valid. The efficiency for reaction 2 is almost 3 times greater than the efficiency reported in the flowing afterglow studies for reaction of Ti^{2+} with methane.[5]

Reactions of $NbCH_2^{2+}$ showed this species to be a powerful proton donor. Proton-transfer experiments indicate $PA(CH_4) = 132$ kcal/mol $< PA(NbCH^+) < 142$ kcal/mol $= PA(CO)$,[16] yielding $PA(NbCH^+) = 137 \pm 7$ kcal/mol. Charge-exchange reactions indicate $IP(C_2H_4) = 10.5$ eV $<$ 2nd $IP(NbCH_2) < 10.6$ eV $= IP(i\text{-}C_4H_{10})$, yielding 2nd $IP(NbCH_2) = 10.55 \pm 0.05$ eV compared to 2nd IP(Nb) = 14.3 eV. These results, together with $\Delta H_f(NbCH^+) = 328 \pm 8$ kcal/mol and $\Delta H_f(NbCH_2^+) = 316 \pm 7$ kcal/mol reported earlier,[15] yield values of $\Delta H_f(NbCH_2^{2+}) = 556 \pm 11$ kcal/mol from the proton affinity experiment and $\Delta H_f(NbCH_2^{2+}) = 559 \pm 7$ kcal/mol from the charge-exchange experiment. Thus, we assign a value of $\Delta H_f(NbCH_2^{2+}) = 558 \pm 10$ kcal/mol, from which the values of $D^0(Nb^{2+}\text{-}CH_2) = 197 \pm 10$ kcal/mol and $D^0(Nb^+\text{-}CH_2^+) = 107 \pm 10$ kcal/mol are derived. For comparison, $D^0(Nb^+\text{-}CH_2) = 109 \pm 7$ kcal/mol has recently been reported.[15]

The novel reactivity of multiply charged early transition metals is now under continued investigation in our laboratory. We hope these ions can be compared to the higher oxidation state species which are observed in solution.

Acknowledgment is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy (DE-ACO2-8OER10689) for supporting the transition-metal ion research and to the National Science Foundation (CHE-8310039) for the continued support of the Fourier transform mass spectrometry instrumentation. S.W.B. gratefully acknowledges the Purdue Research Foundation for providing fellowship support.

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(16) Proton affinity values taken from: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Preparation and Conformation of (*E*,*E*)-1,5-Cyclooctadiene†

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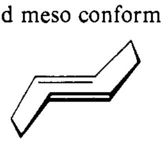
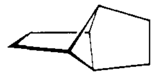
Irradiation of CuCl-complexed (*Z*,*Z*)-1,5-cyclooctadiene and Hofmann elimination of 1,5-bis(trimethylammonio)cyclooctane diiodide furnished 1% and 2.4% of (*E*,*E*)-1,5-cyclooctadiene (**1**) in isomer mixtures;[1] oxidation of isolated **1** gave succinic acid. The constraint of the double bonds in **1** does not allow interconversion of the rac and meso conformations, **1a** and **1b**. The ingenious tentative assignment of **1a** (δ_H 2.43, 4.88 in 2:1 ratio) by Whitesides, Goe, and Cope[1] rested on the photocyclization to **2**. Force field calculations favored the twist form **1a** over the chair **1b** by 5.35 (MM1)[2] or 7.36 kcal mol^{-1} (Ermer-Lifson).[3a] We report a method which makes the elusive **1** available gramwise and present conclusive evidence for the twist conformation **1a**.

1a



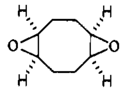
1b



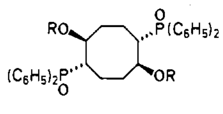
2

Combinations of trans addition and cis elimination have been employed to convert *cis*-cyclooctene into the strained trans isomer.[4] Peracid oxidation of (*Z*,*Z*)-1,5-cyclooctadiene resulted in the pure *cis*-diepoxide **3**.[5] An attempt to convert **3** into **1** had failed.[4b]

We adapted the procedure of Bridges and Whitham[4d] and reacted **3** with 2.1 equiv of lithium diphenylphosphide in THF at 0 °C and, subsequently, with 10% H_2O_2 and acetic acid. The dihydroxy bis(diphenylphosphine oxides) **4** and **5** (78%, 77:23) were separated. The ^{13}C NMR spectra of rac **4**, mp 220–222 °C,[6] and meso **5**, mp 241–242 °C, confirm the C_2 or C_s symmetry; the *J* values suggest the assignment but are not convincing.

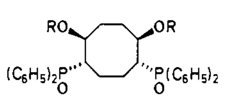


3



4 R = H

6a R = (-)-menthoxyacetyl



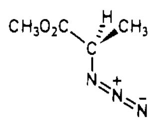
5

7

Two diastereoisomeric bis esters, **6a** and **6b** (only **6a** illustrated), both with C_2 symmetry, are the expected products from rac **4** and 2 mol of (−)-menthoxyacetyl chloride, whereas **5** should provide one bis ester, **7**, lacking symmetry. However, **6a** and **6b** formed 1:1 mixed crystals, mp 226–227 °C, thus thwarting the distinction from **7**, mp 220–221 °C, by counting ^{13}C signals. Fortunately, HPLC[7] separated the 1:1 mixture, **6a** and **6b**, whereas **7** moved as a single zone.

In the base-induced cis elimination of diphenylphosphinate, rac **4** is predestined to produce the twist conformation **1a**, and meso **5** is the logical precursor of **1b**. Treatment of **4** with NaH in DMF at 20 °C, hydrolysis at 0 °C, and extraction with pentane furnished a solution of 35–41% of **1**, *free of isomers* (GC analysis);[8] no volatile olefin emerged from **5** under the same conditions, sparing us the laborious separation of **4** and **5**. We obtained 17–21% of **1** from the mixture on a 40–80-mmol scale. Its distillation as a colorless liquid is accompanied by much polymerization. The pentane solution of **1** keeps well at −78 °C and its transfer to other solvents is achieved via aqueous 0.5 M $AgNO_3$ and extraction after adding KCN at 0 °C.

Beyond the genetic relation **4** → **1a**, we searched for direct evidence for the conformation of **1**. According to inspection of models the "jump rope rotation"[9] should be even more barred for **1a** than for (*E*)-cyclooctene; optical resolution would rule out **1b**. We considered another approach: Cycloaddition of 2 mol of a chiral 1,3-dipole should convert rac **1a** into two pairs of regioisomeric diastereomers, i.e., four bis adducts with C_2 axis each. Two regioisomeric bis adducts without symmetry are anticipated from the chair form **1b**. After reaction of **1** with the azide (*R*)-**8** as well as with the nitrile oxide (*R*)-**9**, two sharp-melting bis



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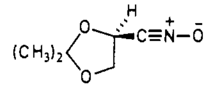
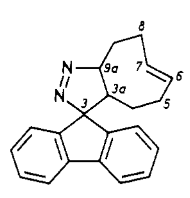


9



10

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† Dedicated to Professor Arthur Lüttringhaus on the occasion of his 80th birthday.

(1) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 2608.

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(6) Satisfactory elemental analysis and spectra were obtained for all new compounds.

(7) Silica gel, C_{18} reversed phase (Zorbax ODS of Du Pont, 25-cm analytical column), THF/H_2O 60:40, 150 bar, flow 1.2 mL/min, retention times 14.7 and 15.5 min.

(8) Packed column, 1 m, with OV17-Silicon on Varioport at 40 °C, injector 80 °C, 2 bar of He, flow 24 mL/min; retention times (min): toluene (weighed standard) 4.3, **1a** 11.1. The calibration factor of (*Z*,*Z*)-cyclooctadiene/toluene was set equal with that of **1a**/toluene.

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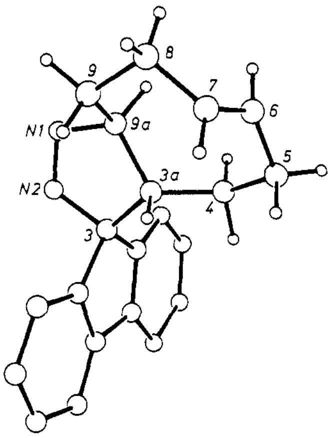

Figure 1. Structure of the diazofluorene adduct **10** of (*E*,*E*)-1,5-cyclooctadiene (one enantiomer). Bond lengths and angles of eight-membered ring: 3a–4 154.5, 4–5 154.8, 5–6 148.6, 6–7 132.3, 7–8 148.7, 8–9 155.3, 9–9a 153.9, 9a–3a 156.0 pm; 3a–4–5 115.0°, 4–5–6 106.4°, 5–6–7 123.1°, 6–7–8 122.4°, 7–8–9 106.1, 8–9–9a 114.2°, 9–9a–3a 119.4°.

adducts were separated in each case. From the structure proof of **1a** given below, we deduce that in all four cases we were dealing with 1:1 mixed crystals of diastereoisomers, this foiling potential distinction of derivatives of **1a** and **1b** by their ^{13}C NMR spectra.

After the failure of the "number game" we resorted to X-ray analysis of a crystalline monoadduct of **1**. The structure of the diazofluorene adduct **10** (Figure 1),[10] colorless monoclinic prisms, reveals provenance from the twist form **1a**. The angle of 69.4° between the 6,7- and 3a,9a-bond (Figure 1) indicates that the monoadduct is still fixed in a twist conformation. Not only the 1,2-bond of (*E*)-cyclooctene but also the 5,6-bond[11] is sterically constrained; force field calculations[3b] show a preference of the "crown" (here twist) over the chair form by 4.0 kcal mol^{-1} and $\Delta H^{\ddagger}$ = 11.6 kcal mol^{-1} for the "jump rope rotation" at the 5,6-bond. The corresponding rotation of the 3a,9a-bond in **10** is blocked by the annelated pyrazoline ring.

The dihedral angle (5–6–7–8) at the trans double bond of **10** is 136.3°, as compared with 137.7° found for (*E*)-cycloocten-3-yl 3,5-dinitrobenzoate (X-ray)[12] and 136.0° for gaseous (*E*)-cyclooctene (electron diffraction).[13] Out-of-plane bending (χ = 24.0°, 28.1°) and torsion (17.7°) in **10** participate to a similar extent in the deformation of the double bond as in the other models.

The ^{1}H NMR spectrum of **1a** in CDCl$_3$ at 0 °C shows two broad signals at δ 2.0–2.9 and 4.8–5.2 in the ratio 2:1. Irradiation at δ 2.45 furnishes a sharp singlet at δ 5.05, demonstrating the equivalence of the four vinyl Hs. Two ^{13}C NMR signals at δ 32.3 and 141.1 confirm the symmetry. The following δ_C values (CDCl$_3$) and (in brackets) J(^{13}C–H) of the olefinic C atoms of cyclooctenes and 1,5-cyclooctadienes suggest a relation with ring strain: (*Z*) 130.1 (154.0), (*E*) 132.8 (151), (*Z*,*Z*) 128.6 (152.7), (*E*,*Z*) 136.0, (*E*,*E*) 141.1 (146 Hz). Strain energies according to force-field MM1:[2,14] (*Z*) 5.3, (*E*) 13.1, (*Z*,*Z*) 8.3, (*E*,*E*) 20.3 kcal mol^{-1}.

Acknowledgment. We thank Dr. D. Männig for assistance in the X-ray work and express our gratitude to the Fonds der Chemischen Industrie for support.

Supplementary Material Available: Tables of atomic coordinates,[15] bond distances, bond angles, parameters of anisotropic temperature factors, and hydrogen coordinates (6 pages); table of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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[10] C$_{21}$H$_{20}$N$_2$, monoclinic, $P2_1/c$, a = 13.797 (3) Å, b = 16.173 (4) Å, c = 15.687 (4) Å, β = 109.42 (2)°, V = 3301 Å^3, Z = 8 (pair of enantiomers in asymmetric unit), D_{calcd} = 1.21 g·cm^{-3}, μ = 0.66 cm^{-1}, Mo Kα, colorless prisms, 0.15 × 0.21 × 0.30 mm, Syntex P3 diffractometer graphite monochromator; $2 < 2\theta < 45°$, ω-scan, 2–29.3°/min; correction for intensity variation of check reflexion (3%). 4926 data collected, 4316 unique and 3275 observed ($I \geqslant 2\sigma(I)$). Direct methods solution, blocked cascade refinement, all non-hydrogen atoms anisotropic, hydrogen atoms refined with fixed isotropic U approximately $1.2U_{\text{eq}}$ of corresponding carbon atom. R_F = 0.0819, R_{wF} = 0.0674, highest difference map peak = 0.248 e/Å^3, number of refined parameters 529; ratio data/parameters 6.2. Comparable bond lengths and bond angles of the two species can be considered as equivalent within the 3σ criterion, but numerical values for the molecule depicted in Figure 1 match more closely standard values than those for the other isomer.

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[15] Atomic coordinates found in the supplementary material are also deposited at the Cambridge Crystallographic Data Center.

1,2-Asymmetric Rearrangements in Chiral Sulfinylcyclopropane Systems: Asymmetric Synthesis of α,α-Disubstituted Cyclobutanones

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Creation of asymmetric quaternary carbon atoms[1] is one of the most important problems for the enantioselective synthesis[2] of natural products such as steroids, terpenoids, and alkaloids. We wish to communicate a potentially valuable method for enantioselective creation of quaternary carbons by thermal 1,2-asymmetric rearrangements in cyclopropane systems possessing a chiral sulfinyl group on the rings.

The thermal rearrangements in cyclopropane systems have received much attention in recent years for the preparation of various kinds of synthetically valuable compounds;[3] however, no work has been reported on asymmetric rearrangements in such systems. This paper presents the first example of asymmetric induction in thermal rearrangements of cyclopropane systems affected by the chirality of optically active sulfoxides.

Addition of the α-carbanion of (R_S)-(+)-*p*-toluenesulfinylcyclopropane (**1**) (100% ee),[4] generated by treatment of (R_S)-(+)-**1** with *n*-butyllithium, to acetophenone (**2a**) at −20 °C for 4 h afforded (S_S)-**3a** in 78% yield (ratio of the diastereomers, 3:2). When (S_S)-**3a** obtained was heated in refluxing benzene for 3.5 h in the presence of a catalytic amount of *p*-toluenesulfonic acid, it underwent a 1,2-asymmetric rearrangement to give (S_S,4*R*)-**4a** in 88% yield. Reduction of the sulfoxide in (S_S,4*R*)-**4a** was carried out by treatment with acetyl chloride[5] in dichloromethane at room temperature for 2 h, affording (*R*)-(−)-**5a** ($[\alpha]^{25}_{D}$ −14.7° (*c* 2.0, EtOH)) in 78% yield. Isolation of the diastereomers of **3a** was successfully accomplished by careful preparative thick-layer chromatography over silica gel (CHCl$_3$–EtOH 25:1). The same sequences of each diastereomer of **3a** were carried out by heating in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid and treatment with acetyl chloride under the same conditions to give (*R*)-(−)-**5a** having the same optical rotation as described above. Hydrolysis of the enol thioether (*R*)-(−)-**5a** obtained was performed by treatment with titanium(IV) chloride (3 equiv)–lead hydroxide (3 equiv)–H$_2$O (6 equiv)[6] in acetonitrile at room temperature for 18 h to produce (*R*)-(−)-2-methyl-2-

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