$n^{25}$D 1.5232; uv max 274, 263.5, 253,5 nm (trans,trans isomer) ($\epsilon$ 3.56, 4.48, 3.18 × $10^4$); nmr ($CCl_4$) identical with that above but shifted due to solvent difference]. Glpc analysis revealed a purity of 99.0% and an isomer distribution of 84.8% trans,trans and 15.2% cis,trans.

**B.**—Half of the above crude bromide (60.5 g, 0.32 mol) was allowed to react with *N*,*N*-dimethylbenzylamine (61 g, 0.45 mol) in 500 ml of toluene at 50–60° for 24 hr. After cooling, the toluene was decanted from the brown glassy salt which was then dissolved in *ca.* 500 ml of water. The resulting yellow solution was added dropwise to a KOH solution (70 g/1200 ml of water) undergoing distillation. The product was worked up in the usual manner[4,5] and distilled yielding **3** (3.5 g, 10%). Glpc analysis revealed a purity of 99% but essentially only one isomer, *trans,-trans*-**3** with only a trace of the *cis,trans*-**3**.

**Registry No.**—*trans*-**1**, 821-07-8; *cis*-**1**, 2612-46-6; **2**, 2196-23-8; *trans,trans*-**3**, 17679-94-6; *cis,trans*-**3**, 18304-16-0; DBN, 3001-72-7.

## Cyclobutene Epoxides. The Stereospecific Lewis Acid Rearrangement[1]

DAVID L. GARIN

*Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121*

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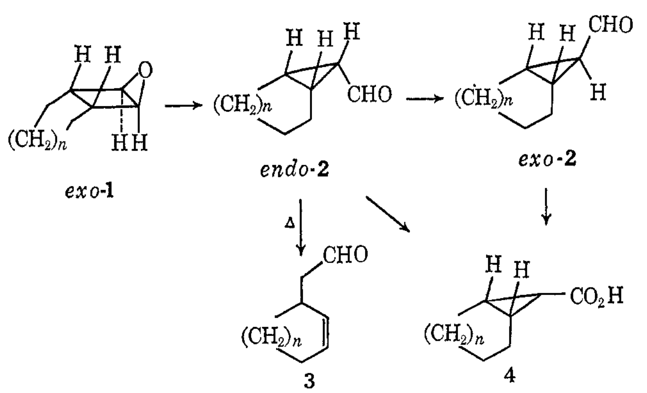
Despite numerous reports on the Lewis acid rearrangement of cyclobutene epoxides to cyclopropyl carbonyl compounds, the possible stereospecificity of the reaction (by analogy to other cycloalkene epoxides) has not been reported.[2-5]

Our investigation was prompted by the fact that the determination of the stereospecificity would enhance the synthetic utility of the reaction and by the availability of two cyclobutene epoxides suitable for such a study, bicyclo[3.2.0]hept-6-ene oxide (**1**, $n$ = 1) and bicyclo[4.2.0]oct-7-ene oxide (**1**, $n$ = 2).[6]

### Results

The epoxides were prepared by the peracid oxidation of the corresponding cyclobutenes giving the exo isomer of **1** ($n$ = 1)[7] and the exo and endo isomers of **1** ($n$ = 2) which were separable by gas chromatography.[8]

Treatment of the exo isomers of **1** ($n$ = 1, 2) with concentrated solutions of anhydrous lithium iodide in ether in a stoppered flask at *ca.* 40° for 1–24 hr produces a rearrangement to the exo and endo isomers of the ring-contracted bicyclic carboxaldehydes **2** ($n$ = 1, 2) in varying amounts. Prolonged reaction time favors the formation of the exo isomer. Product mixtures were analyzed by vpc although the *endo*-carboxaldehydes **2** ($n$ = 1, 2) rearrange on the vpc column to the corresponding $\Delta^2$-cycloalkenyl acetaldehydes **3** ($n$ = 1, 2) under the conditions employed.[9] The *exo*-carboxaldehydes **2** ($n$ = 1, 2) were separated and collected by preparative vpc. Silver oxide oxidation under nonisomerizing conditions gives the known *exo*-carboxylic acids **4** ($n$ = 1, 2).[10,11]



Our results suggested an initial isomerization of the *exo*-epoxides (**1**) to the bicyclic *endo*-carboxaldehydes (**2**) followed by a slower but competitive epimerization of *endo*-**2** to *exo*-**2**. This was verified by utilizing proton nmr spectroscopy to follow the rearrangement. Lithium iodide was added to an nmr sample of *exo*-**1** ($n$ = 2) in $CDCl_3$ at room temperature. After 1 hr, the epoxide proton absorption had decreased and an aldehydic signal at 9.6 ppm had appeared in the spectrum (see Table I). After 4 hr, with 20% of **1** still unreacted, a new aldehyde signal at 9.1 ppm began to appear in the spectrum. After 16 hr, we obtained a ratio of 1:1 for the signals at 9.6 and 9.1 ppm assigned to the endo and exo isomers of **2** ($n$ = 2), respectively. These two products can account for all of the absorptions observed in the spectrum[12] which is in perfect agreement with those of the known compounds.[9]

TABLE I

REARRANGEMENT OF *exo*-**1** ($n$ = 1, 2) WITH LITHIUM IODIDE IN $CDCl_3$[a]

| Time, hr | % of compound[b] | | | | | |
|---|---|---|---|---|---|---|
| | *exo*-**1** | | *endo*-**2** | | *exo*-**2** | |
| | $n$ = 2 | $n$ = 1 | $n$ = 2 | $n$ = 1 | $n$ = 2 | $n$ = 1 |
| 0 | 100 | | 0 | | 0 | |
| 1 | 65 | | 35 | | 0 | |
| 2 | 40 | | 60 | | 0 | |
| 3 | 25 | | 75 | | 0 | |
| 4 | 20 | | 80 | | Trace | |
| 16 | 0 | 90 | 50 | 10 | 50 | |
| 23 | 0 | 85 | 30 | 15 | 70 | |
| 43 | 0 | 80 | 10 | 20 | 90 | |
| 64 | 0 | 70 | 0 | 25 | 100 | 5 |

[a] These data were obtained using 55 mg of *exo*-**1** ($n$ = 1, 2) and 60 mg of lithium iodide in 0.4 ml of $CDCl_3$. [b] Based on integration of epoxide proton *vs.* aldehydic proton absorptions.

A similar experiment utilizing *exo*-**1** ($n$ = 1) produced a slower conversion of epoxide to carboxaldehyde (Table I). Molar amounts of lithium iodide are not essential but lesser amounts reduce the rates of the reactions.

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[1] Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN 137.

[2] J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1965).

[3] J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965).

[4] W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angles, Calif, 1963, 11M.

[5] An extensive review of epoxide chemistry can be found: A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 1-523.

[6] D. L. Garin, *J. Org. Chem.*, **34**, 2355 (1969).

[7] L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Amer. Chem. Soc.*, **89**, 5246 (1967).

[8] A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962).

[9] D. L. Garin, *J. Org. Chem.*, **35**, 2830 (1970).

[10] J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963).

[11] J. A. Berson and E. S. Hand, *ibid.*, **86**, 1978 (1964).

[12] The solid lithium iodide contained ether whose proton absorptions served as an internal standard for integrations.

The *endo*-carboxaldehydes **2** do not epimerize in ether or CDCl$_3$ in the absence of lithium iodide. The nature and extent of this surprisingly facile epimerization is currently under investigation.

In an attempt to avoid the epimerization of the *endo*-carboxaldehydes during the rearrangement of the *exo*-epoxides, another Lewis acid was employed. The reaction of *exo*-**1** ($n = 2$) with a molar excess of lithium thiocyanate in ether gave *endo*-**2** ($n = 2$) with no formation of *exo*-**2**. The exo isomer of **1** ($n = 1$) was stable to prolonged treatment with lithium thiocyanate in ether at 40°.

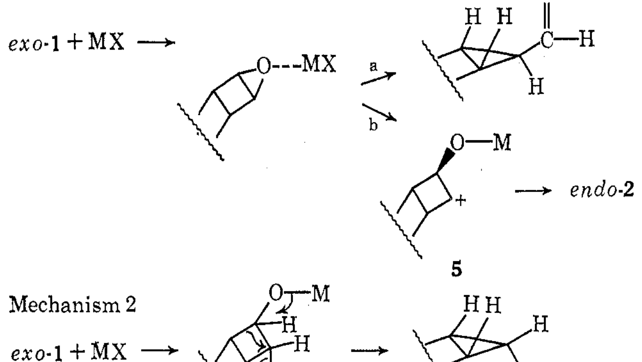
As expected, *endo*-**1** ($n = 2$) reacts with lithium iodide to give *exo*-**2** ($n = 2$). Thus, these Lewis acid rearrangements of cyclobutene epoxides to cyclopropyl carboxaldehydes occur with net retention of configuration at the migration terminus.

## Discussion

At least two possible mechanisms must be considered for the rearrangement. The formation of a Lewis acid–epoxide complex would result in polarization of the C–O bond with subsequent rearrangement to the cyclopropyl carbonyl compound possibly through a cyclobutyl carbonium ion intermediate (mechanism 1). A concerted, unimolecular process (path a) would be expected to occur with inversion.[13,14] A nonconcerted two-step process (path b) would lead to a cyclobutyl carbonium ion. If this is indeed an intermediate, the rearrangement would have to be governed by the stereochemistry of the C–O linkage of **5** since exo and endo species lead to different products, an unlikely possibility.[14] Moreover, the cyclobutyl carbonium ion would be expected to rearrange to olefinic products.[15]

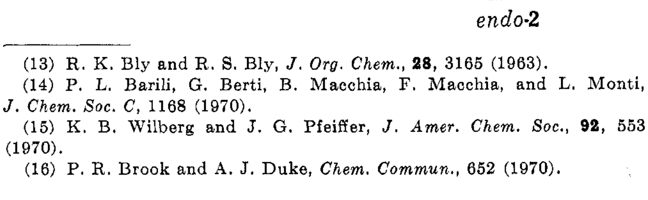
Alternatively, the Lewis acid could add across the epoxide bond to give the lithio salt of the *trans*-iodohydrin followed by rearrangement with alkyl displacement of iodine (mechanism 2). Both steps would be expected to occur with inversion of configuration resulting in net retention. Treatment of α-chlorocyclobutanols with base resulted in the formation of cyclopropyl carboxaldehydes with alkyl displacement of chlorine occurring with inversion of configuration.[16] The addition of lithium iodide to cyclohexene oxide is reported to give the *trans*-iodohydrin lithio salt (isolated as the iodohydrin). Subsequent base treatment of *trans*-cyclohexane iodohydrin resulted in the formation of the ring-contracted cyclopentane carboxaldehyde among other products.[17,17a]

Mechanism 1



5

Mechanism 2



Our attempts to isolate a cyclobutane iodohydrin were unsuccessful. No absorptions attributable to the lithio salts of these compounds were observed in the nmr spectra while the reactions were occurring but high concentrations of these reactive intermediates would not be expected (the reaction of α-chlorocyclobutanols with lithium *tert*-butoxide in chloroform produces the cyclopropyl carboxaldehydes in minutes).[18]

The latter mechanism, which we favor, can account for the discriminatory reactivity of lithium thiocyanate toward **1** as well as the difference in the rates of rearrangement with lithium iodide. Back-side displacement of the large anions on the exo isomer of **1** ($n = 1$) would be more difficult than that of **1** ($n = 2$) due to the greater rigidity of the fused five-membered ring of the former.

### Experimental Section[19]

***exo*- and *endo*-1** ($n = 2$).—The mixture of isomers was synthesized as reported.[6] Separation of isomers was effected on a 20 ft × $^3/_8$ in. Carbowax 20M column (30% of 45–60 Chromosorb W) at 190° with carrier flow *ca.* 85 ml/min. Compounds isolated and retention times in minutes were *endo*-**1** ($n = 2$), 27; *exo*-**1** ($n = 2$), 34; unknown, 31. Approximate ratios of *endo*-**1**:*exo*-**1**:unknown were 2:15:1 from integration of peak areas on the chromatogram.

**Rearrangement and Epimerization Reactions of 1 in Ether. Reactions with Lithium Iodide.**—To 24 mg (18 mmol) of anhydrous lithium iodide[20] in 1.0 ml of anhydrous ether in a 5-ml round-bottom flask was added 155 mg (120 mmol) of *exo*-**1** ($n = 2$). The flask was stoppered and immersed in an oil bath at 42° and the solution was stirred *via* a magnetic bar for 20 hr. After cooling, the crude reaction mixture was poured onto a 6-in. column of silica gel and eluted with benzene. After collection of 200 ml of benzene, the solvent was removed by rotary evaporator giving 152 mg of product. CDCl$_3$ was immediately added and the nmr spectrum taken. Integration of peaks at 9.6, 9.1, and 3.5 ppm showed a ratio of *endo*-**2**:*exo*-**2**:*exo*-**1** ($n = 2$) of 75:15:10. The CDCl$_3$ was removed by a rotary evaporator and the residue added to 240 mg of anhydrous lithium iodide (180 mmol) in 1.0 ml of anhydrous ether in a 5-ml round-bottom flask. The flask was stoppered tightly and placed in an oil bath at 40° for 14 hr with stirring. Similar work-up gave 140 mg of product whose nmr spectrum was now superimposable with that of the known *exo*-**2** ($n = 2$).[9]

In a similar fashion, the reaction of 195 mg of *exo*-**1** ($n = 1$) with 262 mg of lithium iodide in 1.0 ml of anhydrous ether at 42° for 48 hr produced *endo*-**2**:*exo*-**2**:*exo*-**1** ($n = 1$) in the ratio of 25:70:5 as determined by nmr analysis (peaks at 9.5, 9.1, and 3.5 ppm, respectively) in collaboration with peak integration of chromatograms and comparison with the known compounds.[9]

The reaction of 43 mg of *endo*-**1** ($n = 2$) with 63 mg of lithium iodide in 1.0 ml of anhydrous ether at 38° for 16 hr produced 40 mg of a product which was identical with *exo*-**2** ($n = 2$).

Heating *exo*-**1** ($n = 1, 2$) and *endo*-**2** ($n = 1,2$) in ether at 40° for 36 hr in the absence of lithium iodide followed by the normal work-up gave no rearrangement products.

**Reactions with Lithium Thiocyanate.**—To 153 mg of lithium thiocyanate in 1.0 ml of anhydrous ether was added 166 mg of

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[13] R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[14] P. L. Barili, G. Berti, B. Macchia, F. Macchia, and L. Monti, *J. Chem. Soc. C*, 1168 (1970).

[15] K. B. Wilberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 553 (1970).

[16] P. R. Brook and A. J. Duke, *Chem. Commun.*, 652 (1970).

[17] J. K. Heeren, T. C. Flood, and R. H. Cunningham, *J. Organometal. Chem.*, **9**, 18 (1967).

[17a] NOTE ADDED IN PROOF.—For an excellent discussion on the lithium salt catalyzed epoxide–carbonyl rearrangement, see B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **93**, 1693 (1971).

[18] D. L. Garin, unreported results.

[19] All melting points are uncorrected. All nmr spectra were taken in CDCl$_3$ on a Perkin-Elmer R-20 60-Mc instrument utilizing TMS as internal standard. An Aerograph Model A-700 vpc was used extensively.

[20] M. D. Taylor and L. R. Grant, *J. Amer. Chem. Soc.*, **77**, 1507 (1955).

*exo*-**1** ($n = 2$). The flask was stoppered and stirred at 41° for 34 hr. Work-up as described above gave 150 mg of a product whose nmr spectrum was consistant with that of known *endo*-**2** ($n = 2$) and displayed no *exo*-**2** aldehydic signal at 9.1 ppm.[9] Air oxidation of the carboxaldehyde gave an acid identical with authentic bicyclo[4.1.0]heptane-7-*endo*-carboxylic acid (**4**, $n = 2$).[11]

The reaction of 30 mg of *exo*-**1** ($n = 1$) with 11 mg of lithium thiocyanate in 0.5 ml of ether at 40° for 48 hr resulted in the recovery of starting material.

**Rearrangement and Epimerization Reactions of 1 in $CDCl_3$.**—Samples of the epoxides **1** were dissolved in 0.4 ml of $CDCl_3$ and the nmr spectrum was recorded. Solid lithium iodide was then added to the nmr tube which was shaken briefly (the lithium iodide is only partially soluble in $CDCl_3$) and the spectrum was recorded immediately. The lithium iodide contained ether[21] (*ca.* 20% by weight) whose proton absorptions were utilized as an internal standard. Periodic scans showed changes in absorption for the epoxide and aldehydic protons (see Table I). Integration of the peaks in these regions relative to one another allowed a determination of the progress of the reaction, and integration relative to the ether proton signals substantiated the proton count. Data for the individual reactions of 55 mg of *exo*-**1** ($n = 1$) and 55 mg of *exo*-**1** ($n = 2$), both with 60 mg of lithium iodide, are listed in Table I.

A similar experiment with 53 mg of *endo*-**1** ($n = 2$) and 30 mg of lithium iodide produced a 90:10 product mixture of *exo*-**2**:-*endo*-**1** ($n = 2$) after 14 hr as determined by nmr and vpc analyses. The rates of the above reactions in $CDCl_3$ are extremely slow when the molar ratio of lithium iodide to epoxide is less than 1:5.

**Silver Oxide Oxidation of *exo*-2.**—Following reported procedures,[10] 60 mg of *exo*-**2** ($n = 2$) in 0.5 ml of ethanol and 0.60 g of silver nitrate in 1.0 ml of water were placed in a 10-ml round-bottom flask. To this was added dropwise with stirring a solution of 0.20 g of sodium hydroxide in 2.0 ml of water. After being stirred for 1 hr, the reaction mixture was filtered and the filtrate acidified with 3 *N* HCl. The white solid was filtered (46.4 mg) and the aqueous solution extracted with ether to yield, after evaporation, another 15.0 mg of solid. Recrystallization from hexane gave crystals which had mp 95–96° (reported[11] for bicyclo[4.1.0]heptane-7-*exo*-carboxylic acid, mp 95–96.5°).

In identical fashion, *exo*-**2** ($n = 1$) gives a white solid acid, mp 58° (reported[10] for bicyclo[3.1.0]hexane-6-*exo*-carboxylic acid, mp 58°).

**Registry No.**—*exo*-**1** ($n = 1$), 18684-66-7; *exo*-**1** ($n = 2$), 28541-57-3; *endo*-**1** ($n = 2$), 28541-58-4.

**Acknowledgment.**—The author is grateful to the Petroleum Research Fund (1207-G1) and the Research Committee, UMSL, for financial support.

[21] The ether is not essential. Similar results are obtained with commercial anhydrous lithium iodide (Alfa Inorganics, Beverly, Mass.).

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## The Synthesis and Diels–Alder Reactivity of 2-Ferrocenylbutadiene[1a]

RONALD W. NOVAK,*[1b] TRAVIS E. STEVENS,
AND MORRIS HOWARD

*Rohm and Haas Company, Redstone Research Laboratories,
Huntsville, Alabama 35807*

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We wish to report on the synthesis and characterization of 2-ferrocenybutadiene and some of its Diels–Alder adducts. The synthetic approach taken to the title compound was through dehydration of 2-hydroxy-2-ferrocenylbutene. The latter compound may be obtained in good yield from reaction of the readily available acetylferrocene and vinylmagnesium bromide. The dehydration of the alcohol is a delicate procedure because of the acid and heat sensitivity of the diene product; a variety of acid-catalyzed routes to 2-ferrocenylbutadiene were attempted without success. The method of choice is reaction with methyl chloroformate in the presence of pyridine. The intermediate carbonate decomposes under the reaction conditions to give the desired product.

The current interest in α-ferrocenylcarbonium ions[2] coupled with the possible zwitterionic character of the Diels–Alder reaction[3] prompted a study of the Diels–Alder activity of 2-ferrocenylbutadiene. Dienophiles such as maleic anhydride, *p*-benzoquinone, nitrosobenzene, and acryloylferrocene were found to add readily to form 1:1 adducts. The characterization of these compounds is given in Table I. No attempts were made to isolate minor products. Attempted reactions with dimethyl maleate and with cyclohexene were unsuccessful. The former compound appeared to catalyze decomposition of the diene to unidentified products.

TABLE I
PROPERTIES OF THE DIELS–ALDER ADDUCTS
OF 2-FERROCENYLBUTADIENE[a]

| Dienophile[d] | Adduct mp, °C | Adduct nmr, δ |
|---|---|---|
| Maleic anhydride (12504-80-2) | 147 | 5.95 (s, 1, vinyl), 4.26 (m, 4, ferrocenyl), 4.11 (s, 5, ferrocenyl), 3.40 (m, 2, methine), 2.55 (m, 4, methylene) |
| *p*-Benzoquinone (12504-81-3) | 137–138 | 6.69 (s, 2, vinyl), 5.83 (m, 1, vinyl), 4.20 (m, 9, ferrocenyl), 3.30 (m, 2, methine), 2.60 (m, 4, methylene) |
| Nitrosobenzene[b] (12504-82-4) | 86–87 | 7.22 (m, 5, phenyl), 5.92 (m, 1, vinyl), 4.48 (m, 2, methylene), 4.36 (m, 2, ferrocenyl), 4.21 (m, 2, ferrocenyl), 4.11 (s overlapping m, 7, ferrocenyl and methylene) |
| Acryloylferrocene[c] (12504-89-1) | 161–162 | 5.96 (m, 1, vinyl), 4.82 (m, 2, ferrocenyl), 4.51 (m, 2, ferrocenyl), 4.33 (m, 2, ferrocenyl), 4.21 (s, ferrocenyl), 4.10 (s, ferrocenyl); total area 4.21 + 4.10 = 12 |

[a] Satisfactory analysis for C, H, and Fe were obtained for the adducts in this table. The data were made available to the referees and to the editor. [b] The expected product is 2-phenyl-5-ferrocenyl-3,6-dihydro-1,2-oxazine. See ref 2. [c] The expected product is 1-ferrocenyl-4-ferrocenoylcyclohexene-1. See ref 3d. [d] Registry numbers appear in parentheses.

It is concluded that 2-ferrocenylbutadiene is an active diene with a variety of dienophiles. More detailed studies are necessary to adequately weigh the electronic and steric effects of the 2-ferrocenyl group.

[1] (a) This work was sponsored by the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DAAH01-70-C-0146. (b) Rohm and Haas Co., Spring House, Pa. 19477.

[2] See J. Feinburg and M. Rosenblum, *J. Amer. Chem. Soc.*, **91**, 4324 (1969), and references cited therein.

[3] For recent discussions on the mechanism of the Diels–Alder reaction, see (a) S. Seltzer, *Advan. Alicycl. Chem.*, **2**, 1 (1968); (b) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; (c) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (d) J. A. Titov, *Russ. Chem. Rev.*, 267 (1962).