California 93106

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The lithium diethylamide induced rearrangement of a series of propylidenecycloalkane oxides to allylic alcohols exhibits marked regioselectivity, with endocyclic olefin product being formed preferentially. An exception is propylidenecyclohexane oxide which gives 95% of the alternate, tertiary allylic alcohol. A series of ethylidenecycloalkane oxides, where preference for endocyclic elimination competes with proton abstraction from primary carbon, was also examined. The results of both series support a syn elimination mechanism, with very specific cis-coplanar transition state geometrical requirements.

Cope and Tiffany[2] were apparently the first workers to observe an unusual base-catalyzed rearrangement of an epoxide when dealing with cyclooctatetraene oxide. Subsequent work with phenyl-substituted ethylene oxides,[3] medium-ring cycloalkene oxides,[4] and open-chain epoxides[5] established several novel reaction pathways on treatment with strong base. The extensive work of Crandall and his coworkers[6] amplified these and brought to light additional reactions.

This paper deals with our continuing[1,7] study of the lithium diethylamide induced rearrangement of epoxides to allylic alcohols. Formally an elimination, this reaction is remarkable for its very high selectivity, *e.g.*, stereoselectivity (exclusive formation of trans olefin in open-chain systems[5,7]) and regioselectivity[8] (exclusive, or nearly so, abstraction of proton from least substituted carbon[6,7]). Recently deuterium labeling studies[1] have established that syn elimination is the preferred pathway in cyclohexene oxide rearrangements.

The factors which influence the regioselectivity of the base-induced reaction are incompletely understood. We have undertaken a systematic study of substituted epoxides to examine this question; the results obtained with alkylidenecycloalkane oxides are presented here.

Results and Discussion

A series of propylidenecycloalkane oxides (**1**) was prepared by standard procedures and treated with lithium diethylamide in refluxing ether–hexane (eq 1). The course of the reaction was followed by vpc, and the mixture quenched with water when the epoxide was consumed. The results are shown in Table I.

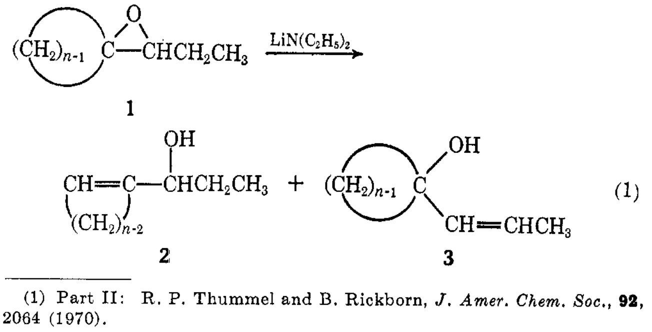

TABLE I

PRODUCT DISTRIBUTION FROM THE REACTION OF PROPYLIDENECYCLOALKANE OXIDES (1) WITH LITHIUM DIETHYLAMIDE

1	*n*	Time, hr[a]	2	3
a	4	6	77	15[b]
b	5	1	100	0
c	6	49[c]	5	95
d	7	5	98	2
e	8	2	100	0
f	12	22	≥84	. . .[d]

[a] The reactions were followed by vpc; this is the time required for effective complete loss of starting epoxide. [b] The product mixture in this case contained 5% cyclobutyl ethyl ketone and 3% unidentified material. [c] At this time 9% unreacted epoxide remained. [d] Not directly determined; see Experimental Section.

In this series, proton abstraction from secondary cyclic carbon competes with that from a secondary acyclic center. The data in Table I show not only high selectivity depending on ring size, but a striking reversal in the direction of elimination in the series cyclopentyl (endocyclic), cyclohexyl (acyclic), and cycloheptyl (endocyclic olefin preferred).

It is apparent that subtle conformational effects can significantly diminish the activation energy for elimination into the carbocyclic ring. The propylidenecyclohexane oxide **1c** serves as a basis for comparison; reaction to form the acyclic double bond (as strongly favored in **1c**) requires in excess of 49 hr for complete conversion. All other systems shown in Table I react more rapidly, from a great deal faster in the completely

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[1] Part II: R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970).

[2] A. C. Cope and B. D. Tiffany, *ibid.*, **73**, 4158 (1951).

[3] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *ibid.*, **80**, 2844 (1958).

[4] (a) A. C. Cope, H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958); (b) A. C. Cope, M. Brown, and H. Lee, *ibid.*, **80**, 2855 (1958); (c) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960).

[5] A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1965).

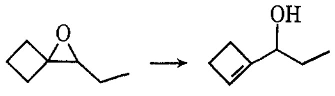
[6] (a) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964); (b) J. K. Crandall and L. Chang, *ibid.*, **32**, 435 (1967); (c) *ibid.*, **32**, 532 (1967); (d) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967); (e) *J. Org. Chem.*, **33**, 2375 (1968).

[7] B. Rickborn and R. P. Thummel, *ibid.*, **34**, 3583 (1969).

[8] The terminology suggested by A. Hassner, *ibid.*, **33**, 2685 (1968).

endocyclic regiospecific reactions of **1b** and **1e** to the moderately faster, somewhat regioselective reaction of **1f**. In the limit a large ring should exhibit open-chain behavior, and the cyclododecyl system **1f** appears from both a rate and product (although incompletely analyzed) standpoint to be progressing in this direction.

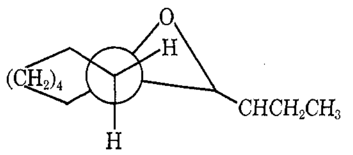
The cyclobutyl system **1a** is of interest in that it leads primarily to the strained cyclobutene product **2a** (eq 2)



1a **2a** (2)

The data in Table I are best interpreted in terms of a syn elimination mechanism as earlier demonstrated in cyclohexene oxides.[1] DePuy and his coworkers[9] have presented convincing evidence of the importance of cis coplanarity of hydrogen and leaving group in the E2 syn elimination mechanism. Although other known syn eliminations do not necessarily serve as good models for the epoxide reaction, transition state cis coplanarity is apparently a dominant feature of the latter as well. Thus a cis coplanar arrangement of β hydrogen and epoxygen in the cyclopentyl compound **1b** is easily attained, whereas trans coplanarity (needed for anti elimination) would involve excessive strain. The fact that **2b** is the exclusive product of this reaction strongly supports the syn elimination mechanism, although the degree of preference for endocyclic elimination is not so easily rationalized.

Compound **1c** offers a convincing demonstration of the importance of coplanarity in the base-induced rearrangement. In neither chair conformer (as seen from Newman projection **4**) of **1c** is cis (or trans) coplanarity of epoxygen with a β hydrogen on the ring attained. Cis coplanarity is attainable with the acyclic β proton; as a consequence, elimination is nearly exclusively in this direction (95%), in a slow reaction as expected for normal secondary proton abstraction. The product, in agreement with earlier work, is the trans olefin **5**. The small amount of endocyclic olefin which is formed in the reaction of **1c** may arise *via* a twist boat conformer, where cis coplanarity is feasible.



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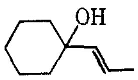
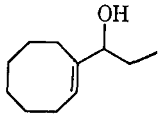


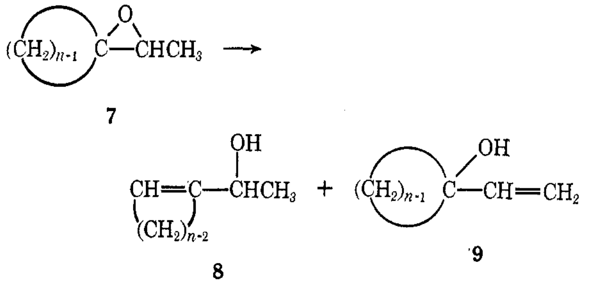
5

It is particularly interesting that the next higher ring system (cycloheptyl, **1d**) gives nearly exclusively endocyclic product. Apparently the cycloheptyl ring is sufficiently flexible that a conformationally favorable cis coplanar transition state is allowed. This behavior is even more pronounced with the cyclooctyloxirane **1e**, which in a quite rapid reaction yields the endocyclic olefin with complete regiospecificity. The product **2e** gives a single peak on vpc, and its nmr spectrum supports the *cis*-cyclooctene structure **6**; the formation of cis endocyclic olefin is of course mechanistically analogous to the generation of trans acyclic material.



6

In view of the decided competitive advantage enjoyed by cyclic secondary proton abstraction over its acyclic equivalent, it was of interest to explore the competition between cyclic secondary and acyclic primary abstraction. It should be recalled that, in an open-chain model, 2-pentene oxide, no base attack at the secondary proton could be detected.[7] The systems studied are indicated in the generalized eq 3, and the results are given in Table II.



(3)

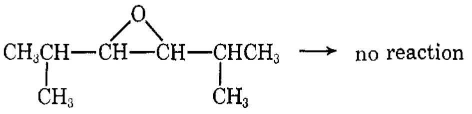
TABLE II

THE LITHIUM DIETHYLAMIDE INDUCED REARRANGEMENT OF ETHYLIDENECYCLOALKANE OXIDES (**7**)

7	*n*	Time, hr	8	9
a	5	1.5	70	30
b	6	2	0	100
c	7	2.5	38	62
d	8	2	66	34

Several points are worth noting. Although the cyclopentyl system **7a** no longer gives regiospecific results, endocyclic olefin formation is still preferred over primary proton abstraction, in contrast to the open-chain model. The ethylidenecyclooctane oxide **7d** gives results which are quite analogous to those obtained with **7a**. This behavior is anticipated from the results for **1b** and **1e** in Table I. Similarly, where the propylidenecycloheptane oxide **1d** gave incomplete specificity, the ethylidene analog **7c** reverts to slight preference for primary proton abstraction. As expected, ethylidenecyclohexane oxide yields only 1-vinylcyclohexanol (**9b**). Thus the results with the two sets of epoxides, ethylidene- and propylidenecycloalkane oxides, are mutually consistent.

We had earlier observed that a system containing only tertiary β protons, *i.e.*, 2,5-dimethyl-3-hexene oxide (**10**), gave no observable reaction when refluxed



$$\underset{\displaystyle CH_3}{CH_3CH}—\overset{\displaystyle O}{CH—CH}—\underset{\displaystyle CH_3}{CHCH_3} \longrightarrow \text{no reaction} \qquad (4)$$

10

for 2 days with lithium diethylamide. Compound **11** was prepared in order to examine the competition between secondary cyclohexyl and tertiary proton abstraction. The reaction was extremely slow; under the conditions normally employed, only 24% of the

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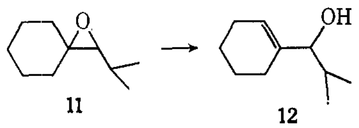
[9] C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, **87**, 2421 (1965).

epoxide had rearranged after 72 hr, giving **12** as the exclusive product. Again this behavior is anticipated



11 **12** (5)

based on the inert nature of **10** and the formation of a small amount of **2c** in the reaction of **1c**.

The results presented here provide another example of the unusual and synthetically useful selectivity of the base-induced rearrangement of epoxides. We are continuing to explore other features of this interesting reaction.

Experimental Section[10]

Olefins.—The method of Schlosser and Christmann,[11] involving the appropriate alkyltriphenylphosphonium bromide, was used to prepare olefins. The cyclic ketones used in this ylide reaction were all, with the exception of cyclobutanone, distilled commercial materials. Cyclobutanone was prepared using a literature method.[12] The product olefins had the following characteristics.

Propylidenecyclobutane (56%):[13] bp 96–104° (83% pure); nmr δ 5.15 (nonet, 1, *J* = 2.5 Hz, C=CH), 2.7 (t, 4, *J* = 7.5 Hz, $CH_2\mathbf{H}_2C{=}CH$), 2.3–1.5 (m, 4), and 0.95 ppm (t, 3); ir 1460, 1300, and 850 cm^{-1}.

Propylidenecyclopentane[14] (44%): bp 56–58° (43 mm); nmr δ 5.08 (nonet, 1, *J* = 2.3 Hz, C=CH), 2.2–1.1 (m, 10), and 0.7 ppm (t, 3); ir 1460, 900, and 850 cm^{-1}.

Propylidenecyclohexane[15] (77%): bp 69–70.5° (70 mm); nmr δ 4.9 (t, 1, *J* = 7 Hz, C=CH), 2.2–1.6 (m, 6), 1.6–1.0 (m, 6), and 0.7 ppm (t, 3); ir 1450, 983, 890, 841, 742, and 695 cm^{-1}.

Propylidenecycloheptane (78%): bp 90° (45 mm); nmr 5.0 (t, 1, *J* = 7 Hz, C=CH), 2.5–1.1 (m, 14), and 0.9 ppm (t, 3); ir 2960 and 1460 cm^{-1}.

Propylidenecyclooctane (75%): bp 93–97° (30 mm); nmr δ 5.23 (t, 1, *J* = 7 Hz, C=CH), 2.5–1.8 (m, 6), 1.55 (broad singlet, 10), and 0.95 ppm (t, 3); ir 2920 and 1460 cm^{-1}.

Propylidenecyclododecane (83%): bp 144–150° (20 mm); nmr δ 5.08 (t, 1, *J* = 7 Hz, C=CH), 2.0 (m, 6), 1.3 (s, 18) and 0.92 ppm (t, 3); ir 1475, 1450, 880, and 725 cm^{-1}.

Ethylidenecyclopentane[16] (24%): bp 52–58° (80 mm); nmr δ 5.1 (m, 1), 2.1 (m, 4), and 1.6 ppm (m, 7); ir 3050, 945, and 805 cm^{-1}.

Ethylidenecyclohexane was a commercial sample purchased from the Aldrich Chemical Co.

Ethylidenecycloheptane[17] (62%): bp 71–74° (53 mm); nmr δ 5.3 (quartet, 1, *J* = 7 Hz, C=CH), 2.25 (broad singlet, 4), and 1.8–1.4 ppm (m, 11); ir 2915, 1450, and 807 cm^{-1}.

Ethylidenecyclooctane (24%): bp 70–72° (50 mm) (81% pure by vpc); nmr δ 5.12 (quartet, 1, *J* = 7 Hz, C=CH) and 2.4–1.1 ppm (broad multiplet, 17); ir 2920 and 1450 cm^{-1}.

Isobutylidenecyclohexane (9%): bp 88–92° (108 mm) (45% pure by vpc, contaminated with cyclohexanone); nmr δ 5.0 (d, 1, *J* = 9 Hz, C=CH) and 0.9 ppm (d, 6).

Epoxides.—The epoxides were prepared from the olefins using peracetic acid[18] and had the following characteristics.

Propylidenecyclobutane oxide (82%): bp 75–77° (108 mm); nmr δ 2.8–0.8 ppm (multiplet); ir 1340, 1120, 920, and 830 cm^{-1}. *Anal.*[19] Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.73; H, 10.97.

Propylidenecyclopentane oxide (82%); bp 75–76° (39 mm); nmr δ 2.7 (t, 1, *J* = 6 Hz, -O-CH[20]), 2.1–1.1 (m, 10), and 0.91 ppm (t, 3); ir 930 and 880 cm^{-1}. *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.32; H, 11.26.

Propylidenecyclohexane oxide (61%): bp 76° (20 mm); nmr δ 2.36 (t, 1, *J* = 6 Hz, -O-CH[20]), 2.1–1.1 (m, 12), and 0.88 ppm (t, 3); ir 1040, 990, and 910 cm^{-1}. *Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.09; H, 11.83.

Propylidenecycloheptane oxide (70%): bp 98° (30 mm); nmr δ 2.48 (t, 1, *J* = 6 Hz, -O-CH[20]), 1.9–1.2 (m, 14), and 1.0 ppm (t, 3); ir 1460 and 910 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.81; H, 11.89.

Propylidenecyclooctane oxide (70%): bp 110–112° (25 mm); nmr δ 2.57 (t, 1, *J* = 6 Hz, -O-CH[20]), 1.6 (s) overlapping 1.5 (quartet, 16), and 1.03 ppm (t, 3); ir 955, 935, and 910 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.24; H, 12.13.

Propylidenecyclododecane oxide (86%): bp 123–126° (3 mm); nmr δ 2.36 (t, 1, *J* = 6 Hz, -O-CH[20]), 1.3 (broad singlet, 24), and 0.9 ppm (t, 3); ir 1255, 948, 885, and 723 cm^{-1}. *Anal.* Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.22; H, 12.79.

Ethylidenecyclopentane oxide (73%): bp 133–136°; nmr δ 3.25 (quartet, 1, *J* = 6 Hz, -O-CH[20]), 2.3–1.5 (m, 8), and 1.4 ppm (d, 3, *J* = 6 Hz, $CH{-}C\mathbf{H}_3$); ir 1165, 1030, 1000, 980, 950, 930, and 865 cm^{-1}. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.71; H, 10.94.

Ethylidenecyclohexane oxide[21] (64%): bp 158–160°; nmr δ 2.7 (quartet, 1), 2.55 (broad singlet, 10), and 1.25 ppm (d, 3); ir 1030, 897, and 849 cm^{-1}.

Ethylidenecycloheptane oxide[22] (83%): bp 80–82° (30 mm); nmr δ 2.7 (quartet, 1, *J* = 6 Hz, -O-CH[20]), 1.65 (broad singlet, 12), and 1.23 ppm (d, 3, *J* = 6 Hz, $CH{-}C\mathbf{H}_3$); ir 1020 and 870 cm^{-1}.

Ethylidenecyclooctane oxide (75%): bp 87–91° (21 mm); nmr δ 268 (quartet, 1, *J* = 5.5 Hz, -O-CH[20]), 1.54 (s, 14), and 1.2 ppm (d, 3, *J* = 5.5 Hz, $CH{-}C\mathbf{H}_3$); ir 1150 and 1100 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.62; H, 11.35.

Isobutylidenecyclohexane oxide (63%): preparative vpc, collected on a Carbowax 6000 column at 125°; nmr δ 2.15 (d, 1, *J* = 8.5 Hz, -O-CH[20]), 1.5 (broad singlet, 11), and 0.95 ppm (two overlapping doublets, 6, *J* = 5.5 Hz, $CH{-}C\mathbf{H}_3$); ir 1010 and 917 cm^{-1}. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.33; H, 11.76.

Epoxide Rearrangements.—All reactions were run in refluxing ether solvent using 0.01 mol of epoxide; 0.025 mol of lithium diethylamide, prepared from the amine and commercial butyllithium in hexane, was used.

Aliquots were withdrawn, quenched with water, and examined by vpc to follow the course of the reaction. Carbowax 6M and 20M columns were employed for vpc analysis. Rearrangement product yields were obtained from vpc peak areas (uncorrected).

After quenching with water and evaporation of solvent, the products from the rearrangement reaction were isolated by preparative vpc and analyzed by nmr and ir. In cases where positive identification was not possible by spectral means, the product was catalytically reduced and then compared by gas chromatography to the saturated alcohols prepared by lithium aluminum hydride reduction of the epoxide or appropriate ketone.

The major products from **propylidenecyclobutane oxide** (66%) were catalytically reduced to give a mixture of 15% 1-propylcyclobutanol (ir 3350, 1270, 1175, 1038, and 963 cm^{-1}, identical with sole product from $LiAlH_4$ reduction of the epoxide), 72% 1-cyclobutylpropanol [nmr δ 3.1 (m, 2), 1.8 (m, 7), 1.25 (m, 2), and 0.9 ppm (t, 3); ir 3350, 1108, 1040, and 973 cm^{-1}], and 9%

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(10) Nmr spectra were obtained in carbon tetrachloride solution using either a Varian A-60 or a Jeolco C-60H spectrometer. Infrared spectra were obtained on neat thin films using a Perkin-Elmer 337 grating spectrometer.

(11) M. Schlosser and K. F. Christmann, *Angew. Chem.*, **76**, 683 (1964).

(12) J. M. Conia and P. Leriverend, *C. R. Acad. Sci.*, **250**, 1078 (1960).

(13) The per cent yield is given in parentheses after the compound name throughout the Experimental Section.

(14) A. F. Plate and A. A. Melnikov, *Zh. Obshch. Khim.*, **29**, 1064 (1959).

(15) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 2847 (1965).

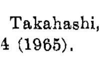
(16) R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

(17) A. Maccioni and M. Secci, *Ann. Chim.* (*Rome*), **54**, 226 (1964).

(18) M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

(19) Analyses were carried out by C. F. Geiger, 312 E. Yale St., Ontario, Calif.

(20) -O-CH is from the grouping



(21) R. Jacquier, M. Mousseron, and R. Zagdourn, *Bull. Soc. Chim. Fr.*, 1042 (1959).

(22) A. Endo, M. Saito, M. Takahashi, K. Nagata, and Y. Fushizaki, *Nippon Kagaku Zasshi*, **86**, 1304 (1965).

cyclobutyl ethyl ketone (ir 1710, 1247, 1132, and 970 cm^{-1}, identical with product from Jones oxidation of 1-cyclobutylpropanol).

Propylidenecyclopentane oxide gave a single product in 84% yield: nmr δ 5.4 (s, 1), 4.0 (t, 1, J = 6 Hz, CH–OH), 2.9 (d, 1, J = 3 Hz, OH, shifts with formic acid), 2.5–1.2 (m, 8), and 0.85 ppm (t, 3, J = 6.5 Hz, CH$_3$); ir 3320, 1090, and 900 cm^{-1}.

Propylidenecyclohexane oxide after 49 hr gave 9% unreacted epoxide and a 69% yield of two products. **3c** (95%): nmr δ 5.35 (m, 2), 2.3 (s, 1, shifts with formic acid, OH), 1.7 (d, 3, J = 5 Hz, CH$_3$), and 1.55 ppm (broad singlet, 10); ir 3370 and 970 cm^{-1}. **2c** (5%): nmr δ 5.47 (t, 1, J = 2.5 Hz, C=CH), 3.7 (t, 1, J = 6.5 Hz, CH–OH), 2.5 (s, 1, OH), 2.2–1.2 (m, 10), and 0.8 ppm (t, 3, J = 7 Hz, CH$_3$); ir 3330, 1003, 960, and 917 cm^{-1}.

Propylidenecycloheptane oxide was consumed within 5 hr, giving 76% of two volatile products. **2d** (98%): nmr δ 6.2 (t, 1, J = 7 Hz, C=CH), 4.1 (t, 1, J = 7 Hz, CH–OH), 2.7–1.3 (m, 13), and 0.9 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3320, 1020, and 850 cm^{-1}. The minor product, **3d** (2%), was identified by catalytic reduction to 1-propylcycloheptanol which was the major product from LiAlH$_4$ reduction of the epoxide.

Propylidenecyclooctane oxide after 2 hr gave 74% of a single product, **2e**: nmr δ 5.75 (t, 1, J = 8 Hz, C=CH), 4.0 (t, 1, J = 7 Hz, CH–OH), 2.2 (m, 4), 1.6 (broad singlet, 9), and 0.9 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3350, 1100, and 850 cm^{-1}.

Propylidenecyclododecane oxide was completely rearranged in 22 hr, yielding 66% of a product mixture. The major component (84%) was shown to be **2f**: nmr δ 6.0 (t, 1, J = 8.5 Hz, C=CH), 4.9 (t, 1, J = 7.5 Hz, CH–OH), 2.6–2.0 (m, 4), 2.0–1.2 (m, 19), and 1.0 ppm (t, 3, J = 8 Hz, CH$_3$); ir 3370, 1090, 1010, and 970 cm^{-1}. Two lesser components, 12 and 4%, were not elucidated.

Ethylidenecyclopentane oxide after 1.5 hr gave 82% of two products. The major product (70%) was **8a**: nmr δ 6.2 (s, 1), 4.85 (quartet, 1, J = 7.5 Hz, CH–OH), 3.5 (s, 1), 2.9–1.8 (m, 6), and 1.4 ppm (d, 3, J = 7 Hz, CH$_3$); ir 3340, 1160, and 1075 cm^{-1}. The remainder (30%) was **9a**: nmr δ 6.1–4.8 (ABC pattern, 3) and 2.0–1.2 ppm (m, 8), OH peak variable; ir 3360, 3080, 990 (doublet), and 920 cm^{-1}.

Ethylidenecyclohexane oxide rearranged to a single product in 66% yield, **9b**: nmr δ 7.0–5.4 (ABC pattern, 3), 2.2 (s, 1, OH), and 1.7 ppm (broad singlet, 10); ir 3370, 3070, 1265, 995, 965, 925, and 910 cm^{-1}.

Ethylidenecycloheptane oxide gave a 74% yield of two allylic alcohols. The minor alcohol (38%) was **8c**: nmr δ 5.85 (t, 1, J = 6.5 Hz, HC=C), 4.16 (quartet, 1, J = 6.5 Hz, CH–OH), 2.8 (s, 1, OH), 2.4–1.9 (m, 4), 1.9–1.3 (m, 6), and 1.16 ppm (d, 3, J = 7 Hz, CH$_3$); ir 3340, 1080, 1063, 986, and 848 cm^{-1}. The major product **9c** comprised 62% of the mixture: nmr δ 6.4–4.9 (ABC pattern, 3), 2.3 (s, 1, –OH), and 1.62 (broad singlet, 12); ir 3370, 1035, 1000, and 920 cm^{-1}.

Ethylidenecyclooctane oxide also led to a mixture of two alcohols in 73% overall yield. **8d** (66%): nmr δ 5.42 (t, 1, J = 8 Hz, HC=C), 4.05 (quartet, 1, J = 6 Hz, CH–OH), 3.2 (s, 1, OH), 2.1 (broad singlet, 4), 1.46 (s, 8), and 1.17 ppm (d, 3, J = 6.5 Hz, CH$_3$); ir 3330, 1160, 1100, 1062, and 848 cm^{-1}. **9d** (34%): nmr δ 6.0–4.6 (ABC pattern, 3) and 1.55 ppm (broad singlet, 15, includes OH); ir 3375, 1160, 995, 972, and 919 cm^{-1}.

Isobutylidenecyclohexane oxide, after 72 hr reflux, was up to 76% unreacted. The sole product was **12**: nmr δ 5.4 (s, 1, HC=C), 4.6 (s, 1, OH), 3.36 (d, 1, J = 7.5 Hz, CH–OH), 2.3–1.2 (m, 9), and 0.83 ppm (two overlapping doublets, 6); ir 3400, 1140, 1014, and 915 cm^{-1}.

Registry No.—Propylidenecyclobutane, 28253-07-8; propylidenecyclopentane, 4810-12-2; propylidenecyclohexane, 2129-93-3; propylidenecycloheptane, 17257-34-0; propylidenecyclooctane, 28256-52-2; propylidenecyclododecane, 28256-53-3; ethylidenecyclopentane, 2146-37-4; ethylidenecycloheptane, 10494-87-8; ethylidenecyclooctane, 19780-51-9; isobutylidenecyclohexane, 28256-56-6; **1a**, 28256-57-7; **1b**, 28256-58-8; **1c**, 28256-59-9; **1d**, 28256-60-2; **1e**, 28256-61-3; **1f**, 28256-62-4; **7a**, 28256-63-5; **7b**, 17328-74-4; **7c**, 28256-65-7; **7d**, 28256-66-8; **11**, 28256-67-9.

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On the Rigidity to Carbanion Inversion of Four-, Five-, and Six-Membered Cyclic Organomagnesium Compounds

ENGELBERT PECHHOLD, DAVID G. ADAMS, AND GIDEON FRAENKEL*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Several 1,1-dimethylcycloalkylmagnesium halides were synthesized and their nmr spectra obtained as a function of temperature. Each reagent gave rise to an equal doublet for the methyl resonance. The nmr spectra were independent of the temperature, and it is concluded that carbanion inversion is slow on the nmr time scale up to 175°. The various effects responsible for this result are discussed in terms of what is known about the mechanism of inversion in primary Grignard reagents. It is concluded that carbon bridging in Grignard dimers is not favored when the bridging group is cycloalkyl.

Inversion rates of carbon bonded to metal in primary organometallic compounds of lithium, magnesium, aluminum, and zinc have been reported.[1–5] However, so far there has been relatively little work on inversion in secondary systems. Letsinger found 2-octyllithium inverted slowly at low temperatures.[6] Jensen and Nakamaye determined the endo/exo ratio for 2-norbornylmagnesium bromide.[7] This reagent also inverted slowly.[7]

While our work on inversion in primary organometallic systems was proceeding, we initiated some experiments on secondary reagents. Meanwhile, Whitesides and Roberts[2] discussed the behavior of the nmr spectra of 3,3-dimethylcyclobutylmagnesium bromide and 2,4-dimethylpentylmagnesium bromide-3 and concluded carbanion inversion to be slow on the nmr time scale.[2] Also, Glaze and Selman have reported 4-*tert*-butylcyclohexyllithium to be configurationally stable.[8]

The approach we have chosen consists of synthesizing various 1,1-dimethylcycloalkylmagnesium halides, I, and obtaining their nmr spectra as a function of tem-

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