(3) s, 8.15 (3) m, and 8.30 (3) m as the major peaks; ultraviolet spectrum: $\lambda\lambda_{max}$ 279 mμ (ϵ 7000) and 522 mμ (ϵ 29) (the extinction coefficients are based on an estimated 60% conversion); infrared spectrum: 2035 cm^{-1} (C=N=N). Part of the reaction mixture was added to an ethereal solution of benzoic acid. Nitrogen was evolved and the solution decolorized. The mixture was washed with sodium bicarbonate and water. After evaporation of the solvent, the residue was distilled under vacuum (60° (0.5 mm)). The distillate gave infrared and nmr spectra identical with those obtained from a sample of 2-methyl-4-benzoyloxy-2-pentene.

2-Methyl-4-benzoyloxy-2-pentene. 2-Methyl-2-penten-4-ol (12 g, 0.12 mole) was allowed to react with benzoyl chloride (16.8 g, 0.12 mole) in pyridine (100 ml) at 0° for 40 min. The reaction mixture was poured on ice, extracted with ether, and dried over sodium sulfate. Distillation yielded a fraction (13.35 g) boiling at 60–80° (0.025 mm) consisting mainly of benzoate. Repeated distillation over a column gave a pure sample boiling at 62° (0.05 mm).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.84. Found: C, 76.26; H, 7.84.

1-Phenyl-1-diazo-3-methyl-2-butene from 3,3-Dimethyl-5-phenyl-3*H*-pyrazole. 3*H*-Pyrazole IV (1.27 g, 7.4 mmoles) in methylene chloride (100 ml) was irradiated at −40° using apparatus B equipped with Corning filter 7-37. No nitrogen evolution was detected. After 80 min, the irradiation was discontinued, and a sample of the solution was analyzed by nmr: 2.7 (5) (m), 7.98 (3) m, and 8.22 (3) m. Based on an integration of the nmr peaks conversion to the diazo compound was 86%; ultraviolet spectrum: $\lambda\lambda_{max}$ 292 mμ (ϵ 18,000) and 522 mμ (ϵ 56) (the extinction coefficients are based on the conversion as determined by nmr); infrared spectrum: 2035 cm^{-1} (C=N=N).

The Stereoselective Rearrangements of Conformationally Mobile Epoxides[1a]

Clair J. Cheer[1b,c] **and Carl R. Johnson**[1d,e]

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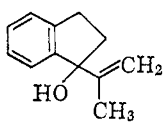
Received May 9, 1967

Abstract: The syntheses and structural assignments of *erythro*- and *threo*-1-methyl-1-(hydroxyindanyl)oxirane are described. The course of the rearrangements of each of these isomers to 1- and 2-tetralone derivatives utilizing homogeneous (boron trifluoride) and heterogeneous (alumina) catalyses have been examined. The latter effects the arrangements in a stereoselective manner lending support to an earlier suggestion that such reactions proceed through conformationally immobile surface absorbed transition states.

As part of a study of ring expansion reactions,[2,3] we have examined the acid-catalyzed rearrangements of the diastereomeric epoxy alcohols derived from the oxidation of 1-isopropenyl-1-indanol (**1**).



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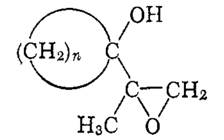
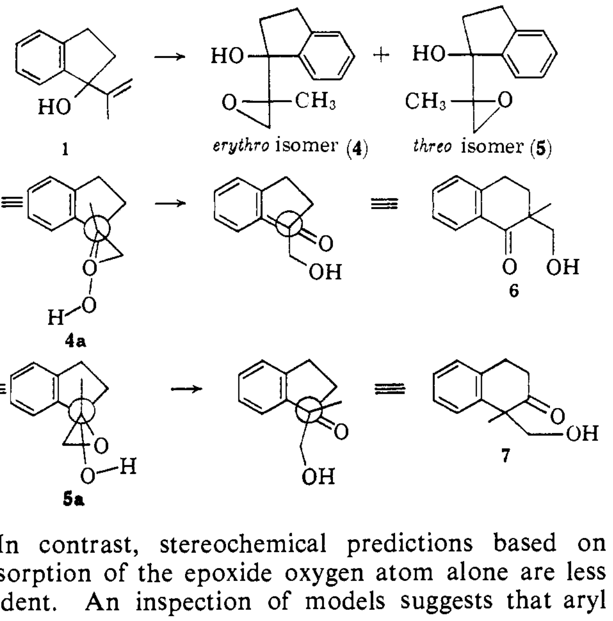


2, *n* = 4
3, *n* = 5

Our interest in this system stemmed from a mechanistic proposal[3] that the alumina-catalyzed ring enlargement of the unsubstituted analogs **2** and **3** proceeded through a transition state in which both oxygen atoms were attached to the surface of the catalyst.

The *erythro*- and *threo*-epoxy alcohols (**4** and **5**) appeared to be particularly suited to demonstrate the stereochemical implications derived from such a conformationally rigid transition state. Adsorption of *both* oxygen atoms onto a surface infers that these atoms are mutually eclipsed (or nearly eclipsed) to allow maximum approach of the nonbonded electrons to the electrophilic surface. Ring opening and rearrangement of these "eclipsed" surface adsorbed conformations (**4a** and **5a**) should then proceed by preferential migration of the group which is held *anti* (methylene in **4a**; aryl in **5a**) to the epoxide oxygen. These processes are depicted in Scheme I.

Scheme I



In contrast, stereochemical predictions based on adsorption of the epoxide oxygen atom alone are less evident. An inspection of models suggests that aryl

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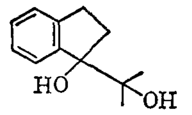
(1) (a) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; (b) to whom inquiries should be addressed at the Department of Chemistry, The University of Arizona, Tucson, Ariz. 85721; (c) U. S. Air Force Academy; (d) Alfred P. Sloan Research Fellow, 1965–1968; (e) Wayne State University.

(2) C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, 29, 3320 (1964).

(3) C. J. Cheer and C. R. Johnson, *ibid.*, 32, 428 (1967).

migration might be expected to predominate in the rearrangement of either diastereomer **4** or **5**. With these considerations in mind, the synthesis of the *erythro*- and *threo*-epoxy alcohols (**4** and **5**) was undertaken.

Epoxidation of **1** with *m*-chloroperbenzoic acid in chloroform solution produces a 1:1 mixture of diastereomeric epoxy alcohols in good yield. Repeated fractional distillation provided separation of the mixture into a lower boiling, solid isomer A and a higher boiling, liquid isomer B. The diastereomeric relationship between these isomers is demonstrated by their conversion in high yield to the same crystalline diol **8** on treatment with lithium aluminum hydride.



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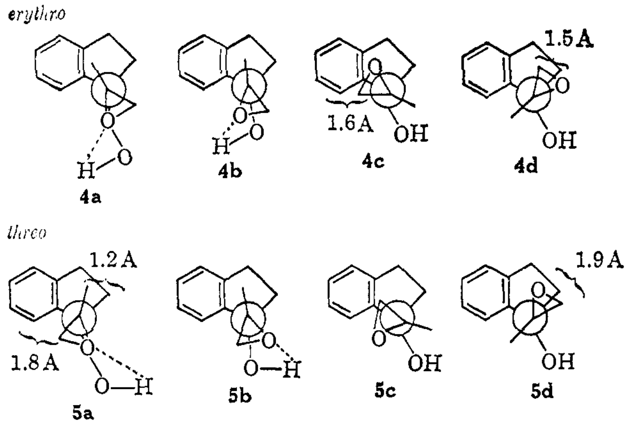
An examination of models indicates that the steric environments of the diastereomers **4** and **5** are significantly different. These differences are visualized by a comparison of the corresponding Newman projections of the various rotamers **4a–d** and **5a–d** of the *erythro* and *threo* isomers, respectively (Chart I).

Chart I



Orbital geometry considerations[4,5] suggest that intramolecular hydrogen bonding should be significant in conformations **4a**, **4b**, **5a**, and **5b** and unimportant in conformations **4c**, **4d**, **5c**, and **5d**. Steric interactions due to nonbonded repulsions between hydrogens are represented in these figures by internuclear distances less than 2 A (measured from Dreiding models). All methyl interactions which are present in both isomers have not been represented. The distances given in **5a** occur on complete eclipsing of the oxygen atoms. The conformations **4a**, **4b**, **5b**, and **5c** appear relatively strain-free while **4c**, **4d**, **5a**, and **5d** all possess steric interactions of varying severity. The substance of these considerations suggests that the *erythro* isomer **4** might be more comfortable in a bonded conformation than the *threo* isomer **5**.

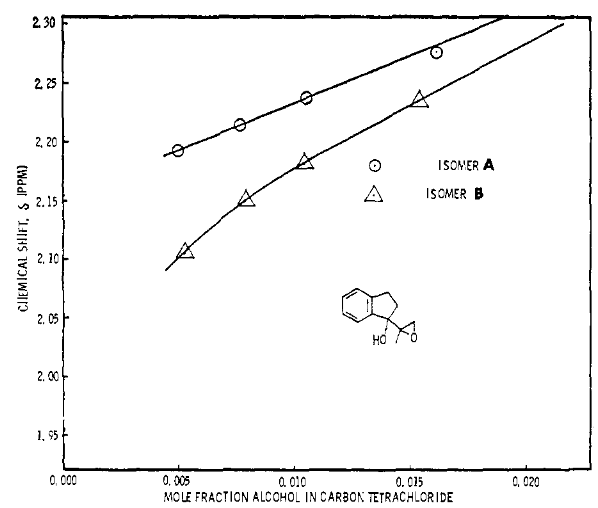


Figure 1. Chemical shift dependence of hydroxyl proton with concentration.

The application of proton magnetic resonance measurements has proved an invaluable aid to studies of hydrogen bonding.[6,7] Ouellette[8] has utilized the linear relationship[7] of hydroxyl proton chemical shift to concentration in carbon tetrachloride in the 0.015–0.002 mole fraction range as a sensitive probe for the study of the steric environment of monohydric alcohols. In this concentration range the chemical shift is influenced almost entirely by a monomer–dimer equilibrium situation, with the limiting slope a function of the equilibrium constant.[7] This study has recently been extended to include substituted olefinic and epoxy alcohols whose ability to intramolecularly hydrogen bond is determined by geometrical factors.[9] Ouellette's results clearly demonstrate that in cases where intramolecular hydrogen bonding can occur in only one of a pair of isomeric alcohols, the bonded isomer exhibits a smaller limiting slope and larger limiting chemical shift. The chemical shift–concentration dependence relationship for the diastereomers A and B is illustrated in Figure 1.

In contrast to the examples chosen by Ouellette wherein only one member of a pair of isomeric alcohols can form an intramolecular hydrogen bond, in the present case both members have the ability to form such bonds but to measurably different degrees. It seems evident from Figure 1 that isomer A is better able to form an intramolecular bond than isomer B. These results are confirmed by the hydroxyl region of the high

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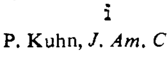
(4) The hydrogen-bonded conformations depicted in **4a** and **5a** represent the conformation in each case which should allow for the formation of the strongest possible hydrogen bond. In these conformations maximum endwise overlap obtains between the directed orbitals on the oxirane oxygens and the s orbital on the hydrogens, *i.e.*, i. We maintain that the additional strength of the hydrogen bond overshadows any unfavorable eclipsing interactions.[5] In the conformations **4a** and **5a** the oxygens are just short of eclipsing. In all other conformations in which hydrogen bonding might occur, *e.g.*, **4b** and **5b**, the orbital overlap for the hydrogen bond formation appears less efficient, *i.e.*, ii.



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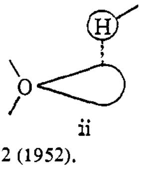


ii

(5) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter 15.

(7) E. D. Becker, U. Liddel, and J. N. Schoolery, *J. Mol. Spectry*, **2**, 1 (1958).

(8) R. J. Ouellette, G. E. Booth, and K. Liptak, *J. Am. Chem. Soc.*, **87**, 3436 (1965).

(9) R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **32**, 2394 (1967).

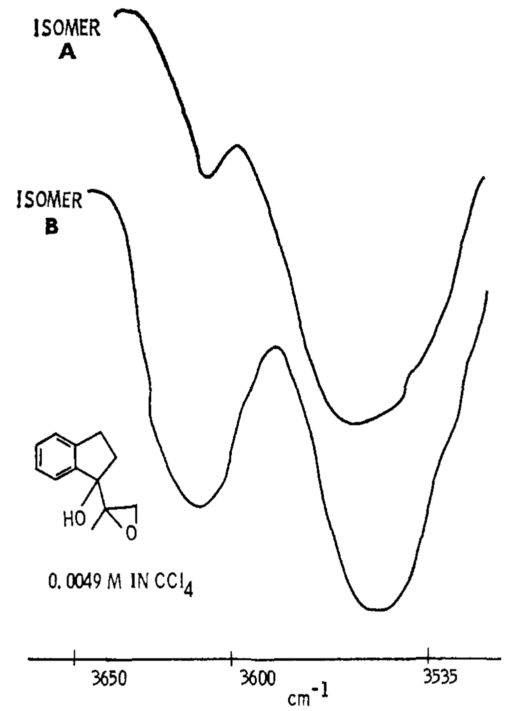


Figure 2. High dilution infrared spectra of diastereomeric epoxy alcohols.

dilution infrared spectra of each isomer (Figure 2). While the spectra of both isomers exhibit strong bands due to intramolecularly bonded hydroxyl functions,[5,10] the liquid isomer B also displays a significant band at 3606 cm^{-1} due to a free hydroxyl absorption.

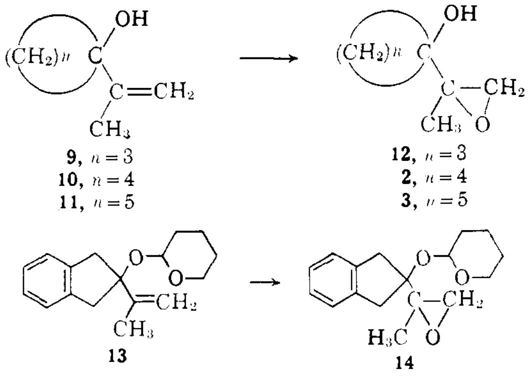
The qualitative agreement between the infrared and nuclear magnetic resonance results, coupled with the consideration of the steric factors outlined above, suggests the tentative assignment of the *erythro* configuration **4** to isomer A and the *threo* configuration **5** to isomer B.[11] This assignment permits a rationalization, albeit tenuous, of the anomalous curvature exhibited by isomer B in Figure 1.[9,12] We suggest that the shape of the curve be explained qualitatively in terms of an anisotropic effect of the aromatic ring on the hydroxyl proton. Owing to its diminished ability to form an intramolecular hydrogen bond, the hydroxyl proton in the *threo* isomer is rotated in the direction of the benzene ring to avoid steric interactions with the methyl and oxirane methylene groups. Visual inspection of the projection of a Dreiding model of the *threo* isomer onto the diagram of Johnson and Bovey,[13] which describes the magnitude of the anisotropic effect of a phenyl ring as a function of spatial orientation, places a maximum value of *ca.* 0.10 ppm on this effect. Support for this argument is found in the measurable anisotropy of the methyl group in the *erythro* isomer. As indicated in Table I, the methyl protons of the isopropenyl group are shifted upfield by 0.40–0.47 ppm on epoxidation. This change is depicted in Scheme II. The upfield shift experienced by the methyl group in the *erythro* isomer, however, is 0.54 ppm.

Table I. Nmr Chemical Shift Values of the Methyl Group in Some Olefins and Corresponding Epoxides

Olefin (δ_{CH_3})	Epoxide (δ_{CH_3})	$\Delta\delta_{CH_3}$
9[a] (1.75)	**12**[a] (1.35)	0.40
10[b] (1.78)	**2**[b] (1.33)	0.45
11[b] (1.75)	**3**[b] (1.28)	0.47
13[c] (1.80)	**14**[c] (1.37)	0.43
1[a] (1.65)	**5** (1.20)	0.45
1[a] (1.65)	**4** (1.11)	0.54

[a] See ref 4. [b] See ref 2. [c] The preparation and properties of compounds in the β-indanyl series will be subject of a forthcoming publication.

Scheme II



The most rewarding demonstration of the *erythro–threo* structural relationship was afforded by the high degree of stereoselectivity observed in their rearrangements with acidic alumina. Examination of the infrared spectra of the crude reaction products provided an indication of the stereospecificity of the over-all reaction. Thus, treatment of the *erythro* isomer (**4**) with acidic alumina in refluxing benzene followed by filtration, washing with chloroform, and concentration produced an oily product whose infrared spectrum exhibited a single carbonyl absorption band at 1691 cm^{-1}. Similar treatment of the *threo* isomer (**5**) afforded a product exhibiting a single carbonyl band in the infrared region, but in this case at 1725 cm^{-1}.

Thin layer chromatographic analysis of these reaction mixtures on silica gel G (9:1 benzene–methanol) revealed the presence of fast-moving, semipolar constituents in both products. The amounts of these materials in the reaction product mixture is increased with longer reaction times. These materials have been identified as the tetralones **15** and **16**. These presumably arise *via* retro-aldol reaction of the initially formed keto alcohols **6** and **7**.

It seemed necessary at this point to compare the stereochemical course of the "surface absorbed" reactions on alumina (which we suggest[3] result in rearrangement through the conformationally rigid transition states **17** and **18**) with rearrangements in a homogeneous

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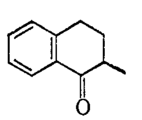
(10) M. Mousseron-Canet and B. Labeeuw, *Compt. Rend.*, 260, 4225 (1965).

(11) It has been suggested by a referee that the noticeably larger Δν value evident in isomer B indicates that this isomer forms a stronger hydrogen bond and actually possesses the *erythro* configuration. We submit that a stronger hydrogen bond (or alternately a shorter >O---H– distance) is not incompatible with the present assignment. The *cis* and *trans* isomers of cyclohexane-1,2-diol exhibit similar behavior.[5] The bonded OH band in the *trans* isomer is considerably stronger than in the *cis* isomer. Yet, the *cis* compound has the larger Δν. This difference in Δν has been ascribed to the fact that it is energetically easier to decrease the >O---H– distance in the *cis* isomer than in the *trans* isomer. The steric interactions illustrated in **5a** may also result in a hydrogen bond shortening relative to **4a**.

(12) C. M. Huggins, G. C. Pimentel, and J. N. Schoolery, *J. Phys. Chem.*, 60, 1311 (1956).

(13) C. E. Johnson and R. F. A. Bovey, *J. Chem. Phys.*, 29, 1012 (1958).



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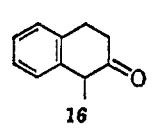

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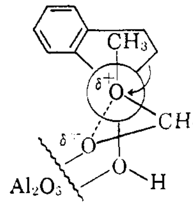

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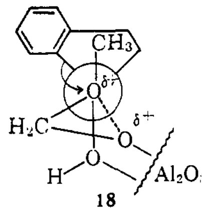

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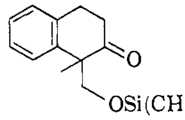
environment. Accordingly, the *erythro-* and *threo*-epoxy alcohols were each rearranged by catalysis with boron trifluoride etherate in methylene chloride solution. In each case a mixture of isomers was produced as evidenced by the presence of two carbonyl bands in the infrared spectra at 1691 and 1725 cm^{-1}. In each case the band at 1725 cm^{-1} was the more intense, indicating a predominance of **7**.[14]

Attempts to determine the product ratios by gas chromatographic analysis of the crude reaction products were unsuccessful, owing to extensive decomposition. However, trimethylsilanation[15] of the reaction mixtures followed by gas chromatography provided an extremely simple and efficient method of analysis. Application of this method to the reaction of the *erythro*-epoxy alcohol (**4**) with boron trifluoride etherate indicated the presence of two products in a ratio of 77:23 with the major component eluting first. Similar treatment of the *threo*-epoxy alcohol affords the same two components in a ratio of 90:10, again with the major component eluting first. On the basis of the infrared spectra, the β-tetralone structure **19** may be assigned to the major component and the α-tetralone structure **20** to the minor component. Correct elemental analyses of both mixtures confirmed the isomeric nature of their components.



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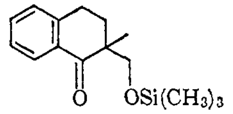

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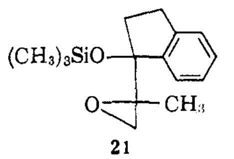
The trimethylsilyl ether derivatives **21** and **22** of the starting epoxy alcohols **4** and **5**, respectively, were prepared to assure their absence in the reaction mixtures. While **21** and **22** were not separated from one another, by gas chromatography they eluted much earlier than **19** and **20** and their absence in the reaction mixture is readily apparent.



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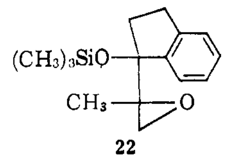

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The ratio of **6** to **7** obtained in the reaction of the *threo* isomer (**5**) with boron trifluoride etherate is probably best explained in terms of relative migratory aptitudes. The studies of Hawthorne, *et al.*,[16] on the Bayer–Villager oxidation of alkyl phenyl ketones demonstrate phenyl migratory preferences of 87:6 when the alkyl group is ethyl, 85:6 when it is *n*-propyl, and 84:9 when it is neopentyl. We suggest that the increased production of the α-tetralone (**6**) in the boron trifluoride catalyzed reaction of the *erythro* isomer (**4**) is a reflection of conformational effects.

An examination of the alumina-catalyzed rearrangement products obtained from **4** and **5** by the trimethylsilanation–gas chromatography technique did not provide a definitive measure of the stereochemical result. The presence of unidentified impurities prevented the accurate measurement of peak areas. These interfering impurities were minimized by omission of the chloroform wash of the alumina after filtration. The chromatogram of the *threo* reaction mixture was also complicated by the incomplete separation of the β-tetralone **19** and its deformylation product **16**.

If it is assumed that the detector response difference between all the compounds in the system is negligible, then we are able to obtain an approximate measure of the stereospecificity of the reaction in the case of the *threo* isomer (**5**). The ratio of β-tetralones (**16** + **19**) to α-tetralone (**20**) in this case is 90:10. On the basis of the infrared spectrum of this mixture and that obtained in the boron trifluoride ethereate catalyzed reaction, we contend that this ratio represents at least a minimum stereochemical value for this reaction.

In the case of the *erythro* isomer (**4**), it was impossible to determine directly the ratio of isomers due to the presence of an unidentified broad peak which obscured the region where both **16** and **19** appear. However, on the basis of the infrared and integrated nmr spectra of the mixture, we contend that the ratio 10:90 represents a minimum stereochemical value in this case also.

While the alumina-catalyzed reactions afford only qualitative results, it is still possible to draw several conclusions concerning this reaction. First, the relative amounts of starting epoxides remaining after 2 hr indicate that the *erythro* isomer (**4**) rearranges somewhat faster than does the *threo* isomer (**5**). This is a result of the lower energy of the conformation **4a** relative to **5a**. Secondly, the loss of formaldehyde from **7** to produce **16** is considerably more rapid than that from **6** to produce **15**. The reason for this facile retro-aldol reaction is not immediately apparent but is undoubtedly related to the high order of stability associated with enols of β-tetralone systems.[17] The stereochemical results of the alumina-catalyzed reactions, coupled with the lack of stereoselectivity in the Lewis acid catalyzed rearrangements, provide credible

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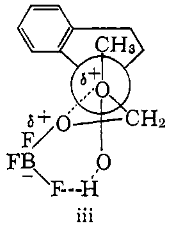
[14] This predominance of 7 in the rearrangement of either epoxide suggests that transition states in which the negatively charged boron fluoride grouping is hydrogen bonded by the hydroxyl proton, *e.g.*, iii, are unimportant.



iii

[15] C. W. Sweeley and B. Walker, *Anal. Chem.*, **36**, 1461 (1964).

[16] M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958).

[17] For a review of examples of some unusual chemistry of β-tetralones, see J. Rundquist, Ph.D. Thesis, Harvard University, 1951.

evidence that these reactions proceed through "surface-adsorbed" transition states as shown in **17** and **18**.

Experimental Section

Melting points were determined using a Kofler micro hot stage and are corrected; boiling points are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra, with the exception of the high dilution studies, were measured with a Beckman IR-4 infrared spectrophotometer. The high dilution spectra were obtained with a Perkin-Elmer Model 521 grating instrument. Nmr spectra were recorded with a Varian A-60 spectrometer and chemical shift values are given in parts per million relative to tetramethylsilane as internal standard. Gas chromatographic analyses were performed on a Beckman GC-4 instrument equipped with a 4 ft × 0.25 in. 20% Carbowax 20M on 60–80 mesh Chromosorb P and a flame ionization detector. All analyses were carried out at 190°.

1-Isopropenyl-1-indanol (1).[18] Magnesium bromide was prepared under nitrogen by the dropwise addition of 1,2-dibromoethane (56.7 g, 0.30 mole) to a mixture of 12.35 g (0.508 g-atom) of magnesium turnings in 400 ml of dry tetrahydrofuran, contained in a 1-l. three-necked flask equipped with a mechanical stirrer, addition funnel, condenser, and nitrogen inlet. The mixture was refluxed for 1 hr after the cessation of gas evolution and cooled, and a solution of 25.2 g (0.208 mole) of freshly distilled 2-bromopropene in 50 ml of dry tetrahydrofuran was added dropwise. The mixture was refluxed gently with stirring until all the magnesium had reacted and cooled to room temperature; a solution of 25.2 g (0.191 mole) of 1-indanone in 50 ml of dry tetrahydrofuran was added dropwise with stirring over a period of 1 hr. The mixture was then warmed to *ca.* 40° and stirred overnight under nitrogen. The mixture was then cooled and decomposed by the addition of a saturated aqueous solution of ammonium chloride and filtered and the precipitate washed several times with benzene. The resulting filtrate and washings were dried over anhydrous potassium carbonate and concentrated under reduced pressure. Distillation through a pyridine washed, jacketed 0.7 × 38 cm Podbielniak column afforded 13.6 g (41%) of the alcohol **1** as a colorless oil: bp 51–53° (0.045 mm); $n^{25}D$ 1.5522. A sample of the material solidified on standing and recrystallization from hexane provided colorless needles, mp 46–47°. The solid material exhibited infrared and nmr spectra superimposable with those of the liquid.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.60; H, 8.10.

erythro- and *threo*-**1-Methyl-1-(1′-hydroxyindanyl)oxirane (4 and 5).** To a chilled solution of 42.5 g (0.25 mole) of 1-isopropenyl-1-indanol (**1**) in 200 ml of chloroform was added with stirring a solution of 50 g (0.25 mole) of 85% *m*-chloroperbenzoic acid in 300 ml of chloroform. The resulting solution was allowed to warm to room temperature and was stirred overnight. The mixture was cooled in an ice bath and the bulk of the *m*-chlorobenzoic acid removed by filtration. The solution was washed successively with aqueous solutions of sodium sulfite and sodium bicarbonate, dried, and concentrated under reduced pressure to leave 46.2 g of a pale yellow oil. Examination of the methyl region of the nmr spectrum of this material indicated the presence of approximately equal amounts of both *erythro* and *threo* isomers, **4** and **5**. Careful fractionation of the mixture through a jacketed 36 × 0.5 cm Podbielniak column produced the following fractions: a, 5.2 g of semisolid forerun, bp 44–64° (0.03 mm); b, 23.4 g of a semicrystalline *erythro* rich mixture of isomers, bp 64–70° (0.03–0.06 mm); c, 7.2 g of the *threo* isomer, bp 70–72° (0.06 mm). Fraction b was filtered and the filter cake pressed between several pieces of filter paper to remove the majority of the liquid portion. Two recrystallizations from light petroleum (bp 20–40°) afforded 8.6 g of *erythro* isomer **4** (isomer A) as colorless crystals: mp 56–57°; nmr, δ_{CH_3} 1.11 ppm.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.92; H, 7.51.

Redistillation of fraction c produced the pure *threo* isomer **5** (isomer B) as a pale yellow oil: bp 73–75° (0.05 mm); nmr, δ_{CH_3} 1.20 ppm.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.87; H, 7.52.

2-(1-Hydroxyindanyl)-2-propanol (8). A. Reduction of *erythro*-Epoxy Alcohol 4 with Lithium Aluminum Hydride. An ethereal solution of 190 mg (1 mmole) of *erythro*-epoxy alcohol **4** was refluxed with 38 mg (1 mmole) of lithium aluminum hydride for 2 hr. The excess hydride was decomposed by the addition of a saturated aqueous solution of potassium sodium tartrate, the ether decanted, and the residue washed several times with fresh ether. The combined ether washings were dried over sodium sulfate and concentrated to leave 195 mg of a white crystalline solid. Recrystallization from hexane afforded 140 mg (73%) of the diol **8** as colorless needles, mp 120.5–121.5°.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.94; H, 8.54.

B. Reduction of *threo*-epoxy Alcohol 5 with Lithium Aluminum Hydride. Reduction of the *threo* isomer **5** by the same procedure as that used for the *erythro* isomer **4** produced the diol **8** in 75% yield after recrystallization from hexane. The material had mp 120–121° and the melting point was not depressed on admixture with a specimen obtained from reduction of the *erythro* isomer. The diols also had identical infrared and nmr spectra.

Rearrangement of *erythro*-Epoxy Alcohol 4. A. Reaction with Boron Trifluoride Etherate in Methylene Chloride. To a stirred solution of 95 mg (0.5 mmole) of epoxy alcohol **4** in 3 ml of methylene chloride chilled to *ca.* −5° with an ice–acetone bath was added 0.005 ml of boron trifluoride ethereate. The solution was allowed to stir for 10 min and was then poured into 5 ml of ice-cold aqueous sodium bicarbonate solution. The layers were separated and the aqueous layer was extracted several times with methylene chloride. The extracts were combined, dried over sodium sulfate, and concentrated to leave 90 mg of a pale yellow oil. The infrared spectrum of this material contained carbonyl bands at 1725 and 1691 cm^{-1} with the band at 1725 cm^{-1} slightly more intense. To this crude material was added a mixture of 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilane in 1 ml of dry pyridine[15] and the resulting cloudy solution was allowed to stand at room temperature for 30 min. The reaction mixture was concentrated under reduced pressure, taken up in methylene chloride, filtered, and reconcentrated to leave 114 mg of a pale yellow oil. This oil was subjected to gas chromatographic analysis. The chromatogram indicated the presence of only two peaks with retention times of 17.0 (major) and 20.7 min (minor). Planimetric integration yielded a ratio of 77:23. Distillation afforded the mixture of keto trimethylsilyl ethers **19** and **20** as a colorless oil, bp 78–80° (0.03 mm).

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.64; H, 8.50.

B. Reaction with Acidic Alumina. A magnetically stirred mixture of 500 mg of Merck acid-washed alumina in 10 ml of benzene was refluxed overnight under a Dean–Stark trap. The mixture was cooled slightly, 95 mg (0.5 mmole) of *erythro*-epoxy alcohol **4** was added; the mixture was reheated to reflux, and stirred for 2 hr. The reaction mixture was cooled, filtered, and washed with *ca.* 1 ml of benzene. Concentration left 63 mg of a pale yellow oil. The infrared spectrum showed a single carbonyl peak at 1691 cm^{-1}. The crude product was trimethylsilanated by the same procedure as described above and analyzed by gas chromatography. The chromatogram indicated three main peaks with retention times of 9.1, 15.2, and 21.1 min in an approximate ratio of 2:3:4. The structures **21**, **15**, and **20** were assigned to these materials, respectively. The region between **15** and **20** was obscured by the presence of a broad peak which overlapped considerably with both of these materials, making accurate planimetric integration impossible.

When the rearrangement was carried out on a preparative scale, it was possible to prepare the *p*-nitrobenzoate derivative as a crystalline solid. Treatment of the oily material obtained by rearrangement of 1.155 g (6 mmoles) of *erythro*-epoxide **4** with *p*-nitrobenzoyl chloride in pyridine followed by the usual work-up, and chromatography on 35 g of basic alumina (activity I) afforded 43 mg of the ketone 2-methyl-1-tetralone (**15**) by elution with benzene; infrared, ν_{max} neat 1691 cm^{-1}; nm, doublet (CH_3) at 1.20 ppm, J = 7 cps. The semicarbazone had mp 198–201° (lit.[19] mp 203–205°). Elution with 1:1 benzene–ether afforded 208 mg of **2-hydroxylmethyl-2-1-tetralone *p*-nitrobenzoate** as a colorless solid. Recrystallization from hexane produced analytically pure material as small needles, mp 77–79°.

Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.42; H, 5.15; N, 4.09.

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[18] The synthesis of **1** represents an improved method for the preparation of allylic alcohols of this type. This method will de discussed fully in a forthcoming publication.

[19] M. C. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940).

Continued elution with chloroform produced 321 mg of an oil which consisted predominantly of 2-hydroxylmethyl-2-methyl-1-tetralone (**6**) as evidenced by infrared and nmr spectra and trimethylsilanation and gas chromatographic analysis.

Rearrangement of *threo*-Epoxy Alcohol 5. A. Reaction with Boron Trifluoride Etherate in Methylene Chloride. Treatment of 196 mg (1.03 mmole) of the *threo*-epoxy alcohol **5** with boron trifluoride etherate in methylene chloride by the same procedure as described above for the *erythro* isomer **4** afforded 180 mg of a pale yellow oil. The infrared spectrum of this material contained carbonyl bands at 1691 and 1725 cm^{-1}, with the latter the more intense. Trimethylsilanation by the same procedure described above followed by gas chromatography indicated the presence of only two components with retention times of 17.1 (major) and 20.8 min (minor) in a ratio of 89.6:10.4 by integration of peak areas. Distillation provided the mixture of keto trimethylsilyl ethers **19** and **20** as a colorless oil, bp 80–84° (0.03 mm).

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.57; H, 8.42.

B. Reaction with Acidic Alumina. The *threo* isomer **5** was rearranged on treatment with acidic alumina under exactly the same conditions as described above for the *erythro* isomer **4**. Concentration of the benzene solution afforded 64 mg of a pale yellow oil whose infrared spectrum indicated a single carbonyl band at 1725 cm^{-1}. Examination of the gas chromatogram of the trimethylsilanated material indicated the presence of three components with retention times of 9.3, 16.8, and 21.1 min. These peaks had planimetrically integrated ratios of 9:9:1 and were assigned the structures **22**, **16** + **19**, and **20**, respectively, by comparison with authentic samples. The position of the second peak (**16** and **19**) is only approximate since a mixture of these two compounds appears as a single nonsymmetric peak whose maximum depends on the ratio of the two components. For analytical purposes the entire peak is integrated and no effort was made to determine the ratio of **16** to **19**, although in all cases the deformylation product **16** was present in large excess.

When the rearrangement was carried out for a period of 16 hr employing 950 mg (5 mmoles) of the *threo* isomer and 5 g of alumina in 100 ml of benzene, filtration and evaporation of the solvent left 645 mg of a pale yellow oil which on distillation yielded 227 mg of 1-methyl-2-tetralone (**16**) as a colorless oil, bp 136–140° (15 mm) (lit.[20] bp 138–142° (20 mm)). The infrared and nmr spectra of the distillate were identical with that of an authentic sample.[20] The semicarbazone crystallized from ethanol had mp 189–193° (lit.[21] mp 177–178 and 200–203°). The melting point was not depressed on admixture with an authentic sample.[21]

***erythro*-1-Methyl-1-(1′-trimethylsilanoxyindanyl)oxirane (21).** To 100 mg (0.53 mmole) of *erythro*-epoxy alcohol **4** in a 5-ml flask was added a freshly made solution of 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilazane in 1.0 ml of pyridine and the flask was stoppered and allowed to stand for 30 min at room temperature with occasional shaking. The crude reaction mixture was then concentrated under reduced pressure, triturated with methylene chloride, filtered, and reconcentrated to leave 114 mg of the trimethylsilyl ether **23** as a colorless oil. The material eluted as a symmetrical peak with a retention time of 8.8 min. Short-path distillation provided an analytical sample: bp 78–80° (0.03 mm); $n^{25}\text{D}$ 1.5004.

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.74; H, 8.41.

***threo*-1-Methyl-1-(1′-trimethylsilanoxyindanyl)oxirane (22).** Application of the above described trimethylsilanation procedure to 100 mg (0.53 mmole) of the epoxy alcohol **5** produced 110 mg of crude trimethylsilyl ether **22**. The ether was homogeneous on gas chromatographic analysis and had a retention time of 9.0 min. Short-path distillation provided the pure trimethylsilyl ether **22** as a colorless oil: bp 76–78° (0.03 mm); $n^{25}\text{D}$ 1.5024.

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.64; H, 8.38.

Chemical Shift of Hydroxyl Protons. The data exhibited in Figure 2 were obtained by the procedure of Ouellette.[8] The Varian A-60 spectrometer was equipped with a V-6020 closed-loop water circulator and operated at probe temperature of 45°. The samples were prepared gravimetrically. The chemical shifts were measured after the sample had equilibrated to probe temperature with an average value of five to ten scans for each concentration. Deviations are less than ±0.5 cps.

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A Novel Rearrangement of Some Phenoxyphosphonium Salts[1]

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Abstract: Treatment of tris(diethylamino)phenoxyphosphonium chloride (Ia) and tris(diethylamino)-*p*-methoxyphenoxyphosphonium chloride (IIa) with lithium diethylamide in benzene–hexane led to the rearranged betaines (III and VI). The structures of these materials were demonstrated by alternate syntheses of derivatives of them. Treatment of the hexafluorophosphate (Ib) in benzene–hexane and hexane alone with lithium diethylamide yielded III in the benzene–hexane reaction; however, in hexane alone, N,N-diethylaniline and tris(diethylamino)phosphine oxide were formed along with III. The amine and oxide probably arise by benzyne formation. The mechanism of the reaction is discussed.

The preparation and chemistry of pentasubstituted phosphorus compounds is of considerable interest from both the theoretical and practical points of view.[2] Compounds with five nitrogens bonded to phosphorus are not known, although some compounds with three nitrogens and two oxygens bonded to phosphorus have been prepared recently.[3]

A possible route to pentadialkylaminophosphoranes involves preparation of a tetrakis(dialkylamino)phos-

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