yield. Methylation of **6** followed by reaction with potassium *tert*-butoxide in tetrahydrofuran gave the Stevens rearrangement product **7**, as a mixture of isomers, in 22% yield. Remethylation of **7** followed by treatment again with potassium *tert*-butoxide in tetrahydrofuran effected a double Hofmann elimination to give the diene **8**, mp 220–221°, in 19% yield (Scheme I).

Scheme I

1, X = —Br
2, X = —CH₂=O
3, X = —CH₂OH
4, X = —CH₂Br

6   7

8   9   10
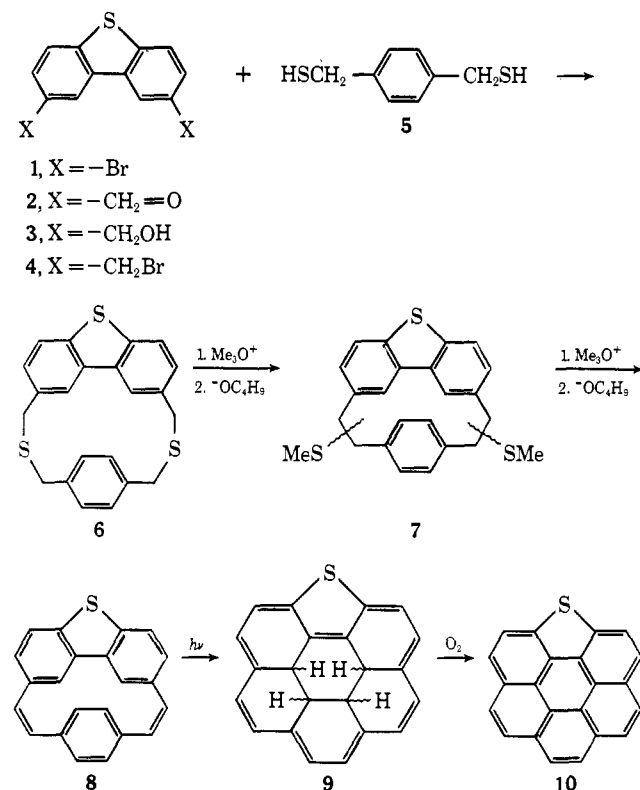
Since we had previously shown that irradiation of [2.2]metacyclophane-1,9-diene gives *trans*-15,16-dihydropyrene,[9] which is stable in degassed solution but is quickly oxidized by air to pyrene, we expected **8** to behave similarly. Irradiation of **8** in degassed perdeuteriobenzene gave a deep orange solution. When the reaction was followed by nmr, it could be seen that the signals for the photoproduct were arising both at higher and lower field than the starting material. The nmr spectrum of the photoproduct is presented in Figure 1. Its striking feature is the signal in the high-field range of τ 15.0–15.69. Furthermore, the integrated area of this region corresponds to four protons, whereas the region of τ 1.16–1.54 corresponds to ten protons, as expected. The only reasonable structure to account for such high-field protons is a bridged [18]annulene such as **9** where the high-field protons are the interior protons.

Although the splitting patterns of the low-field protons of the photoproduct are readily interpretable in terms of the perimeter protons of **9**, the splitting pattern of the upfield protons cannot be interpreted readily in terms of a single stereoisomer. It would appear that the double photocyclization may occur stepwise and, after the first ring closure, conformational flipping is possible so that the second photocyclization can lead

(9) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3510 (1970).
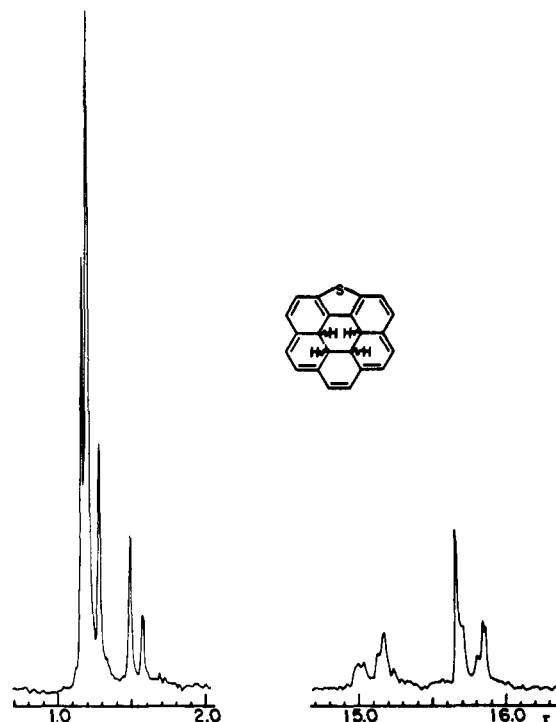

Figure 1. The nmr spectrum of **9** in degassed perdeuteriobenzene as measured using a Varian XL-100-Hz instrument with Fourier transform. Chemical shift values are in τ.

to more than one stereoisomer. Alternatively, the initial photoproduct from **8** may undergo a subsequent irradiation-induced stereoisomerization or tautomerization, possibly involving isomers where the interior double bond has shifted. The overall structure of **9** seems quite certain, but the exact assignment for the internal protons as well as the interior ring is not yet clear.

When the irradiated solution of **9** was exposed to air, oxidative removal of the internal hydrogens occurred and thiacoronene (**10**) was formed. The ultraviolet and visible spectrum of **10** corresponds very closely to that of coronene itself, and the nmr spectrum of **10** is in full accord with its assigned structure.

J. Lawson, R. DuVernet, V. Boekelheide*
*Chemistry Department, University of Oregon
Eugene, Oregon 97403*

A Stereoselective Method for the Synthesis of Both Olefinic Isomers from a Single Precursor. The Conjugate Reduction of α,β-Unsaturated Epoxides

Sir:

The need for stereoselective methods for the synthesis of olefins that are convenient and of general applicability is attested to by numerous recent publications in this area.[1] The available methods generally have sought to optimize stereoselectivity but as a consequence have suffered a loss of generality, *viz.*, only

(1) Recent reviews include: D. J. Faulkner, *Synthesis*, 175 (1971); J. Reucroft and P. J. Sammes, *Quart. Rev., Chem. Soc.*, **25**, 135 (1971).

one isomer of the olefin is obtainable from a single precursor, albeit in a state of high yield and purity. We wish to report a novel method for the synthesis of olefins based on the conjugate reduction of α,β-unsaturated epoxides using either diisobutylaluminum hydride (DIBAH) or dissolving metal–ammonia.[2] This method is convenient, and depending on the choice of reducing agent, allows the synthesis of either olefinic isomer of the related allylic alcohol in good yield with high stereoselectivity in many cases.

The major results of our findings are given in Tables I and II. The reduction of 2-methyl-1,2-oxido-3-
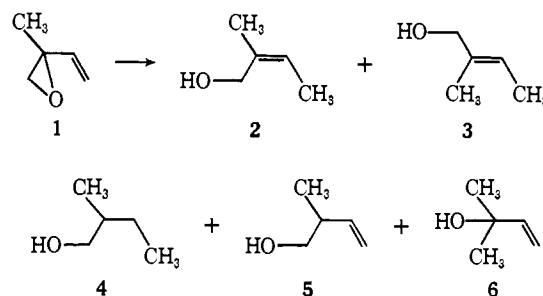
Table I. Reduction Products of 2-Methyl-1,2-oxido-3-butene (1)

Reducing agent	Solvent	Temp, °C	Total[a] yield, %	Product distribution, rel % 2	3	4	5	6
DIBAH	Hexane	68	71	95	5	0	0	0
DIBAH	Hexane	0	65	90	10	0	0	0
DIBAH	Benzene	80	33	83	3	14	0	0
DIBAH	THF	65	62	34	0	0	66	0
DIBAH	THF	0	59	16	0	0	84	0
DIBAH–TEA[b]	Hexane	68	55	63	0	0	22	15
LiAlH₄	Ether	35	48	0	0	0	0	100
Ca	NH₃	−33	64	8	92	0	0	0
Na	NH₃	−33	82	13	87	0	0	0
Li	NH₃	−33	79	20	80	0	0	0

[a] Distilled yield. [b] 2 equiv of TEA per DIBAH.

Table II. Stereoselectivity and Per Cent Conjugate Reduction in the Reduction of Unsaturated Epoxides

Unsatd epoxide	% stereoselectivity[a] [% conjugate reduction[b]][c] DIBAH–hexane	Ca–NH₃	Li–NH₃
1	90 [100]	−84 [100]	−60 [100]
7	78[d] [73]	−86 [99]	−80 [91]
8	17[e] [46]	−78 [54]	−83 [59]
9	12[f] [100]	−86 [100]	−70 [100]

[a] Stereoselectivity, S = (relative % Z isomer) − (relative % E isomer); it is related to the ratio of isomers R (% Z/% E), by R = $(100 + S)/(100 - S)$; see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 10. [b] Per cent of total isolated product made up of isomers $Z + E$. [c] Total isolated yields ranged from 59 to 85%, except reduction of epoxide 7 with DIBAH (27%). [d] Quantitation of isomeric alcohols was best done by glpc (Carbowax 4000), relative retention times $Z:E$ 1.00:0.87. [e] Isomeric alcohols were quantitated by nmr after shaking with D₂O. Hydroxymethylene signals (quartets): E, δ 4.05; Z, δ 4.86. Authentic samples of the allylic alcohols were prepared by the method of H. O. House and R. S. Ro, J. Amer. Chem. Soc., 80, 2428 (1958). [f] Isomer quantitation by glpc (Carbowax 4000), relative retention times $Z:E$ 1.00:1.14.

butene (1)[3] to the alcohols 2–6[4] (Table I) with both DIBAH and dissolved metals was studied extensively to establish optimum reaction conditions. As is evident in Table I, the solvent dependence of the DIBAH reductions of this epoxide is pronounced. Conjugate

(2) For reports on the conjugate addition of alkyl groups to α,β-unsaturated epoxides, see (a) H. C. Brown, N. Miyaura, M. Itoh, A. Suzuki, G. W. Holland, and E. Negishi, J. Amer. Chem. Soc., 93, 2792 (1971); (b) R. J. Anderson, ibid., 92, 4978 (1970); (c) R. W. Herr and C. R. Johnson, ibid., 92, 4979 (1970); (d) J. Staroscik and B. Rickborn, ibid., 93, 3046 (1971); (e) D. M. Wieland and C. R. Johnson, ibid., 93, 3047 (1971).

(3) Synthesized from isoprene according to the procedure of E. J. Reist, I. G. Junga, and B. R. Baker, J. Org. Chem., 25, 1673 (1960).

(4) All new compounds exhibited nmr spectra consistent with the assigned structures and gave satisfactory microanalysis.

reduction using DIBAH in refluxing hexane is highly stereoselective, giving a ratio of the Z isomer (2)[5]

to the E isomer (3)[6] of 95:5,[7] respectively. The same reduction at 0° gave comparable yields but slightly reduced stereoselectivity. At both temperatures, the reduction was allowed to run 1–2 hr, and the products were isolated by a standard aqueous work-up. Reduction in refluxing benzene has a stereoselectivity comparable to that in hexane; but the yield is lower, and the product is contaminated with substantial amounts of the saturated alcohol 4. This by-product, which may result from further reduction of either alcohol 2, 3, or 5, can be cleanly separated from the unsaturated alcohols by chromatography on 15% silver nitrate–silica gel.

A dramatic alteration in product distribution occurs when the reduction with DIBAH is conducted in tetrahydrofuran (THF); although the Z isomer 2 is formed with no trace of 3, the predominant product is the homoallylic alcohol 5, resulting from a direct, Markovnikov addition of hydride to the epoxide. Direct reduction predominates 2:1 over conjugate reduction at 65° and 5:1 at 0°. As it is known that DIBAH forms a complex with THF,[8] the stronger complexing agent triethylamine (TEA) was used. Reduction with DIBAH–TEA (1:2) in refluxing hexane does indeed give some of the direct reduction product 5, but less than DIBAH in THF. Furthermore, some of the anti-Markovnikov product 6 is also produced. Lithium aluminum hydride (LiAlH₄) reduction of 1 gives, as expected, exclusively the tertiary allylic alcohol 6.[9] It is interesting that the reduction characteristics of DIBAH can be modified to such a large extent through solvent and complexing agents, and that the DIBAH–THF reagent can be used to give reduction, at least in this case, opposite to that given by LiAlH₄.

In contrast to the reduction of 1 by DIBAH in hexane that gave almost exclusively the Z isomer 2, dissolving metal reduction of 1 gives almost exclusively the E isomer 3. Thus, treatment of 1 dissolved in liquid ammonia–THF with calcium metal until the blue color persisted, followed by the addition of solid ammonium chloride, evaporation of the ammonia, and a standard aqueous work-up, allowed the isolation of the alcohol 3, contaminated by only 8% of the Z

(5) A sample of this isomer was prepared by lithium aluminum hydride reduction of angelic acid prepared according to R. E. Buckles and G. V. Mock, J. Org. Chem., 15, 680 (1950).

(6) A sample of this isomer was obtained by lithium aluminum hydride reduction of tiglic acid.

(7) Quantitation of the isomer ratios was best accomplished by comparison of the hydroxymethyl signals in the nmr spectra (2, δ 3.94; 3, δ 3.78) after D₂O shake. The detection limit is less than 1%.

(8) G. Bruno, Ed., "The Use of Aluminum Alkyls in Organic Synthesis," Ethyl Corp., Baton Rouge, La., 1970, p 3.

(9) M. N. Rerick, "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 53.

isomer 2 (Table I). Similarly, reduction of 1 with either lithium or sodium metal in liquid ammonia gave 3 in higher yield but with reduced stereoselectivity.[10]

With the results from the aforementioned system in mind, we have investigated several other α,β-unsaturated epoxide systems to see if analogous reductions could be carried out when the substitution pattern on the unsaturated epoxide was varied. To this end, the reductions of 1,2-oxido-3-butene (7),[11] (E)-3-methyl-1,2-oxido-3-pentene (8),[12] and 3-methyl-2,3-oxido-4-pentene (9)[13] with DIBAH in refluxing hexane and with lithium and calcium metal dissolved in liquid ammonia were studied. The results are summarized in Table II, with data from system 1 included for comparison.

conjugate reduction
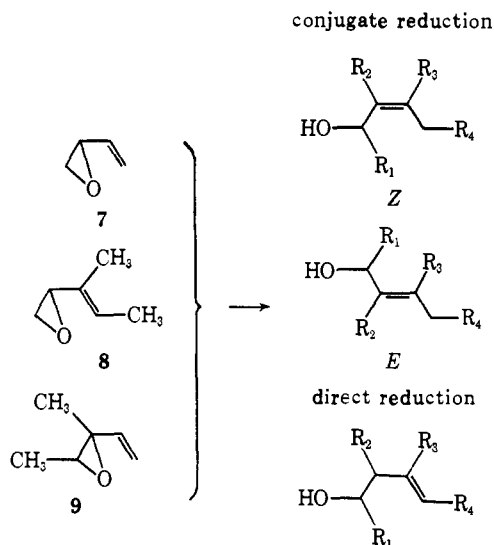
direct reduction

Comparison of the reactions of these four systems can best be made by considering first the extent to which reduction occurs in a conjugate, as opposed to a direct, fashion, and then the degree to which the conjugate reduction is stereoselective. Systems 1 and 9 have substituents that hinder the oxirane function, but none that hinder the double bond; reduction of both these systems with the three reagents studied proceeds cleanly in a conjugate fashion. System 7, which is hindered at neither function, experiences predominantly conjugate reduction, but more so with the dissolving metals than with DIBAH. System 8, with the double bond quite severely hindered but the oxirane accessible, undergoes about 50% direct attack on the epoxide function with all three reagents. Thus, the course of the reduction, conjugate vs. direct, seems in these systems to be simply a function of the relative degree to which the two functional groups are hindered, conjugate reduction being somewhat more favored with the dissolving metal reagents than with DIBAH.

The stereoselectivity of the conjugate reduction with the two dissolving metals favors the E isomer and is very high in all four systems, calcium generally being more selective than lithium. With DIBAH, the stereoselec-

tivity favors the Z isomer but is much more variable; it is high in systems 1 and 7, but low in 8 and 9, and does not appear to depend upon either the overall hindrance of the system or the ease with which the system undergoes conjugate reduction.

It is tempting to speculate on the mechanistic factors that result in the opposing stereoselectivities of the DIBAH and dissolving metal reductions. With DIBAH in nonpolar medium, the aluminum may be internally solvated by the epoxide oxygen. Delivery of hydride within this complex could be accomplished only in that rotamer (A) having the vinyl group positioned syn to the hydride source, to give the Z isomer; the minor isomer could result from hydride delivery by uncomplexed reagent to the other rotamer (B). With the dissolving metal reductions, negative charge in the transition state is most likely distributed over the four atoms; the more extended conformer D, which minimizes charge repulsion, would be stabler, so that the E isomer would predominate.

Work is currently in progress on the extension of this reaction to other systems and application to the synthesis of certain natural products.

Ronald S. Lenox, John A. Katzenellenbogen*
*The Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801*
Received September 5, 1972

Unusual Polarographic Behavior of Arylaziridinium Salts[1]

Sir:

Previous polarographic studies of aziridinium ions (generated *in situ*) emphasized either quantitative analysis[2a,b] or the nature of the reduction process.[2c-f]
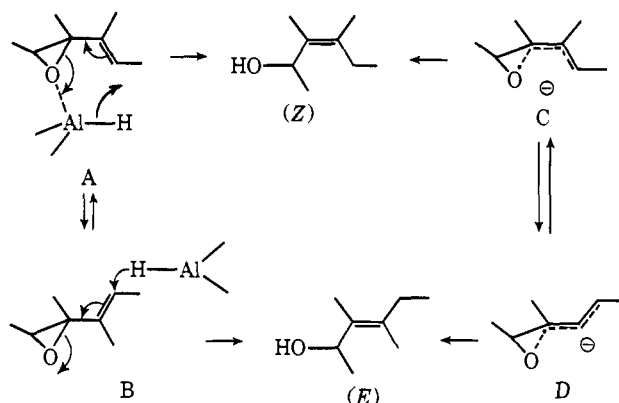
(10) These dissolving metal reductions are quite similar to a recently described reaction of an unsaturated cyclic oxide: D. Joulain and F. Rouessac, *J. Chem. Soc. D*, 314 (1972).

(11) Commercially obtained material was used (Columbia Chemical Co.).

(12) Prepared from the corresponding bromohydrin synthesized according to the method of D. R. Dalton and R. M. Davis, *Tetrahedron Lett.*, 1057 (1972).

(13) Prepared from *trans*-3-methyl-1,3-pentadiene and *m*-chloroperbenzoic acid in methylene chloride.

(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 28, 1972, Abstracts of Papers, ORGN-17.

(2) (a) N. G. Lordi and J. E. Christian, *J. Amer. Pharm. Ass.*, **45**, 530 (1956); (b) R. Mantsavinos and J. E. Christian, *Anal. Chem.*, **30**, 1071 (1958); (c) A. Anhalt and H. Berg, *J. Electroanal. Chem.*, **4**, 218 (1962), and references therein; (d) E. Bauer and H. Berg, *Chem. Zvesti*, **18**, 454 (1964); (e) B. Jambor, I. P. Horvath, and L. Institoris, *Magy. Kem. Foly.*, **73**, 332 (1967); *Chem. Abstr.*, **67**, 102840 (1967); (f) D. A. Tyssee and M. M. Baizer, *J. Electrochem. Soc.*, **118**, 1420 (1971).