# The Stereochemistry of Epoxidation of Rigid Methylenecyclohexane Systems. Determination of Stereochemistry of Exocyclic Epoxides in Rigid Cyclohexanes by Nuclear Magnetic Resonance Half Band Widths

Robert G. Carlson and Norman S. Behn

*Department of Chemistry, University of Kansas, Lawrence, Kansas 66044*

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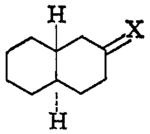
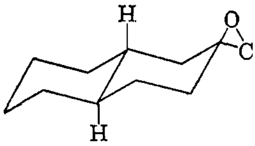
The stereochemical results of the epoxidation of four rigid methylenecyclohexane systems have been studied with a variety of per acids and the alkaline hydrogen peroxide–benzonitrile system. Epoxidation of unhindered methylenecyclohexanes with per acids gave predominantly axial attack, whereas epoxidation with the alkaline hydrogen peroxide–benzonitrile system gave predominantly equatorial attack. The measurement of half band widths of the methylene group in epoxide rings exocyclic to rigid cyclohexanes allows an unambiguous assignment of stereochemistry. Measurements of $\Delta W_{h/2}$ for four pairs of epimeric epoxides gave an average value of $\Delta W_{h/2} = 0.15 \pm 0.07$ cps for equatorial methylene groups and $\Delta W_{h/2} = 1.41 \pm 0.14$ cps for axial methylene groups.

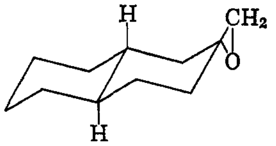
During the course of studies on the stereochemistry of some ring-expansion reactions we were confronted with the problem of obtaining appreciable quantities of two epimeric epoxides 2 and 3. The recent reports[1] of the contrasting stereoselectivity in the conversion of rigid cyclohexanones to the corresponding epoxides by dimethyloxosulfonium methylide and dimethylsulfonium methylide led us to attempt the preparation of 2 and 3 by these methods. The reaction of *trans*-2-decalone (1) with dimethyloxosulfonium methylide was indeed highly stereoselective, giving a mixture of epoxides which contained 2 and 3 in the ratio 9:1. The reaction of 1 with dimethylsulfonium methylide, however, proceeded in low yield and gave a mixture of epoxides 2 and 3 in the ratio 2:3.



**1**, X = O
**4**, X = $CH_2$



**2**



**3**

The failure of this reaction to produce 3 in a state of high purity and the difficulty of separation of the epoxide mixture[2] led us to examine the epoxidation of *trans*-2-methylenedecahydronaphthalene (4). Previous studies of the epoxidation of olefins by per acids have indicated that attack of the per acid usually occurs from the less hindered side of the molecule.[3] Exceptions to this general rule have been noted, particularly when a hydroxyl group is present with which the peracid can hydrogen bond in the transition state leading to the epoxide,[3a,f,4] and recent work has demonstrated that polar effects also exert an influence on the stereochemistry of epoxidation.[3a,f,5] During the course of this study Henbest[3f] reported a study of the epoxidation of two rigid methylenecyclohexane systems, 4-*t*-butylmethylenecyclohexane and 3,3,5-trimethylmethylenecyclohexane, with percamphoric acid and showed that the results paralleled the stereochemistry observed in addition reactions to the corresponding ketones. Favre and Gravel[3g] obtained similar results in the epoxidation of 4-*t*-butylmethylenecyclohexane with perbenzoic acid in chloroform.

We have examined the epoxidation of methylenecyclohexane systems **4**, **6**, **10**, and **14** with several per acids and with the alkaline hydrogen peroxide–benzonitrile system.[6] (See Chart I.) The olefins were prepared from the corresponding ketones by a modified Wittig reaction.[7] Authentic samples of epoxides **2**, **7**, **11**, and **15** were prepared by the reaction of the corresponding ketone with dimethyloxosulfonium methylide[1a] and the stereochemical results of these reactions are summarized in Table I.

Table I
Addition Reactions of Ketones. Per Cent Axial Attack

| | | Ketone | | | |
|---|---|---|---|---|---|
| Entry | Reagent | 1 | 5 | 9 | 13 |
| 1 | $(CH_3)_2SOCH_2$ | 9 | 0[a] | 11 | 5 |
| 2 | $(CH_3)_2SCH_2$ | 55 | 83[a] | . . | . . |
| 3 | $NaBH_4$ | . . | 87[b] | 85[c] | 40[c] |
| 4 | $LiAlH_4$ | . . | 92[d] | . . | . . |

[a] Values taken from ref 1a. [b] Value taken from P. T. Lansbury and R. C. MacLeay, *J. Org. Chem.*, **28**, 1940 (1963). [c] Values taken from ref 19b. [d] Values taken from E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

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(1) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); (b) C. E. Cook, R. C. Corley, and M. E. Wall, *Tetrahedron Letters*, 891 (1965).

(2) A method, albeit very inefficient, for the separation of **3** from a mixture of the epoxides was devised by taking advantage of the greater reactivity of **2** with hydroxide ion in dimethyl sulfoxide. See the Experimental Section.

(3) See, *inter alia*, (a) H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963); (b) H. B. Henbest and J. J. McCullough, *ibid.*, 74 (1962); (c) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963); (d) E. J. Corey and R. L. Dawson, *J. Am. Chem. Soc.*, **85**, 1782 (1963); (e) G. I. Fray, R. J. Hilton, and J. M. Teire, *J. Chem. Soc. Org. Sect.*, 592 (1966); (f) H. B. Henbest in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London 1965, p 83; (g) H. Favre and D. Gravel, *Can. J. Chem.*, **41**, 1452 (1963).

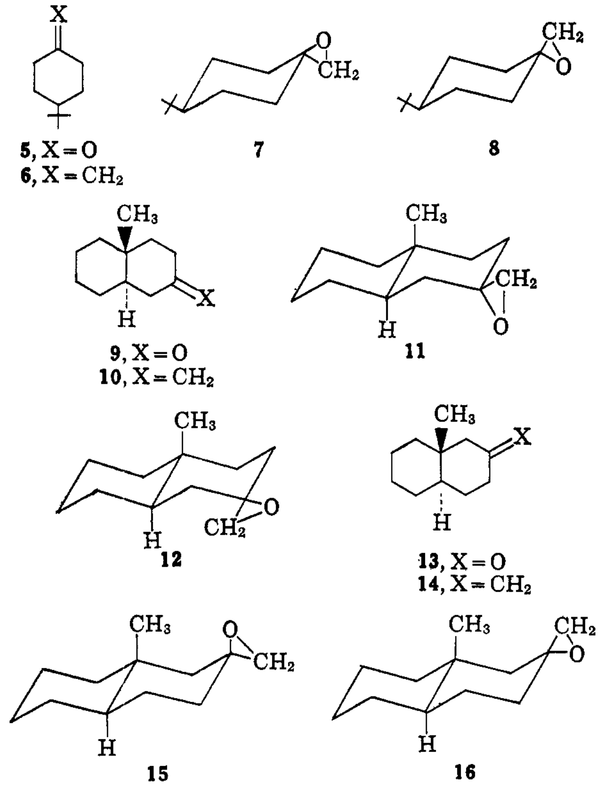
(4) (a) M. Mousseron, M. Mousseron-Canet, and G. Philippe, *Compt. Rend.*, **258**, 3705 (1964); (b) M. Mousseron, M. Mousseron-Canet, and J. Guilleux, *ibid.*, **258**, 3861 (1964); (c) M. L. Sassiver and J. English, *J. Am. Chem. Soc.*, **82**, 4891 (1960); (d) R. Albrecht and Ch. Tamm, *Helv. Chim. Acta.*, **40**, 2216 (1957).

(5) (a) N. S. Crossley, A. C. Darby, H. B. Henbest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Letters*, 398 (1961); (b) A. P. Gray and D. E. Heitmeier, *J. Org. Chem.*, **30**, 1226 (1965); (c) G. I. Poos and J. D. Rosenau, *ibid.*, **28**, 665 (1963).

(6) (a) G. B. Payne and P. H. Williams, *ibid.*, **26**, 651 (1961); (b) G. B. Payne, P. H. Deming, and P. H. Williams, *ibid.*, **26**, 659 (1961); (c) G. B. Payne, *ibid.*, **26**, 663 (1961); (d) G. B. Payne, *Tetrahedron*, **18**, 763 (1962); (e) Y. Ogata and Y. Sawaki, *ibid.*, **20**, 2065 (1964).

(7) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

CHART I



**Determination of Epoxide Stereochemistry.**—Previous workers have determined the stereochemistry of exocyclic epoxides in rigid cyclohexanes by lithium aluminum hydride reduction to the corresponding alcohols which were either known compounds or whose structures could be assigned by dehydration studies.[1,3g] Although in our case the problem was simplified somewhat by the availability of the isomeric epoxide with the methylene group equatorial[8] from the reaction of the corresponding ketone with dimethyloxosulfonium methylide, we sought an instrumental technique capable of defining the stereochemistry which did not require the availability of both isomers for an unambiguous structural assignment.

We consequently turned to nmr spectroscopy to solve this problem. Initially we sought to make use of the generalization that a substituent will absorb at higher field when it is axial than when it occupies an equatorial position.[9,10] This generalization did hold for the methylene group in several of the pairs of epoxides studied (Table II). The differences were very slight, however, and unless both epoxides were available it would not be possible to make an unambiguous assignment. Furthermore, in one pair of epoxides (**15** and **16**) the isomer with the methylene group equatorial absorbed at higher field than the corresponding axial isomer. In the case of the axial isomer (**16**), a paramagnetic shift of the methylene group absorption arises from its 1,3-diaxial interaction with the angular methyl group.[9,11]

TABLE II

CHEMICAL SHIFTS OF METHYLENE GROUPS OF EPOXIDES

| Epoxide | Position of $CH_2$ | Chemical shift, cps[a] |
|---|---|---|
| 2 | Equatorial | 146.4 |
| 3 | Axial | 143.7 |
| 7 | Equatorial | 148.0 |
| 8 | Axial | 143.5 |
| 11 | Equatorial | 146.0 |
| 12 | Axial | 143.0 |
| 15 | Equatorial | 137.0 |
| 16 | Axial | 148.2 |

[a] Chemical shifts are in cycles per second downfield from tetramethylsilane (TMS). Spectra were determined in carbon tetrachloride solution.

During the determination of the nmr spectra at narrow sweep widths in order to obtain accurate chemical shift data we were struck by the very obvious differences in line widths for the isomeric pairs of epoxides. The recent publications describing the use of line widths of angular methyl groups for the assignment of stereochemistry in *cis*- and *trans*-decalins and related systems[12] points out the obvious potential of such measurements for stereochemical assignments which are difficult to obtain by other physical and chemical methods. The application of this method to our systems provided an unambiguous method for stereochemical assignments.

The data in Table III were obtained employing a 50-cycle sweep width and are the averages of at least four determinations made over a period of several months. In order to allow for variations in spectrometer resolution the half band width of the internal standard tetramethylsilane was measured in each determination and subtracted from the half band width of the methylene group of the epoxide. In this way the average deviations of the experimentally determined $\Delta W_{h/2}$ were quite small. The average $\Delta W_{h/2}$ for the four epoxides with the methylene group axial is 1.41 ± 0.14 cps and the average $\Delta W_{h/2}$ for the four epoxides with the methylene group equatorial is 0.15 ± 0.07 cps. Although the data in Table III are limited, they indicate that the measurements of half band widths for

TABLE III

HALF BAND WIDTHS FOR METHYLENE GROUP OF EPOXIDES

| | $W_{h/2}$, cps | | |
|---|---|---|---|
| Compd | $CH_2O$ | TMS | $\Delta W_{h/2}$,[a] cps |
| 2 | 0.77 ± 0.32 | 0.63 ± 0.28 | 0.14 ± 0.03 |
| 3 | 1.83 ± 0.11 | 0.53 ± 0.19 | 1.30 ± 0.07 |
| 7 | 0.61 ± 0.03 | 0.46 ± 0.02 | 0.15 ± 0.05 |
| 8 | 1.69 ± 0.04 | 0.46 ± 0.02 | 1.23 ± 0.06 |
| 11 | 0.68 ± 0.10 | 0.53 ± 0.09 | 0.16 ± 0.04 |
| 12 | 2.05 ± 0.08 | 0.56 ± 0.09 | 1.49 ± 0.12 |
| 15 | 0.63 ± 0.03 | 0.42 ± 0.09 | 0.15 ± 0.09 |
| 16 | 2.14 ± 0.11 | 0.54 ± 0.10 | 1.61 ± 0.16 |
| Av eq $CH_2$ | 0.67 + 0.05 | ... | 0.15 ± 0.07 |
| Av ax $CH_2$ | 1.93 ± 0.17 | ... | 1.41 ± 0.14 |

[a] $\Delta W_{h/2} = (CH_2O)W_{h/2} - (TMS)W_{h/2}$. The average deviation is that for the experimentally measured $\Delta W_{h/2}$.

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[8] In compounds with an epoxide ring exocyclic to a six-membered ring, neither the oxygen nor the methylene group can occupy true axial or equatorial positions. The substituent in the "axial" position is bent away from the center of the ring by *ca.* 30° and the "equatorial" substituent is also bent upward from a true equatorial position. For convenience, however, we shall refer to these positions as axial and equatorial.

[9] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, Calif., 1964.

[10] Exceptions to this generalization have been noted; see, for example, K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961).

[11] G. Slomp and B. R. McGarvey, *ibid.*, **81**, 2200 (1959).

[12] (a) C. W. Shoppee, F. P. Johnson, R. E. Lack, and S. Sternhell, *Chem. Commun.*, 347 (1965); (b) M. J. T. Robinson, *Tetrahedron Letters*, 1685 (1965); (c) K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966).

this type of epoxide may provide a very useful criteria for the assignment of stereochemistry.

The differences in $W_{h/2}$ for the epimeric epoxides must arise from long-range coupling with protons in the cyclohexane ring.[13] Theoretical calculations[14] indicate that the magnitude of the long-range coupling constants for protons separated by three carbons is dependent on the dihedral angle between the interacting protons. Measurements of the appropriate dihedral angles from Dreiding models predict that there should be a difference in the magnitude of the long-range coupling constants for the epoxides with the methylene group axial and equatorial. For an epoxide with the methylene group in an axial position, the dihedral angle between the hydrogens of the methylene group and an equatorial hydrogen on the carbon adjacent to the carbon bearing the oxygen in the cyclohexane ring is $\phi_1'$ (eq) $= ca.\ 15°$[15] and with the corresponding axial hydrogen $\phi_1'$ (ax) $= ca.\ 140°$. According to the theoretical calculations[14] the corresponding coupling constants should be $J = 0.9$ and 0.8 cps, respectively. For an epoxide with the methylene group in an equatorial position the dihedral angles are $\phi_1'$ (eq) $= 330°$ and $\phi_1'$ (ax) $= 80°$, leading to predicted coupling constants of $J = 0.8$ and 0.3 cps.

**Stereochemistry of the Epoxidations.**—The stereochemical results of the olefin epoxidations are summarized in Table IV which lists the average values for two or more determinations. Examination of these results shows that for all of the per acids and solvents employed, the relatively unhindered olefins (*i.e.*, **4**, **6**, **10**) in which there are two 1,3 interactions with hydrogen for axial attack, the predominant product of the reaction arose from axial attack. With the more hindered olefin **14**, in which there is one 1,3 interaction with hydrogen and one 1,3 interaction with the angular methyl group, all of the per acids gave predominantly equatorial transfer of oxygen. The amount of axial attack is somewhat solvent dependent and in agreement with Henbest's results,[3f] the use of methylene chloride and chloroform as solvents for the peracid epoxidation afforded the least amount of axial attack.

TABLE IV

OLEFIN EPOXIDATIONS. PER CENT AXIAL ATTACK[a]

| Entry | Reagent | Olefin 4 | Olefin 6 | Olefin 10 | Olefin 14 |
|---|---|---|---|---|---|
| 1 | *m*-Chloroperbenzoic acid in $CH_2Cl_2$ | 59 | 69 | 65 | 2 |
| 2 | *m*-Chloroperbenzoic acid in $CH_3CN$ | 66 | .. | .. | .. |
| 3 | *m*-Chloroperbenzoic acid in $Et_2O$ | 65 | .. | .. | .. |
| 4 | *m*-Chloroperbenzoic acid in $CH_3OH$ | 68 | .. | .. | .. |
| 5 | *m*-Chloroperbenzoic acid in *t*-BuOH | 64 | .. | .. | .. |
| 6 | Monoperphthalic acid in $Et_2O$ | 69 | 79 | 76 | 17 |
| 7 | Peracetic acid in $CH_2Cl_2$ | 60 | 66 | 61 | 4 |
| 8 | $H_2O_2$–PhCN–$KHCO_3$ in $CH_3OH$ | 14 | 32 | 33 | 2 |
| 9 | $H_2O_2$–PhCN–$KHCO_3$ in $CH_3OH$ with $PO_4^{3-}$ | .. | 30 | 29 | .. |
| 10 | $H_2O_2$–PhCN–$K_2CO_3$ | .. | 27 | .. | .. |

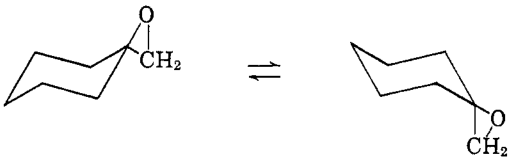
[a] All values are averages of two or more runs.

In contrast to the results obtained with the peracids, epoxidation with the alkaline hydrogen peroxide–benzonitrile system in methanol gave predominantly equatorial oxygen transfer with all of the olefins studied. Addition of phosphate ion, which has been claimed to complex with the intermediate peroxyimidic acid,[6e] or changing the base to potassium carbonate had only a minor effect on the stereochemistry of the epoxidation.

The stereochemical results of the peracid epoxidations parallel the results obtained in the metal hydride reductions of the corresponding ketones (Table I, entries 3 and 4), although a smaller amount of axial attack is observed with the per acids.

The stereochemical results of metal hydride reductions of cyclohexanones are commonly discussed in terms of two factors, "steric approach control" and "product development control."[16] Thus, equatorial approach is assumed to involve approach from the less hindered side ("steric approach control") and produces the less stable alcohol. This type of behavior is observed with relatively hindered cyclohexanones in which there is substantial steric interference between a $\beta$-axial substituent and the attacking reagent in the transition state. To explain the preponderant formation of equatorial alcohol with relatively unhindered cyclohexanones, it is assumed that the relative stability of the product is reflected in the transition state and the more stable product is formed ("product development control").

If these hypotheses are extended to the results obtained for the epoxidation of the methylenecyclohexanes, it would appear that the products of the peracid epoxidations result from product development control and would predict that the exocyclic oxirane ring is more stable with the methylene group "equatorial" by *ca.* 0.3–0.8 kcal/mole. Unfortunately, the relative stability of the two conformers **17a** and **17b** is not known.[17] The decreased amount of axial attack with a peracid in chloroform or methylene chloride could then be ascribed to tighter solvation of the transition state, effectively increasing the bulk of the reagent.



**17a** **17b**

The preferred equatorial attack in the alkaline hydrogen peroxide–benzonitrile system, which presumably involves peroxybenzimidic acid (**18**) as the

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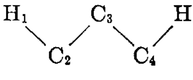
(13) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(14) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

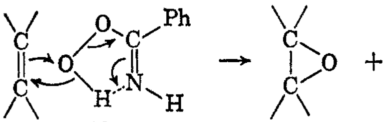
(15) The dihedral angle $\phi_1'$ is defined[14] as the angle between the plane



described by $H_1$, $C_2$, and $C_3$ and the plane described by the three carbon atoms, and is measured in a clockwise direction.

(16) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

(17) We have attempted to determine the conformational preference of the epoxide group (*i.e.*, **17a** $\rightleftharpoons$ **17b**) by an nmr technique using the positions of absorptions of the methylene group in pure epoxides **2** and **3** as models for the absorptions expected for pure conformers **17a** and **17b**. This study, however, was frustrated by the very small differences ($\sim$2.7 cps) in chemical shifts for the "equatorial" and "axial" methylene group in **2** and **3** making it impossible to obtain an accurate value. We are currently attempting to determine the conformational preference by low-temperature nmr studies.



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epoxidizing agent[6,18] can be explained by assuming that peroxybenzimidic acid has a greater steric bulk than the per acids and the resulting epoxides arise from a sterically controlled process.

Recently an alternative explanation has been advanced to explain the stereochemical results observed in addition reactions to cyclohexanones.[19] In this hypothesis it is suggested that the preference for axial attack in unhindered cyclohexanones is due to steric interactions with axial substituents on the $\alpha$ carbon. Measurements from Dreiding models indicate that if the attacking species must approach the carbonyl group very closely in the transition state an axial substituent on the $\alpha$ carbon will exert more steric interference than an axial substituent on the $\beta$ carbon. At longer distances, however, interference with the $\beta$ axial substituent becomes more important.

A similar argument can be used to explain the results of this study. Measurements taken on a Dreiding model of methylenecyclohexane on a line perpendicular to the plane of the double bond at the center indicate that at distances of less than *ca.* 1.8 A from the carbon–carbon double bond, the axial hydrogen on the $\alpha$ carbon is closer than the axial hydrogen on the $\beta$ carbon. Thus the preferential axial attack with the per acid may indicate that the per acid must closely approach the double bond in the transition state and the axial hydrogen on the $\alpha$ carbon destabilizes the transition state for equatorial attack. With peroxybenzimidic acid, however, the transition state may be reached at a somewhat longer distance, and the hydrogen on the $\beta$ carbon becomes the more important substituent.

These measurements also predict that with axial methyl groups on *both* the $\alpha$ and $\beta$ carbons, the $\beta$-methyl group should exert more steric interference than the $\alpha$-methyl group. We are currently examining the epoxidation of compounds of this type to test the validity of this hypothesis.

## Experimental Section[20]

**Preparation of Ketones.** *trans*-**2-Decalone (1).**—Oxidation of an acetone solution of *trans*-2-decalol[21] with a 2.67 *M* solution of chromium trioxide in aqueous sulfuric acid[22] at 10–15° afforded **1**, purified by distillation on a 24-in. spinning-band column (92% yield), bp 65° (0.4 mm), $n^{19}$D 1.4812 [lit.[23] bp 127–128° (28 mm), $n^{23}$D 1.4820]. Gas chromatography[24] revealed the presence of less than 3% of the *cis* isomer.

*trans*-**10-Methyl-2-decalone (9).**—To a solution of 8.20 g (1.25 g-atoms) of lithium in 1200 ml of liquid ammonia was added, with stirring, a solution of 34.0 g (0.208 mole) of 10-methyl-1(9)-octalone[25] and 180 g of *t*-butyl alcohol in 400 ml of dry ether over a 2-hr period. After the addition was complete, the reaction mixture was stirred for an additional 15 min and the excess lithium was destroyed by the addition of ammonium chloride. Evaporation of the ammonia followed by the addition of 600 ml of water and extraction with ether afforded 36.5 g of crude alcohols. Oxidation of an acetone solution of the alcohols with 2.67 *M* chromium trioxide in aqueous sulfuric acid[22] afforded 28.7 g (83%) of the ketone **9**, bp 74–76° (0.5 mm) [lit.[26] bp 130–133° (21 mm)]. Gas chromatographic analysis[27] showed the ketone to be >97% pure.

*trans*-**9-Methyl-2-decalone (13).**—This ketone was prepared by the method of Marshall and Carroll[19b] and after careful fractional distillation had bp 65–67° (0.3 mm) [lit.[19b] bp 83–84° (1.5 mm)]. The ketone showed only a single peak on gas chromatography.[27]

**Preparation of Olefins.**—The olefins were prepared from the corresponding ketones and methylenetriphenylphosphorane using the general procedure described by Corey[7] and purified by distillation on a 24-in. spinning-band column. All olefins were >97% pure by gas chromatography.[27]

*trans*-**2-Methylenedecahydronaphthalene (4)** had bp 70–71° (6 mm), $n^{19}$D 1.4858 [lit.[28] bp 82° (10 mm), $n^{25}$D 1.4841]. The product exhibits infrared absorption[29] at 3080, 1647, and 884 cm$^{-1}$, and nmr absorption[29] at $\delta$ 4.50 (singlet, 2 H, $C{=}CH_2$) and unresolved absorption in the region 1.9–3.4 (16 H).

**4-*t*-Butylmethylenecyclohexane (6)** had bp 62° (7 mm), $n^{21}$D 1.4626 (lit[30] bp 185–187°, $n^{25}$D 1.4604). The product exhibits infrared absorption[29] at 3040, 1650, and 893 cm$^{-1}$, and nmr absorption[29] at $\delta$ 4.49 (singlet, 2 H, $C{=}CH_2$), 0.85 (singlet, 9 H, $CH_3$), and unresolved absorption in the region 1.0–2.5 (9 H).

*trans*-**10-Methyl-2-methylenedecahydronaphthalene (10)** had bp 99–103° (13 mm). The product exhibits infrared absorption[29] at 3060, 1664, and 884 cm$^{-1}$, and nmr absorption[29] at $\delta$ 4.52 (2 H, singlet, $>C{=}CH_2$), 0.90 (3 H, singlet $CH_3$), and unresolved absorption in the region 1.02–2.5 (13 H).

*Anal.* Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.47; H, 12.21.

*trans*-**9-Methyl-2-methylenedecahydronaphthalene (14)** had bp 101–103° (17 mm). The product exhibits infrared absorption[29] at 3080, 1648, and 886 cm$^{-1}$, and nmr absorption[29] at $\delta$ 4.58 (2 H, doublet, $J$ = 5 cps, $C{=}CH_2$), 1.85 [2 H, singlet $CCH_2C({=}CH_2)$], 0.72 (3 H, singlet, $CH_3$), and unresolved absorption in the region 1.2–2.4 (13 H).

*Anal.* Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 88.01; H, 12.19.

**Preparation of Epoxides.**—The following epoxides were prepared from the corresponding ketones and dimethyloxosulfonium methylide in dimethyl sulfoxide following the general procedure of Corey and Chaykovsky.[1a] Epoxides **7** and **8** were reported by these workers.

**Epoxide 2 from *trans*-2-decalone** had bp 55° (0.23 mm), $n^{28}$D 1.4791 [lit.[28,31] bp 114° (15 mm), $n^{25}$D 1.4759]. Gas chromatographic analysis[24] showed the presence of 91% **2** and 9% **3**. A sample of pure **2** obtained by distillation on an Annular Still exhibited nmr absorption[29] at $\delta$ 2.42 (2 H, singlet, $>\overbrace{C{-}CH_2}^{O}$) and unresolved absorption in the region 0.9–2.0 (16 H).

*Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.33; H, 10.86.

**Epoxide 11 from *trans*-10-methyl-2-decalone (9)** had bp 70° (0.80 mm). Gas chromatographic analysis[24] revealed the presence of 89% **11** and 11% **12**. The product exhibits nmr absorption[29]

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(18) The mechanism of epoxidation by the alkaline hydrogen peroxide–benzonitrile system has not been rigorously established and for the purpose of this discussion we will assume that it is similar to the Bartlett mechanism for per acid epoxidations.

(19) (a) J. C. Richer, *J. Org. Chem.*, **30**, 324 (1965); (b) J. A. Marshall and R. D. Carroll, *ibid.*, **30**, 2748 (1965).

(20) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Nmr spectra were recorded on a Varian A-60 instrument using tetramethylsilane as an internal standard. Gas chromatography studies utilized an Aerograph A-90-P gas chromatograph and a Beckman Ten-Inch recorder equipped with a Disc integrator. The microanalyses were performed by Huffman Laboratories. Unless otherwise stated, magnesium sulfate was employed as the drying agent.

(21) Columbia Organic Chemicals Co., Inc.

(22) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(23) R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

(24) A 10 ft × 0.25 in. column packed with 10% DEGS on 60–80 mesh Chromosorb W was employed.

(25) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

(26) M. Yanagita and K. Yamakawa, *ibid.*, **21**, 500 (1956).

(27) A 5 ft × 0.25 in. gas chromatography column packed with SF-96 on 60–80 mesh firebrick was employed.

(28) M. Mousseron, *Bull. Soc. Chim. France*, 629 (1946).

(29) Determined as a solution in carbon tetrachloride.

(30) S. Siegel and B. Dmuchovsky, *J. Am. Chem. Soc.*, **84**, 3132 (1962).

(31) The epoxide reported by these workers[28] is presumably a mixture of epoxides **2** and **3**.

at δ 2.42 (2 H, singlet, $>\overset{\ulcorner O \urcorner}{C{-}CH_2}$), 0.88 (3 H, singlet, $CH_3$), and unresolved absorption in the region 1.1–2.1 (15 H).

*Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.92; H, 10.99.

**Epoxide 15 from *trans*-9-methyl-2-decalone (13)** had bp 55° (0.23 mm). Gas chromatographic analysis[29] revealed the presence of 95% **15** and 5% **16**. The product exhibits nmr absorption[29] at δ 2.26 (singlet, 2 H, $>\overset{\ulcorner O \urcorner}{C{-}CH_2}$), 0.93 (singlet, 3 H, $CH_3$), and unresolved absorption in the region 1.1–2.1 (15 H).

*Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.16; H, 11.20.

**Epoxidation Studies.**—All epoxide mixtures were analyzed by gas chromatography[24] under carefully controlled conditions and it was necessary to use a glass liner in the injection port to prevent rearrangement. Samples of the epoxide mixtures were collected and their infrared spectra were examined to ensure that rearrangement did not occur. The values listed in Table IV are the average values for at least two runs and the results were reproducible to ±2%.

**Epoxidation with *m*-Chloroperbenzoic Acid.**—To 0.100 g of the appropriate olefin in 2 ml of distilled methylene chloride at 0° was added a 20% excess of *m*-chloroperbenzoic acid in 2 ml of methylene chloride. The reaction mixture was stirred at 0° for 2 hr and the excess per acid was destroyed with 10% sodium sulfite solution. Saturated sodium bicarbonate solution was added and the aqueous layer was separated and extracted with two portions of methylene chloride. The combined organic layers were washed with brine and dried. Removal of the solvent afforded the crude epoxide mixture which was analyzed by gas chromatography.

Similar procedures were used for epoxidations in acetonitrile, ether, and methanol. When methanol was used as the solvent the reaction was carried out to *ca.* 20% completion because the epoxides underwent further reaction. Under these conditions no ring opening of the epoxide occurred.

**Epoxidation with Monoperphthalic Acid.**—To 0.100 g of the appropriate olefin in 4 ml of ether was added a 10% excess of an ethereal solution of monoperphthalic acid[32] which contained 0.1 g/ml of per acid and the reaction mixture was stirred at room temperature for 20 hr and worked up as above.

**Epoxidation with Alkaline Hydrogen Peroxide–Benzonitrile.**—A solution of 0.100 g of the appropriate olefin, 0.5 ml of methanol, 70 mg of benzonitrile, 15 mg of potassium bicarbonate, and 0.08 ml of 30% hydrogen peroxide was stirred at room temperature for 20 hr and worked up as above. The addition of phosphate ion or changing the base to potassium carbonate had little effect on the stereochemistry of the reaction.

**Reaction of *trans*-2-Decalone (1) with Dimethylsulfonium Methylide.**—Following the general procedure of Corey and Chaykovsky,[1a] treatment of 10.0 g (66 mmoles) of **1** with dimethylsulfonium methylide from 16.3 g (80 mmoles) of trimethylsulfonium iodide afforded 8.84 g of product, bp 53–55° (0.14 mm). Gas chromatographic analysis[24] revealed the presence of 52% unreacted **1**, 21% **2**, and 26% **3**.

**Separation of Pure Epoxide 3.**—To a solution of 15.0 g of a mixture of epoxides containing 64% **2** and 36% **3** in 340 ml of dimethyl sulfoxide was added a solution of 22.8 g of potassium hydroxide in 68 ml of water. The solution was stirred at room temperature and aliquots were periodically removed and analyzed by gas chromatography. When all of epoxide **2** had reacted (76 hr) the reaction mixture was worked up in the usual manner to afford 0.60 g of pure **3**, bp 56–58° (0.3 mm). The product exhibits nmr absorption at δ 2.37 (singlet, 2 H, $C{=}CH_2$) and unresolved absorption in the region 0.8 to 2.0 (16 H).

*Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.42; H, 10.66.

**Measurement of Half Band Widths.**—All spectra were measured on a Varian A-60 spectrometer at a 0.1-cps sweep time, 50-cycle sweep width, a filter band width of 4 and radio frequency field setting of 0.04. The samples were 10–20% (w/v) in carbon tetrachloride containing 2% TMS as an internal reference. The band widths were measured at half-height to the nearest 0.01 cps and the average deviations are given in Table III.

**Registry No.**—**4**, 7787-72-6; **10**, 7787-73-7; **14**, 7787-74-8; **2**, 7787-75-9; **11**, 7787-76-0; **15**, 10022-32-9; **3**, 7787-77-1; **7**, 7787-78-2; **8**, 7787-79-3; **12**, 7787-80-6; **16**, 7787-81-7.

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# Kinetics of the Base-Induced Conversion of 2-Pyrazolines to Cyclopropanes[1]

W. M. JONES,[2] PAUL O. SANDERFER, AND D. G. BAARDA

*University of Florida, Gainesville, Florida*

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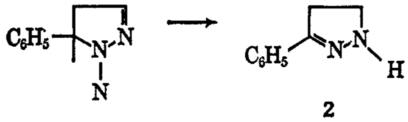
A kinetic study of the base-induced thermal conversion of 5,5-diaryl-3-carboalkoxy-2-pyrazolines to cyclopropanes has been made. Electron-donating groups on the aryl rings cause slight rate retardations, and electron-withdrawing groups cause acceleration. Changes in base concentration cause rate changes that are consistent with a mechanism involving slow formation of a 1-pyrazoline followed by rapid loss of nitrogen. Scrambling experiments and the effect of added base on the rate of decomposition of selected 3,5-dicarboalkoxy-2-pyrazolines lead to the conclusion that these, too, decompose *via* the 1-pyrazoline but in this case the slow step is loss of nitrogen.

The mechanism of the thermal conversion of 2-pyrazolines to cyclopropanes[3] has been a subject of interest in these laboratories for some time.[4] However, to date, the direct evidence for the steps involved in this type of conversion is meager. Perhaps the most definitive investigation that has been reported is that of Beech, Turnbull, and Wilson,[5] who studied the effect of various catalysts on the conversion of 3- and 5-phenyl-2-pyrazolines and 3,5-diphenyl-2-pyrazolines to the corresponding cyclopropanes. In addition to finding that basic catalysts were required to effect the conversions, they also noted that 5-phenyl-2-pyrazoline (1) readily underwent conversion to 3-phenyl-2-



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[1] Taken from dissertations submitted by P. O. Sanderfer and D. G. Baarda to the Faculty of the University of Florida, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Alfred P. Sloan Fellow, 1963–1967.

(3) For a review of this area, see T. L. Jocobs in "Heterocyclic Compounds, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) *Cf.* W. M. Jones, *J. Am. Chem. Soc.*, **82**, 3136 (1960), and previous papers.

(5) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).