these values lead to the prediction of four weak lines spaced in two pairs about the center of each quartet. These are not present when J_{ab} is nil. Reexamination of the spectrum under high amplitude showed the weak lines to be present exactly as predicted. The same lines were found to be present in the spectra of the adducts from dimethyl and diphenylfulvene. Thus, *all our systems have been shown to have* a bridgehead to bridgehead proton coupling constant of ~1.9 Hz.

Conclusions

The condensation of acetone with methylcyclopentadiene yields as the major product 2,6,6-trimethylfulvene which is readily characterized by the TCNE adduct. The nmr spectra of cyclopentadiene and fulvene TCNE adducts are extremely useful for structure determination work since they are readily prepared *in situ* and display large chemical shift differences between the various types of protons.

Experimental Section[12]

Reaction of Methylcyclopentadiene with Acetone.—Methylcyclopentadiene dimer (Enjay) was cracked by distillation. The product was then redistilled to give a mixture of methylcyclopentadienes. This material (20 ml) was mixed wth 17.5 ml of acetone, and 7.5 ml of 20% potassium hydroxide in ethanol was added in 2-ml portions with swirling and cooling. The mixture was stored cold overnight and poured into water (75 ml), and the oily layer was collected. Steam distillation separated the more volatile components (about 25 g) from some tar. The distilled oil was dried over anhydrous $MgSO_4$.

Vacuum distillation caused an appreciable polymerization of the products which appear to be less stable than dimethylfulvene in all respects. Fractionation was effected by vpc over 20% Carbowax on Celite. Six bands were observed which, by retention times, appeared to be methylcyclopentadiene, acetone, dimethylfulvene, and the methylcyclopentadiene dimer(s), and a major and minor band of product. The latter two bands comprised *ca.* 50% of the mixture. The major and minor bands were trapped readily from the vpc and characterized as below.

The major isomer gave nmr (CCl_4) δ 1.99 (3 H, s, CH_3), 2.08 (6 H, s, $C(CH_3)_2$), and 6.08–6.58 (3 H, multiplet, ring H); mass spectrum *m/e* (rel intensity) 120 (43), 105 (100), 91 (34), 80 (34), 79 (60), 77 (45), 51 (44), 41 (38), 39 (65), and 27 (42).

The minor isomer was characterized by nmr (CCl_4) δ 2.19 with shoulder at 2.21 (9 H, s, CH_3 and $C(CH_3)_2$) and 6.03–6.53 (3, H, multiplet, ring H); mass spectrum *m/e* (rel intensity) 120 (45), 105 (100), 91 (36), 79 (45), 77 (41), 51 (42), 41 (39), 39 (64), and 27 (39).

Under the same conditions dimethylfulvene gives δ 2.13 (6 H, s, $C(CH_3)_2$) and 6.30 (4 H, s, ring); mass spectrum *m/e* (rel intensity) 106 (49), 91 (100), 66 (23), 65 (28), 51 (28), 50 (20), 41 (21), and 39 (53).

No attempt was made to obtain C and H analyses on the products due to their avidity for oxygen.

TCNE Adducts were prepared by reacting small amounts of the fulvene or cyclopentadiene with an excess of TCNE in either tetrahydrofuran or acetonitrile at room temperature. Sometimes the reaction was carried out in the nmr tube in the probe. Recrystallization was from a benzene–ether mixture.

Melting points were determined in sealed capillary tubes and were difficult to ascertain because of decomposition. The onset of melting for the TCNE adducts of the major isomer, minor isomer, and dimethylfulvene were 118, 127, and 133°, respectively.

Carbon, hydrogen, and nitrogen analyses were as follows.

Anal. Calcd for $C_{15}H_{12}N_4$ (major isomer): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.26; H, 4.73; N, 22.53.

Anal. Calcd for $C_{15}H_{12}N_4$ (minor isomer): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.34; H, 4.71; N, 22.39.

Anal. Calcd for $C_{14}H_{10}N_4$ (6,6-dimethylfulvene): C, 71.78; H, 4.30; N, 23.92. Found: C, 72.01; H, 4.31; N, 23.84.

The mass spectral data for the adducts in all three cases consisted of that for the parent hydrocarbon plus that for TCNE. No parent ion peak for the adduct could be observed.

Registry No.—I, 30953-08-3; II, 30883-04-6; III, 30883-05-7; IV, 30883-06-8; 6,6-dimethylfulvene, 2175-91-9, 30883-08-0 (TCNE adduct); acetone, 67-64-1; methylcyclopentadiene, 26519-91-5.

Acknowledgment.—We wish to express our appreciation to The Robert A. Welch Foundation for the support of this work and to the National Science Foundation for a grant for the HA-100.

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[12] Melting points are uncorrected. Nmr spectra were determined in carbon tetrachloride solutions for the fulvenes and perdeuterioacetonitrile for the TCNE adducts on Varian A-60A and HA-100 instruments. Spectral analysis was aided by the Laocoon computer program of S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). Mass spectra were determined on a Finnegan 1015/SL. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Hydroazulenes. I. A Thermal Epoxide Rearrangement

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Received February 3, 1971

The epimeric 1,2-epoxy-2-methyl-3-methylenebicyclo[4.4.0]decanes **1** and **2** have been prepared and their thermal rearrangements studied. Pyrolysis of **1** gives a 75% yield of *cis*-1-methyl-10-methylenebicyclo[5.3.0]-decan-2-one (**10a**) while its epimer **2** affords 1-methyl-9-methylenebicyclo[4.3.1]decan-10-one (**9a**) in 47% yield. Magnesium bromide catalyzed rearrangement of **2** failed to yield **9a**.

Until recently, the hydroazulenic sesquiterpenes have represented one of the more neglected areas of study in terpene chemistry. In recent years, however, these compounds have attracted more attention and the number of sesquiterpenes known to contain the hydroazulene ring system has increased substantially.[2] As a part of our work in sesquiterpene synthesis, we have been concerned with techniques for the stereoselective preparation of functionalized and highly substituted hydroazulenes. A few solutions to this problem have been reported,[3] but unfortunately, a wide selection of methods is not yet available to meet the diversity of

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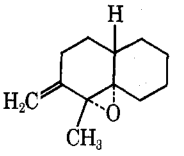
[1] National Science Foundation College Teacher Research Participant, summer 1969 and 1970.

[2] T. Nozoe and S. Itô, *Progr. Chem. Org. Natur. Prod.*, **19**, 32 (1961); J. Romo and A. R. de Vivar, *ibid.*, **25**, 90 (1967); W. Parker and J. S. Roberts, *Quart. Rev., Chem. Soc.*, **21**, 331 (1967); G. Ourisson, S. Munavalli, and C. Ehret, "Sesquiterpenoids," Pergamon Press, Oxford, 1966; J. Romo, *Pure Appl. Chem.*, **21**, 123 (1970).

[3] *Cf.* J. A. Marshall and W. F. Huffman, *J. Amer. Chem. Soc.*, **92**, 6358 (1970); J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970); J. A. Marshall and J. J. Partridge, *Tetrahedron*, **25**, 2159 (1969); C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968); J. B. Hendrickson, C. Ganter, D. Dorman, and H. Link, *Tetrahedron Lett.*, 2235 (1968); E. H. White and J. N. Marx, *J. Amer. Chem. Soc.*, **89**, 5511 (1967); G. Büchi, W. Hofheinz, and J. V. Paukstelis, *ibid.*, **88**, 4113 (1966).

structure encountered in nature. In an effort to develop a new approach to this problem, we have prepared and studied the rearrangement of epoxides **1** and **2**.



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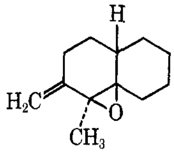

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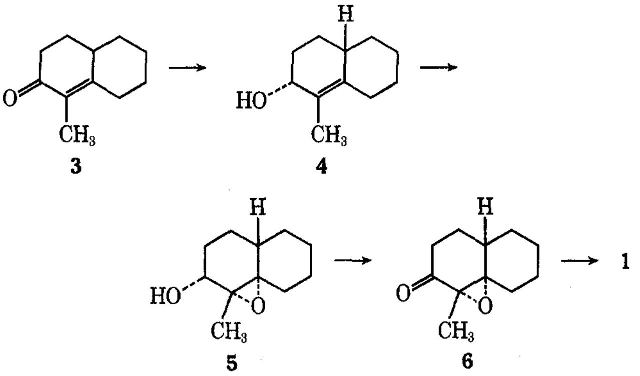
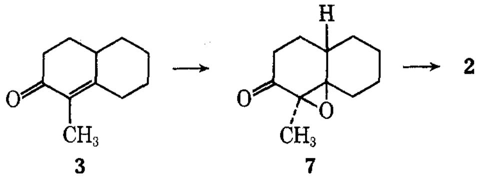
The starting material for these epoxides was enone **3**, prepared by reaction of ethyl vinyl ketone with the pyrrolidine enamine of cyclohexanone.[4] Reduction of the ketone **3** with LiAlH$_4$ afforded a mixture of epimeric alcohols from which a single pure isomer could be obtained in 20% yield by fractional crystallization. (Scheme I). The nmr spectrum of this compound contained a broad signal for the C-3 proton at δ 3.80 with a width at half height of 10 Hz. This indicates, on the basis of the Karplus relationship, that the alcohol has structure **4** in which the C-3 hydroxyl group occupies a quasiaxial position.[5] Stereospecific epoxidation[6] of **4** with *m*-chloroperbenzoic acid yielded the corresponding epoxy alcohol **5**, whose nmr spectrum showed a width at half-height of 8 Hz for the C-3 proton at δ 3.65. This corroborates[5] the previous stereochemical assignment and quasiaxial nature of the hydroxyl group. Oxidation of **5** with chromium trioxide in pyridine then afforded α,β-epoxy ketone **6**, which was subsequently converted to epoxide **1** in 84% yield by reaction with methylenetriphenylphosphorane.

Scheme I



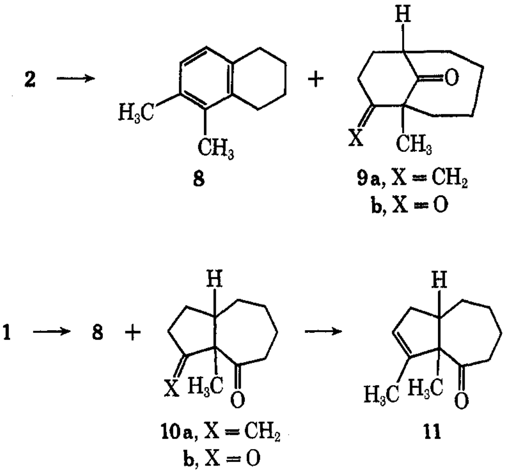
Preparation of the epimeric olefinic epoxide **2** was accomplished in a two-step sequence, beginning with epoxidation of octalone **3** (Scheme II) with hydrogen peroxide under basic conditions at 0–5°. This reaction was stereoselective and provided a 90% yield of product, which was shown by integration of the C-2 methyl signals in the nmr to consist of a 88:12 mixture of α,β-epoxy ketone **7** and its epimer **6**. This mixture of epimeric epoxides could not be further enriched in **7** and was subsequently used without further purification. The stereochemistry of **7** follows from its nonidentity with **6** and the fact that its methyl signal comes at slightly lower field in the nmr spectrum than that of the epimeric compound **6**.[7] Reaction with methylenetriphenylphosphorane then resulted in conversion to olefinic epoxide **2**, which was contaminated with about 14% of its epimer.

Scheme II



Treatment of epoxide **2** with anhydrous magnesium bromide in ether afforded 5,6-dimethyltetralin (**8**) as the principal product (Scheme III). The infrared spectrum of the crude product obtained in this reaction contained only trace absorption at 1710 cm^{-1} in the carbonyl region, indicating that insignificant rearrangement to ketone had occurred. However, when **2** was pyrolyzed over glass wool at 480–560° in a nitrogen atmosphere at 8.0-mm pressure, two major products were obtained. Tetralin **8** was again obtained but only in 8% yield. The principle product, isolated in 47% yield, was ketone **9a** in which C-10 alkyl migration had occurred. Trace amounts of hydroazulene **10a** were also detected by nmr in the pyrolysis product but were not isolated. The ratio of **8** to **9a** produced on pyrolysis was found to be a sensitive function of the nature and history of the material over which pyrolysis was conducted. The results obtained in a series of experiments are indicated in Table I. The structure of **9a** was verified by ozonolysis to diketone **9b**, which had infrared carbonyl absorption at 1692 and 1726 cm^{-1} consistent with the bicyclo[4.3.1]decane ring system.

Scheme III



Pyrolysis of epoxide **1** over sand at 380° in a nitrogen atmosphere at 4-mm pressure afforded a 75% yield of hydroazulene **10a**, in which C-6 alkyl migration had occurred. The only other product detected was tetralin **8**, which was shown by nmr to comprise less than 9% of the crude product. An attempt to examine the crude product by gas chromatography was unsuccessful

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[4] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

[5] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); E. W. Garbish, Jr., *J. Org. Chem.*, **27**, 4249 (1962).

[6] *Cf.* H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).

[7] H. Wehrli, C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1336 (1964).

TABLE I

THERMAL REARRANGEMENT OF OLEFINIC EPOXIDES 1 AND 2

Epoxide	Pyrolysis bed	Pressure,[a] mm	Temp, °C	Yield,[b] %		
				8	**9a**	**10a**
2[c]	Glass wool	8.0	480–560	8[d]	47[d]	2
2[c]	Sand	4.0	380	47	44	9
2[c]	"Conditioned" sand[e]	4.0	380	14	75	11
2[c]	60–80 mesh firebrick	8.0	480	100[f]	0	0
1	Sand	4.5	380	9		91 (75[d])
1	"Conditioned" sand[e]	4.0	380	3		97

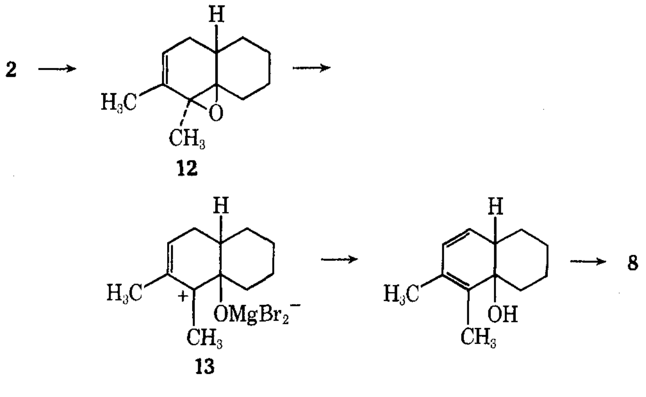
[a] Nitrogen atmosphere. [b] Per cent of isolated product determined by nmr except where indicated. [c] Containing 14% of the epimeric epoxide 1. [d] Isolated yield. [e] Conditioned by use in a previous pyrolysis. [f] Per cent of isolated product determined by infrared analysis.

and resulted in isomerization of **10a** to **11**. A slight dependence of product distribution on pyrolysis conditions is suggested by the results in Table I. The structure of **10a** was confirmed by ozonolysis. This afforded diketone **10b** which showed carbonyl absorption in the infrared at 1739 and 1699 cm^{-1} indicating the presence of a five- and seven-membered ring. The stereochemistry of **10a** and **10b** follows from the assumption that inversion of configuration occurs at the migration terminus.

Discussion

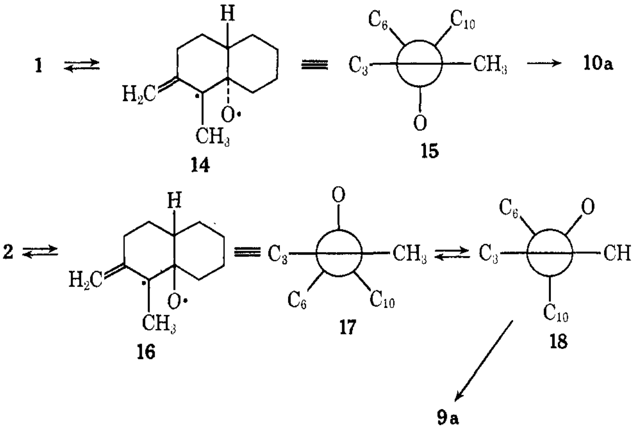
The thermal and acid-catalyzed rearrangement of epoxides has been well investigated, and an extensive literature exists on the subject.[8] These two rearrangement procedures have generally been found to yield identical products, although in somewhat different ratios.[9] The rearrangement of epoxide 2 seems to present an exception, however, since treatment with magnesium bromide fails to produce ketone **9a**, the principal pyrolysis product. Magnesium bromide catalyzed rearrangement of 2 may involve initial isomerization to give **12** (Scheme IV), containing an internal carbon–carbon double bond. Subsequent proton loss from the carbonium ion **13**, generated by cleavage of the allylic C–O bond, followed by loss of water would result in formation of the observed 5,6-dimethyltetralin, **8**. This transformation finds some analogy in the BF$_3$-catalyzed conversion of certain steroidal epoxides to dienes.[10] The formation of tetralin **8** in the pyrolysis of both epoxides 1 and 2 may proceed by a similar process, since surface effects have been shown to be important (Table I).

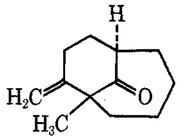
SCHEME IV



The stereochemistry of the thermal rearrangement of epoxides 1 and 2 can be explained either on the basis of a synchronous mechanism or by initial cleavage of the allylic C–O epoxide bond to give a discrete intermediate[11] (Scheme V). Homolytic bond cleavage is indicated, but the results can also be accommodated on the basis of a heterolytic cleavage. Epoxide **1** could afford **14** as a discrete intermediate, whose stereochemistry is partially indicated by the Newman projection **15**. Migration of C-10 with inversion of configuration at the migration terminus is improbable, since this would afford the very highly strained, trans-bridged, bicyclo[4.3.1]decane derivative **19**. As a result, only C-6 migration is observed. Pyrolysis of epoxide **2** could give diradical **16**. As a consequence of the cis-

SCHEME V





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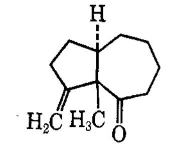

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(8) A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 1–523; R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); S. Winstein and R. B. Henderson, *Heterocycl. Compounds*, **1**, 1 (1950); A. P. Meleshevich, *Russ. Chem. Rev.*, 213 (1970).

(9) D. L. Garin, *J. Org. Chem.*, **34**, 2355 (1969); Y. Deux, *C. R. Acad. Sci.*, **213**, 209 (1941); **207**, 920 (1938); **206**, 1071 (1938); M. Tiffeneau, P. Weill, J. Gutman, and B. Tchoubar, *ibid.*, **201**, 277 (1935); S. M. Naqvi, J. P. Horowitz, and R. Filler, *J. Amer. Chem. Soc.*, **79**, 6283 (1957).

(10) H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.*, 4596 (1957).

(11) Discrete carbonium ion intermediates have been implicated in the boron trifluoride catalyzed rearrangement of 1,1-disubstituted ethylene oxides.[12]

(12) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, *J. Amer. Chem. Soc.*, **92**, 2574 (1970); J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *Tetrahedron*, **25**, 3925 (1969); B. N. Blackett, J. M. Coxon, M. P. Hartshorn, B. L. J. Jackson, and C. N. Muir, *ibid.*, **25**, 1479 (1969).

ring fusion, **16** must be regarded as a mixture of conformers **17** and **18**, if it represents a discrete intermediate. The geometry of **18** is such that C-10 is perfectly situated for migration, which results in formation of **9a**. Hydroazulene **20**, which could result from C-6 migration, was not observed as a pyrolysis product.[13] The traces of hydroazulene **10a** obtained on pyrolysis of **2** are, presumably, derived from small amounts of epimeric epoxide **1**, which is present as a contaminant in the starting material.

Experimental Section[15]

Preparation of Allylic Alcohol 4.—A solution of 25.0 g (0.152 mol) of enone **3**, bp 132–137° (14 mm), in 100 ml of anhydrous ether was added under nitrogen with magnetic stirring over a period of 56 min to a suspension of 5.78 g (0.152 mol) of lithium aluminum hydride in 150 ml of anhydrous ether at ice bath temperature. The resulting mixture was stirred at room temperature for 1 hr and then decomposed at ice-bath temperature by careful addition of 30 ml of saturated, aqueous Na_2SO_4. After drying and filtration, concentration of the solution *in vacuo* afforded a partially crystalline residue. Crystallization from hexane afforded 10.3 g of colorless needles, mp 86.5–100.0°. Two recrystallizations from aqueous dioxane afforded 4.94 g (19.5%) of the pure alcohol **4** as colorless needles: mp 116.0–117.0°; ir (KBr) 3203 (OH) and 1661 cm^{-1} (C=C); nmr (CCl_4) δ 1.72 (3 H, s, vinyl CH_3) and 3.80 (1 H, br, W_H = 10 Hz, CHOR).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.39; H, 10.91.

Preparation of Epoxide 5.—To a solution of 4.516 g (27.2 mmol) of allylic alcohol **4** in 350 ml of chloroform was added 5.750 g (30.0 mmol) of 89.8% *m*-chloroperbenzoic acid, and the solution was maintained at 5° for 20 hr. The resulting mixture was washed once with 75 ml of 10% aqueous KI, once with 75 ml of 10% aqueous $Na_2S_2O_3$, twice with 75-ml portions of 5% aqueous K_2CO_3, and once with 75 ml of water and dried. Concentration *in vacuo* afforded 5.006 g of white solid, mp 70.0–71.5°. Recrystallization from hexane afforded 4.222 g (85%) of the pure epoxide **5** as white, fibrous needles: mp 72.0–73.0°; ir (KBr) 3267 cm^{-1} (OH); nmr (CCl_4) δ 1.33 (3 H, s, CH_3) and 3.65 (1 H, br, W_H = 8 Hz, CHOR).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.45; H, 9.99.

Preparation of Epoxy Ketone 6.—To 100 ml of pyridine at ice-bath temperature was added 6.665 g (66.6 mmol) of chromium trioxide with mechanical stirring. After warming to room temperature, a solution of 4.038 g (22.1 mmol) of epoxy alcohol **5** in 125 ml of pyridine was added dropwise at room temperature over a period of 27 min with mechanical stirring. Stirring was then continued for 22 hr. The resulting mixture was diluted with 100 ml of ethyl acetate, filtered through an alumina column, eluted with ethyl acetate, concentrated, and distilled to give 3.732 g of colorless liquid, bp 68.0–71.0° (0.25 mm). The impure product was chromatographed on a 40-g column of silica gel, and the fractions (3.604 g) eluted with benzene were combined, concentrated, and distilled to give 3.316 g (83%) of pure epoxy ketone **6** as a colorless liquid: bp 69.5–70.5° (0.30 mm); ir (neat) 1707 cm^{-1} (C=O); nmr (CCl_4) δ 1.28 (3 H, s, CH_3).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.08; H, 8.93.

Preparation of the Unsaturated Epoxide 1.—To the basic solution[16] prepared from 0.845 g (35.2 mmol) of NaH and 25 ml of dimethyl sulfoxide was added at ice-bath temperature 11.914 g (35.5 mmol) of methyltriphenylphosphonium bromide, and the mixture was warmed at 40° under nitrogen for 45 min. A solution of 3.144 g (17.4 mmol) of the epoxy ketone **6** in 25 ml of dimethyl sulfoxide was then added, and the mixture was allowed to stir under nitrogen at a bath temperature of 50° for 2 hr. The resulting solution was diluted with 350 ml of water and extracted four times with 75-ml portions of hexane. The combined hexane extracts were dried, filtered through a 40-g alumina column, and eluted with 900 ml of hexane. Concentration of the resulting solution followed by distillation afforded 2.615 g (84%) of the unsaturated epoxide **1** as a colorless liquid: bp 52.5–54.0° (0.25 mm); ir (neat) 3085, 1638, and 888 cm^{-1} (C=CH_2); nmr (CCl_4) δ 1.39 (3 H, s, CH_3), 4.98 (1 H, m, vinyl CH), and 5.23 (1 H, br, vinyl CH).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.22; H, 10.19.

Preparation of the Epoxy Ketone 7.—To a solution of 5.000 g (30.4 mmol) of enone **3** in 525 ml of methanol at ice-bath temperature were added 42 ml of 30% hydrogen peroxide and 42 ml of 4 *N* sodium hydroxide solution. The resulting mixture was stored at 5° for 18 hr, then diluted with 1500 ml of water, and extracted three times with 250-ml portions of benzene. The combined benzene extracts were washed twice with 250-ml portions of water, dried, concentrated *in vacuo*, and distilled to give 4.907 g (90%) of the epoxy ketone **7** as a colorless liquid: bp 71.5–73.0° (0.30 mm); ir (neat) 1703 cm^{-1} (C=O); nmr (CCl_4) δ 1.35 (3 H, s, CH_3). The ketone was homogeneous by thin layer chromatography (silica gel G, elution with 5:95 ethyl acetate-benzene) and by gas chromatography on two different columns.[17] A small singlet in the nmr at δ 1.29, however, suggested the presence of *ca.* 12% of the epimeric epoxide **6**.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.10; H, 9.01.

Preparation of the Unsaturated Epoxide 2.—To the basic solution[16] prepared from 0.654 g (27.2 mmol) of NaH and 20 ml of dimethyl sulfoxide was added at ice-bath temperature 9.510 g (26.6 mmol) of methyltriphenylphosphonium bromide, and the mixture was warmed at 40° under nitrogen for 45 min. A solution of 2.510 g (13.9 mmol) of the epoxy ketone **7** in 20 ml of dimethyl sulfoxide was then added, and the mixture was allowed to stir under nitrogen at a bath temperature of 50–56° for 2 hr. The resulting solution was diluted with 300 ml of water and extracted four times with 75-ml portions of hexane. The combined hexane extracts were washed once with 75 ml of water, dried, filtered through a 30-g alumina column, and eluted with 1.2 l. of hexane. Concentration of the resulting solution followed by distillation afforded 2.088 g (84%) of the unsaturated epoxide **2** as a colorless liquid: bp 58.5° (0.30 mm); ir (neat) 3092, 1634, and 897 cm^{-1} (C=CH_2); nmr (CCl_4) δ 1.44 (3 H, s, CH_3), 5.00 (1 H, m, vinyl CH), and 5.19 (1 H, br, vinyl CH). Integration of the small nmr singlet at δ 1.39 indicated a 14% contamination by the epimer **1**.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.19; H, 10.35.

Magnesium Bromide Catalyzed Rearrangement of the Unsaturated Epoxide 2.—A solution of 1.38 g (8.6 mmol) of bromine in 15 ml of anhydrous ether was added to 0.21 g (8.6 g-atoms) of magnesium turnings at ice-bath temperature, and the mixture was stirred at 0° for 45 min. To this was added a solution of 1.00 g (5.6 mmol) of the unsaturated epoxide **2** in 10 ml of anhydrous ether, and stirring at 0° was continued for an additional 2 hr. The resulting pale orange mixture was diluted with 15 ml of water, the phases were separated, and the aqueous layer was

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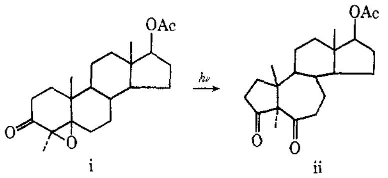
[13] It is interesting that this type of rearrangement does occur in the photochemical conversion of i to ii.[7,14] In our hands, however, this reaction was unsatisfactory on a preparative scale when applied to the analogous 1,2-epoxy-2,7-dimethylbicyclo[4.4.0]decan-3-one.



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[14] O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

[15] Melting points are uncorrected. Unless otherwise stated, magnesium sulfate was employed as a drying agent. The infrared spectra were determined with either a Beckman IR-8 or a Perkin-Elmer 257 infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as internal standard. The mass spectra were obtained with a Hitachi (Perkin-Elmer) mass spectrometer. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich. Baker reagent silica gel, 60–200 mesh, was used as adsorbent for column chromatography.

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

[17] A 5 ft × 0.25 in. column packed with 15% Carbowax 20M on Chromosorb P and a 5 ft × 0.25 in. column packed with 15% sil icone SF-96 on Chromosorb P were employed.

extracted with three 15-ml portions of ether. The combined ether extracts were washed twice with 25-ml portions of saturated $NaHCO_3$ solution, dried, and then concentrated *in vacuo*. The residue was distilled to give 0.46 g of clear, colorless liquid, bp 71.0–72.0° (0.4 mm); the ir (neat) showed only trace absorption in the carbonyl region at 1710 cm^{-1}. The product was then chromatographed on 20 g of silica gel, and the fractions eluted with hexane were combined to give 0.34 g of colorless liquid, which was shown by gas chromatography[18] to consist of three components. Tetralin **8**, the major component, represented 80% of the mixture and was separated by preparative gas chromatography[18] as a colorless liquid: ir (neat) 803 cm^{-1} (aromatic CH); nmr (CCl_4) δ 2.02 (3 H, s, CH_3), 2.17 (3 H, s, CH_3), and 6.71 (2 H, s, aromatic CH).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.90; H, 10.12.

Pyrolysis of the Unsaturated Epoxide 2. A. Over Glass Wool at 480–560°.—The unsaturated epoxide **2** (0.8889 g) was slowly distilled through a 20-cm column packed with glass wool in a nitrogen atmosphere at 8.0 mm pressure. Three passes through the column at temperatures of 480, 530, and 560° were required for complete conversion. The product consisted of 0.5426 g of an amber-colored oil which was chromatographed on 20 g of silica gel. The fractions eluted with hexane contained 0.0648 g (8%) of tetralin **8**. Fractions eluted with 1:1 hexane–benzene and with benzene contained 0.4151 g (47%) of ketone **9a** as an oil: ir (neat) 3079, 1643 ($C{=}CH_2$), and 1708 cm^{-1} ($C{=}O$); nmr (CCl_4) δ 4.87 (1 H, m, vinyl H), 4.78 (1 H, m, vinyl H), and 1.14 (3 H, s, CH_3); mass spectrum (70 eV) *m/e* (rel intensity), 178 (M^+, 93) 163 (14), 150 (21), 135 (89), and 79 (100). Ketone **9a** was characterized by conversion to its oxime, mp 91–93°.

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91. Found: C, 74.32; H, 10.19.

Examination of later chromatography fractions by nmr indicated the formation of hydroazulene **10a** in *ca.* 2.4% yield.

B. Over Sand at 380–385°.—The unsaturated epoxide **2** (0.190 g) was slowly distilled through a freshly packed 20-cm column of sand (J. T. Baker, purified) at 380–385° in a nitrogen atmosphere at 4 mm pressure. The product, 0.174 g (92% recovery) of a pale yellow liquid, was shown by nmr to contain no starting material and to consist of **8**, **9a**, and **10a** in a ratio of 47:44:9.

C. Over "Conditioned" Sand at 380–385°.—The unsaturated epoxide **2** (0.181 g) was pyrolyzed exactly as above, except that the sand had been used once before in the previous experiment. The product consisted of 0.162 g (90% recovery) of a pale yellow liquid. This was shown by nmr to contain no starting material and to consist of **8**, **9a**, and **10a** in a ratio of 14:75:11.

D. Over 60–80 Mesh Firebrick at 480°.—The pyrolysis was carried out as before, but over a 20-cm column of 60–80 mesh firebrick at 480° and in a nitrogen atmosphere at 8.0-mm pressure. The infrared spectrum of the product contained no carbonyl absorption and was essentially identical with that of authentic tetralin **8**.

Ozonolysis of the Unsaturated Ketone 9a.—A stream of ozonized oxygen was bubbled through a solution of 0.1411 g (0.792 mmol) of ketone **9a** in 10 ml of methanol at Dry Ice–acetone bath temperature until the solution developed a pale blue coloration indicative of the presence of excess ozone. After the solution was degassed with nitrogen, 3.0 ml of dimethyl sulfide was added, and the mixture was allowed to stir at room temperature for 19 hr. After concentration *in vacuo*, the residual oil was dissolved in 50 ml of ethyl acetate, washed once with 10 ml of water and once with 20 ml of saturated sodium chloride solution, and dried. Removal of solvent *in vacuo* afforded 0.1253 g of a viscous yellow oil which was chromatographed on a 5.0-g column of silica gel. The fractions eluted with benzene and 2:98 ether–benzene were combined to give 0.0953 g (61%) of diketone **9b** as a colorless resin: ir ($CHCl_3$) 1692 and 1726 cm^{-1} ($C{=}O$); nmr (CCl_4) δ 1.12 (3 H, s, CH_3). This material was characterized by conversion to the dioxime which crystallized from ethanol as small, colorless prisms, mp 225–226° dec.

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.80; H, 8.91; N, 13.12.

Pyrolysis of the Unsaturated Epoxide 1. A. Over Sand at 380–385°.—The unsaturated epoxide **1** (0.167 g) was slowly distilled through a freshly packed 20-cm column of sand (J. T. Baker, purified) at 380–385° in a nitrogen atmosphere at 4.5-mm pressure. The product, collected in a trap maintained at Dry Ice–acetone bath temperature, consisted of 0.129 g of a slightly cloudy, colorless liquid which was shown by nmr to contain 9% of tetralin **8** and no starting material. This material was chromatographed on 20 g of silica gel and the fractions eluted with benzene were combined to give 0.125 g (75%) of hydroazulene **10a**. Short-path distillation (0.25 mm and 80° bath) afforded the analytical sample as a colorless liquid: ir (neat) 3064, 1649 ($C{=}CH_2$), and 1694 cm^{-1} ($C{=}O$); nmr (CCl_4) δ 1.18 (3 H, s, CH_3), 4.64 (1 H, m, vinyl CH), and 4.91 (1 H, m, vinyl CH).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.04; H, 10.31.

In a comparable experiment, an attempt to purify the crude product by preparative gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicone (Fluoro) QF-1 on 60–80 Chromosorb P at a column temperature of 247° resulted in a complete conversion of **10a** to hydroazulene **11**, which was obtained as a colorless liquid: ir (neat), 3027, 1659 ($C{=}CH$), and 1695 cm^{-1} ($C{=}O$); nmr (CCl_4) δ 5.49 (1 H, m, vinyl CH), 1.5 (3 H, m, vinyl CH_3), and 1.12 (3 H, s, CH_3).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.00; H, 10.23.

Ozonolysis of the Unsaturated Ketone 10a.—Ozonolysis of 0.0780 g (0.438 mmol) of ketone **10a**, following the general procedure described above, afforded 0.0650 g of crude product which was chromatographed on 20 g of silica gel. The fractions eluted with 8:92 and 16:84 mixtures of ethyl acetate and benzene were combined to give 0.0400 g (51%) of a pale yellow liquid with spectral characteristics consistent with the diketone **10b**: ir (neat) 1739 and 1699 cm^{-1} ($C{=}O$); nmr (CCl_4) δ 1.24 (3 H, s, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 180 (M^+, 34), 162 (8), 152 (63), 137 (14), 123 (100), 110 (98), and 55 (84).

Registry No.—**1**, 30538-53-5; **2**, 30538-54-6; **4**, 30538-55-7; **5**, 30538-56-8; **6**, 30538-57-9; **7**, 30538-58-0; **8**, 20027-77-4; **9a**, 30545-93-8; **9a** oxime, 30545-94-9; **9b**, 30597-78-5; **9b** dioxime, 30545-95-0; **10a**, 30538-59-1; **10b**, 30538-60-4; **11**, 30538-61-5.

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[18] A 5 ft × 0.25 in. column packed with 15% silicone SF-96 on Chromosorb P was employed.