Scheme II

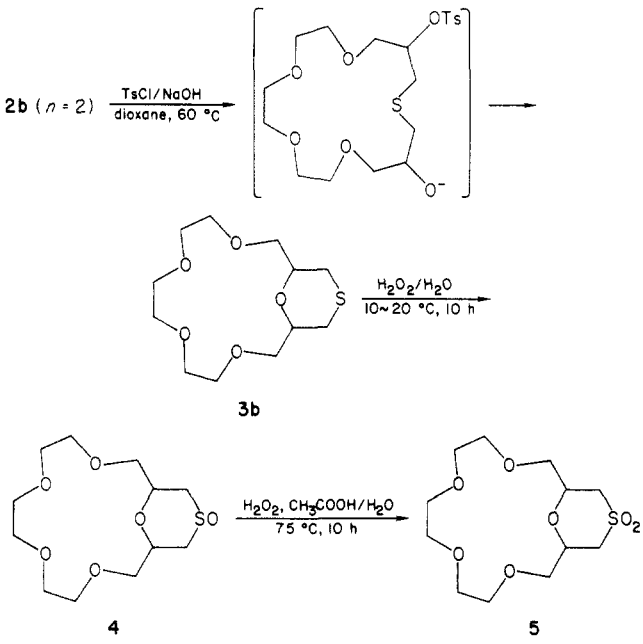

Table I. Stability Constants for Crown Ethers toward Na^+ and K^+ by Potentiometric Titration[a]

compd	log $K'(Na^+)$	log $K'(K^+)$
2a	<1	<1
2b	<1	<1
2c	1.95	2.48
3b	3.38	3.41
4	2.84	3.03
5	2.59	2.78
15-crown-5	3.31[b]	3.34[b]

[a] Reference 12, measured in MeOH at 25 °C. [b] Reference 13.

posed by sodium thiosulfate. Water (50 mL) was added to the mixture, and the mixture was extracted with dichloromethane (200 mL × 3). The dichloromethane solution was concentrated and distilled in a Kugelrohr apparatus (140 °C (0.1 torr)) to give a slightly yellow viscous oil (1.42 g, 61%): IR (neat) 2900, 1460, 1410, 1360, 1300, 1260, 1130, 1050, 950, 880 cm^{-1}; NMR ($CDCl_3$) δ 2.32-3.25 (m, 4 H), 3.25-4.76 (m, 18 H); MS, *m/e* (relative intensity) 294 (M^+, 5), 238 (8), 189 (19), 145 (15), 133 (22), 101 (43), 89 (39), 73 (34), 57 (51), 45 (100), 41 (91).

Anal. Calcd for $C_{12}H_{22}O_6S$: C, 48.96; H, 7.53; S, 10.89. Found: C, 48.71; H, 7.70; S, 10.64.

3,6,9,12,18-Pentaoxa-16-thiabicyclo[12.3.1]octadecane 16,16-Dioxide (5). To a mixture of compound **4** (1.14 g, 0.0039 mol) and acetic acid (0.96 g, 0.016 mol) was added 35% hydrogen peroxide solution (1.55 g, 0.016 mol) by portions at 75 °C and the mixture was stirred for 10 h. Water (50 mL) was added to the mixture, and the mixture was extracted with dichloromethane (200 mL × 3). The organic layer was concentrated and distilled in a Kugelrohr apparatus (160 °C (0.01 torr)) to give a slightly yellow waxy solid (0.99 g, 82%): IR (neat) 2900, 1460, 1350, 1300, 1250, 1125, 1020, 940, 860 cm^{-1}; NMR ($CDCl_3$) δ 2.74-3.36 (m, 4 H), 3.36-4.78 (m, 18 H); MS, *m/e* (relative intensity) 311 (M^+ + 1, tr), 310 (M^+, tr), 267 (1), 223 (5), 189 (19), 133 (9), 101 (35), 89 (30), 87 (32), 73 (33), 59 (32), 57 (47), 45 (75), 41 (100).

Anal. Calcd for $C_{12}H_{22}O_7S$: C, 46.44; H, 7.14; S, 10.33. Found: C, 46.57; H, 7.21; S, 10.09.

Registry No. **1a**, 4206-61-5; **1b**, 1954-28-5; **1c**, 17626-93-6; **2a**, 100228-56-6; **2a**·Na^+, 100205-45-6; **2a**·K^+, 100205-46-7; **2b**, 100205-57-0; **2b**·Na^+, 100205-47-8; **2b**·K^+, 100205-48-9; **2c**, 100205-58-1; **2c**·Na^+, 100205-49-0; **2c**·K^+, 100205-50-3; **3b**, 100205-59-2; **3b**·Na^+, 100205-51-4; **3b**·K^+, 100205-52-5; **3c**, 100205-60-5; **4**, 100205-61-6; **4**·Na^+, 100205-53-6; **4**·K^+, 100205-54-7; **5**, 100205-62-7; **5**·Na^+, 100205-55-8; **5**·K^+, 100205-56-9.

On the Relation between Ring Size and Geometry of 2-Bromo-2-cycloalkenyl Acetates Formed from Dibromobicyclo[*n*.1.0]alkanes by Silver Acetate Catalyzed Reactions. Use of ^3J(C-H) Couplings To Assign the Geometry of Trisubstituted Olefins

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As part of a study[1] of the chiroptical properties of medium-ring cycloalkenyl *p*-bromobenzoates, several cis- and trans-2-substituted 2-cycloalkenyl acetates were required. Reese and Shaw[2] have shown that (*Z*)-2-bromo-2-cyclooctenol and (*Z*)-2-bromo-2-cyclononenol can be conveniently prepared by silver perchlorate promoted solvolyses of the corresponding dibromobicyclo[*n*.1.0]alkanes in aqueous acetone. In order to obtain directly the desired acetates, we modified the Reese and Shaw procedure by reacting the dibromobicyclo[*n*.1.0]alkane with silver acetate in acetonitrile containing a small quantity of acetic acid (see Scheme I). We were surprised to find that compounds **1**, **2**, and **3** obtained under our conditions were not the anticipated *Z* isomers but instead the *E* stereoisomers. The reaction of silver acetate in acetonitrile containing acetic acid with higher homologues of dibromobicyclo[*n*.1.0]alkanes yielded 2-bromo-2-cycloalkenyl acetates in which the size of the ring appeared to influence the geometry about the double bond. The geometry of the double bond in two new compounds has been assigned from data on ^3J(C-H) coupling constants obtained from a new 2D NMR pulse sequence developed by Bax and Freeman.[3]

Results

A series of *gem*-dibromobicyclo[*n*.1.0]alkanes was prepared by the reaction of dibromocarbene with cis- and trans-olefins.[4] Treatment with silver acetate in acetonitrile containing acetic acid afforded 2-bromo-2-cycloalkenyl acetates. Proton NMR spectra (220 MHz) of the crude reaction mixtures established the formation of a single 2-bromo-2-cycloalkenyl acetate; the presence of as little as 5% of the other isomer would have been observable. A comparison of the chemical shifts and splitting patterns of the olefinic proton in the purified acetates (**1a**, **2a**, and **3a**) shows them to be very similar. Enzymic hydrolysis[5] converted the esters into the corresponding alcohols (**1b**, **2b**, and **3b**); the geometries of the latter were assigned as *E* by a comparison of proton NMR data with data in the literature.[2,6] The chemical shifts of the methine protons of the allylic acetates **4a**, **5a**, and **6a** and the splitting pattern of the olefinic proton differed from those observed for **1a**, **2a** and **3a** (see Table I). Since compounds **5a** and **6a** were new, it was necessary to assign unambiguously the geometry about the double bond. Compound **4a** was likewise new, but NMR data for **4b** had previously been reported.[2,6] However, for the reasons given below, the

(1) Ito, S.; Ziffer, H.; Silverton, J. V., unpublished work.
(2) Reese, C. B.; Shaw, A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2422.
(3) Bax, A.; Freeman, R. *J. Am. Chem. Soc.* **1982**, *104*, 1099.
(4) Skottebol, L.; Solomon, S. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 306.
(5) (a) Kasai, M.; Kawai, K.; Imuta, M.; Ziffer, H. *J. Org. Chem.* **1984**, *49*, 675. (b) Ziffer, H.; Kawai, K.; Kasai, M.; Froussios, C. *Ibid.* **1983**, *48*, 3017.

Scheme I

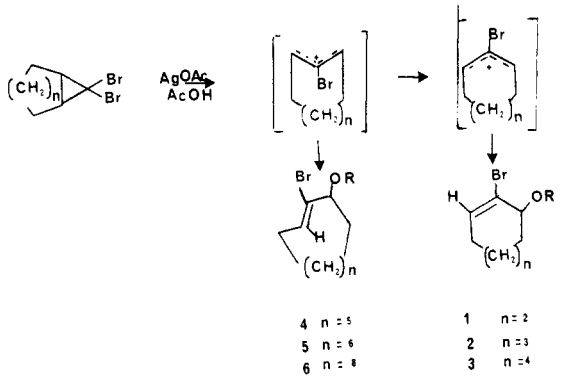

Table I. Chemical Shift and Coupling Constants of Olefinic and Methine Protons of 2-Bromo-2-cycloalkenyl Acetates

compd	ring size	olefinic H (mult, J values)	methine H
1a	7	6.42 (t, 6.5 Hz)	5.56 (br d, 7.5 Hz)
2a	8	6.21 (t, 8.5 Hz)	5.62 (dd, 11.0, 5.0 Hz)
3a	9	6.22 (t, 8.5 Hz)	5.74 (dd, 10.5, 5.0 Hz)
4a	10	6.26 (dd, 8.4, 6.4 Hz)	5.16 (dd, 9.2, 5.2 Hz)
5a	11	6.19 (dd, 9.0, 5.8 Hz)	5.17 (dd, 8.5, 5.0 Hz)
6a	13	6.10 (dd, 9.4, 5.4 Hz)	5.25 (dd, 10.2, 4.0 Hz)

assignment of the double-bond geometry appeared inconclusive. In a comprehensive study of the silver perchlorate catalyzed reactions of the dibromocarbene adducts of cycloheptene and cyclooctene, Reese and Shaw[2] provided an extensive discussion of methods available for assigning the stereochemistry of the carbon–carbon double bond in the products formed. In addition to using infrared spectroscopy and chemical reactivities, they employed NMR data on the relative chemical shifts of the methine proton in their alcohols to assign the geometry of the carbon–carbon double bond. The signal of the methine proton in the E isomer was reported to occur 0.3–0.75-ppm downfield from that of the corresponding Z isomer,[2] but since the geometric isomers of **5a** and **6a** were unknown, we were unable to use the relative chemical shift of the methine protons in assigning the geometry of the double bond. Furthermore, since changes in the ring size of these compounds markedly alter their conformations, it was possible that these changes would also affect the relative chemical shifts of the methine proton. Loozen et al.[6] suggested that the geometry of the double bond in various 2-substituted 2-cycloalkenols could be assigned by NMR from the multiplicity of the signal from the olefinic proton. They found that the proton in the E isomers showed a triplet pattern while in Z isomers the pattern was a doublet of doublets.

In order to assign the geometry of the double bond in **4a**, the compound was hydrolyzed by using *Rhizopus nigricans*[5] and the NMR data for the resulting alcohol were compared with literature data.[2,6] The comparison indicated that the alcohol had previously been assigned a Z geometry. However, the assignment was questionable since the reported pattern of the olefinic proton was a triplet. If Loozen et al. were correct in assigning the geometry of the double bond from the pattern of the olefinic proton, an E assignment was in order, but the relative chemical shifts of the methine proton in the two isomers requires a Z geometry. Thus, different geometric assignments can be made depending upon whether the chemical shift differences of the methine proton or the pattern of the olefinic proton were used. Therefore, to resolve this uncertainty a new approach was developed.

Table II. Summary of ^3J(C–H) Coupling Constants

compd	ring size	stereochemistry of olefin	^3J(C–H), Hz	geometry of C–H couplings
1a	7	E	8.8	trans
2a	8	E	8.5	trans
3a	9	E	8.9	trans
4a	10	Z	5.0	cis
5a	11	Z	4.7	cis
6a	13	Z	4.9	cis

In reviewing the literature on long-range proton–carbon coupling constants, Hansen[7] has indicated that three-bond couplings have been used in studies of the conformation of amino acids. These couplings are sensitive to the substitution pattern, the electronegativity of the substituents, their position along the coupling path, and the geometric relationship of the atoms in question. Vogeli and von Philipsborn[8] have shown that the numerical value of trans couplings (^3J(C–H)) (see top of Figure 1a) are larger than those of cis couplings between the same substituents (Figure 1b). Thus, in our series of compounds an E olefin should exhibit a large proton–carbon coupling constant. While the size of the long-range proton–carbon coupling constant (olefinic proton and the carbon bearing an acetoxy group) could in principle establish the geometry about the double bond, the measurement has been difficult to make by conventional techniques. Recently, however, Bax and Freeman[3] reported a new NMR technique that is specifically designed to facilitate such measurements. This socalled selective proton flip experiment, a low power 180° proton pulse is employed to invert selectively, all resonance lines of a particular multiplet (olefinic proton in these compounds). In the resulting two-dimensional spectrum, resonances from ^{13}C nuclei that are not coupled to the olefinic proton appear as singlets, while the resonances from ^{13}C nuclei which are coupled with J values of 0 to 25 Hz show as doublets in the F1 dimension of the 2D NMR spectrum. The method is sensitive, since nuclear Overhauser enhancement is obtained and the carbon resonances appear as either singlets or doublets. Moreover, with this method it is unnecessary to assign the many long-range proton–carbon coupling constants present in ^1H-coupled ^{13}C spectra thus providing tremendous simplification. The observed patterns for the E olefin and the Z isomer are shown in Figure 1.[9] Values of the proton–carbon coupling constants (Table II) demonstrate that for the olefins bearing a bromine atom, cis-^3J(C–H) varies from 4.7 to 5.0 Hz, while the trans value varies from 8.5 to 8.9 Hz. These values are consistent with the work of Vogeli and von Philipsborn and require a Z geometry for our 2-bromo-2-cyclodecenols in agreement with the earlier assignment. Since there is no overlap in the numerical values for ^3J(C–H) coupling constants in the E and Z isomers, information on the size of these coupling constants can be used to assign the geometry of trisubstituted olefins. The numerical values of these coupling constants in olefins with different substituents may differ somewhat from those reported here.[11]

(6) (a) Loozen, H. J. J.; Robben, W. M. M.; Richter, T. L.; Buck, H. M. *J. Org. Chem.* **1976**, *41*, 384. (b) Loozen, H. J. J.; de Haan, J. W.; Buck, H. M. *J. Org. Chem.* **1977**, *42*, 418.

(7) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175.

(8) Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617.

(9) During a study of the chiroptical properties of *p*-bromobenzoates of these allylic alcohols, it became necessary to assign the absolute stereochemistry of (+)-**5b**. An X-ray crystallographic analysis of the camphanate ester confirmed the trans geometry of the double bond in **5a**.[1]

(10) Sandler, S. R. *J. Org. Chem.* **1967**, *32*, 3876.

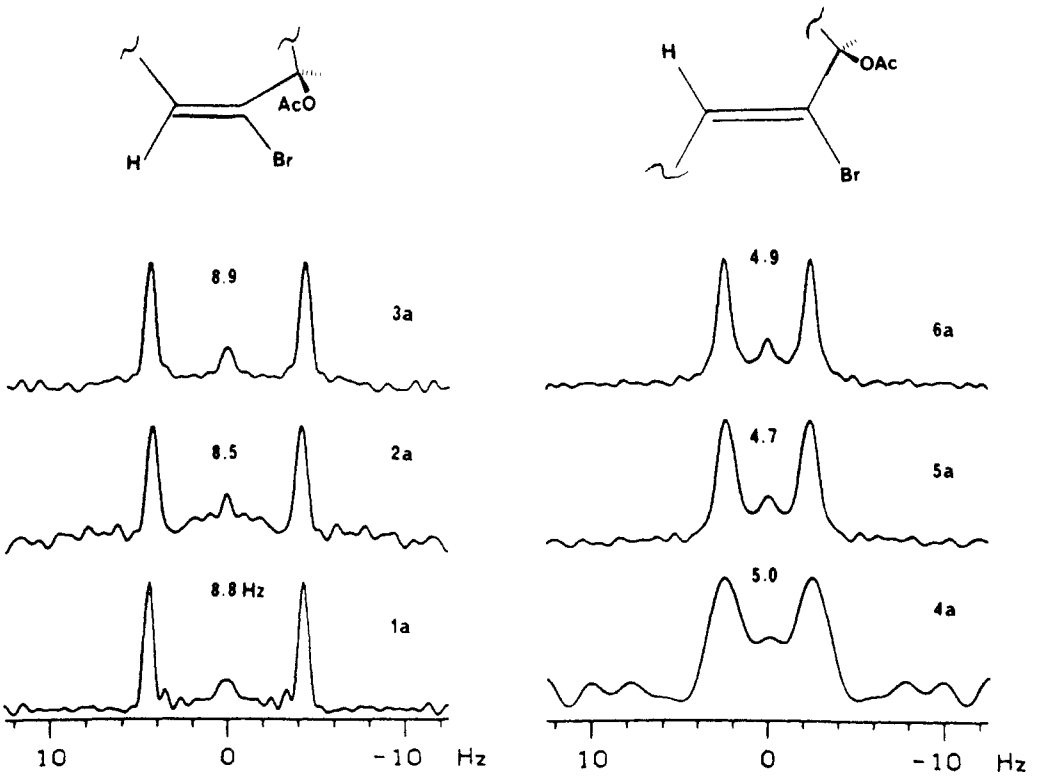

Figure 1. The relation between the geometry about the double bond and the size of ^3J(C–H). Each of the doublets represents a cross-section through the 2D selective proton-flip NMR spectrum, taken parallel to the F_1 axis at the F_2 frequency of the brominated olefinic carbon. The measuring times for the 2D spectra was approximately 1 h each.

Table III. Comparison of ^{1}H Chemical Shift Values (ppm) for 2b, 3b, and 4b with Literature Values (Coupling constants are given in hertz)

proton	*E* isomer		*Z* isomer
		2b	
methine	4.71 (dd, J = 10, 5)[6]	4.65 (bd, J = 10)	4.18 (dd, J = 5, 10)[6]
olefinic	6.21 (t, J = 8.5)	6.17 (t, J = 9.5)	6.11 (dd, J = 4.5, 10.5)
		3b	
methine	4.71 (dd, J = 5, 10)	4.72 (dd, J = 7.5, 8.5)	4.18 (dd, J = 5, 10)
olefinic	6.18 (t, J = 11)	6.17 (t, J = 9.0)	6.11 (dd, J = 5, 10)
		4b	
methine	4.82 (t, J = 8)[6]	4.12 (br m)	4.18 (dd, J = 9, 5)[6]
olefinic	5.98 (dd, J = 12, 6)	6.21 (dd, J = 6.4, 7.6)	6.24 (t, J = 9)
methine	4.67 (dd, J = 6, 9)[2]		4.07 (dd, J = 5, 8)[2]
olefinic	5.86 (dd, J = 5, 12)		6.18 (t, J = 8)

Discussion

The early studies[2,6] of silver ion promoted reactions of dibromocyclopropane derivatives were done at a time when there was considerable interest in concerted reactions. The reaction conditions employed by Reese and Shaw and others generated the less stable *Z* double-bond isomers and were therefore consistent with expectations for concerted reactions. Several compounds prepared by Loozen et al.[6] were assigned as *Z* primarily upon these expectations. However, an examination of NMR data published by these authors reveals inconsistencies between the splitting pattern of the olefinic proton and the assigned geometries about the double bond. Data on ^3J(C–H) coupling constants could be used to verify the earlier assignments.

Studies of Loozen et al.[6] and Shaw and Reese[2] demonstrated clearly that both *E* and *Z* isomers are formed from dibromobicyclo[7.1.0]decane; the results were best explained by assuming formation of intermediate free cations that could isomerize ($Z \rightarrow E$) or react with nucleophiles (see Scheme I). Furthermore, Sandler[10] reported that the same product, a *trans*-pentadiene, is formed from the reaction of two isomeric 1,1-dibromo-2,3-dimethylcyclopropanes with silver acetate in acetic acid, but oddly enough the logical inferences of this observation were not pursued. While the importance of this observation was not apparent at the start of our studies, it is entirely consistent with the postulate that these silver acetate and acetic acid catalyzed reactions probably proceed via free cations rather than via concerted reactions. Although our reaction conditions differ from those employed by Sandler, Shaw and Reese, and Loozen et al., these authors also have employed polar solvents. Therefore, the differences in the geometry of the cyclooctene and cyclononene derivatives formed in their studies and ours probably do not reflect different reaction mechanisms but rather may arise only from differences in the rates of the isomerization of the *Z* cation and the reaction rates of each cation with acetate. The *Z* geometries of the 11- and 13-membered 2-cycloalkenyl acetates also differ from that anticipated for a concerted reaction where the predominant isomer should have been the (*E*)-2-bromo-2-cycloalkenyl acetate. All our

(11) Highet[12] has recently described a procedure for obtaining these coupling constants with a simpler spectrometer.

observations are consistent with the postulate that the reaction rate of acetate with the carbocation is relatively slow in comparison with that by which the initially formed ion isomerizes to the more stable one. Calculations and experimental data on the heats of hydrogenation[13] indicate that cyclic cis olefins with nine or fewer carbons are more stable than the corresponding trans isomer. For cyclodecene and larger cyclic olefins the trans compound is the more stable. Our results on the geometry of the allylic acetate formed in these reactions as a function of ring size parallel the calculated and experimentally observed stabilities of the most stable cyclic olefins.

Conclusion

This study has shown that is is possible to control the stereochemistry of the eight- and nine-membered olefins formed from silver ion promoted solvolyses of the same intermediates by modifying the reaction conditions. Our results suggest that these solvolyses yield the most stable cycloalkenes. Three-bond proton–carbon coupling constants, obtained using the selective proton-flip experiment, have been shown to permit a facile assignment of the geometry of trisubstituted olefins. Since three-bond proton–carbon coupling constants have been shown to be useful for stereochemical assignments increased use of this NMR technique may be anticipated.

Experimental Section

EI–mass spectra were obtained by the NIH microanalytical laboratory. ^{1}H NMR spectra were collected on a Varian H-220 spectrometer, and ^{13}C NMR spectra were measured with a Nicolet 270 spectrometer (67.8 MHz). $CDCl_3$ was used for measuring ^{1}H NMR spectra and acetone-d_6 for ^{13}C NMR spectra.

Dibromocyclopropane derivatives were prepared by the procedure of Skottebol and Solomon.[4] General procedure for silver ion catalyzed solvolysis: An acetonitrile solution (5 ml) of the dibromo compound (5 mmol) was heated in the presence of 1.1 equiv of AgOAc and 1 mL of AcOH on a steam bath for 2 h. The solution was filtered and the precipitate washed with ether. The combined filtrates were washed with aqueous $NaHCO_3$, dried, and concentrated. The crude acetates were purified by column chromatography on silica gel.

(*Z*)-2-Bromo-2-cyclodecen-1-yl Acetate (4a). Cyclononene was prepared from cyclononenone (5 g) by reduction with sodium borohydride in methanol to yield cyclononanol, which was dehydrated at 170 °C, by heating with 85% H_3PO_4 for 1 h. The reaction mixture was cooled, diluted with water, and extracted into hexane. The hexane solution was passed through silica gel to remove polar impurities. The crude olefin (3.17 g) was used to prepare dibromobicyclo[7.1.0]decane (2.48 g, bp 129–134 °C/2.6 torr) by treatment with potassium *tert*-butoxide and bromoform as described by Skottebol and Solomon.[4] Solvolysis of the dibromobicycloalkane with AgOAc, MeCN, and AcOH as described above yielded, after chromatography on silica gel, 731 mg of **4a**: colorless oil; EI–MS, found 195.1384 ($C_{12}H_{19}O_2$, M^+ – Br); ^{1}H NMR 1.06–1.84 (m, 12 H), 2.08 (s, 3 H), 2.06–2.23 (m, 1 H), 2.25–2.45 (m, 1 H), 5.16 (dd, J = 5.2, 9.2 Hz, 1 H), 6.26 (dd, J = 6.4, 8.4 Hz, 1 H).

(*Z*)-2-Bromo-2-cycloundecen-1-yl Acetate (5a). Cyclodecene was prepared by heating cyclodecanol (obtained from sodium borohydride reduction of the ketone) with 85% H_3PO_4 at 170 °C for 1 h. The crude olefin was isolated and reacted with potassium *tert*-butoxide and bromoform as described above. Solvolysis of the crude dibromobicyclo[8.1.0]undecane as described above yielded after chromatography a sample of pure **5a**: colorless oil; EI–MS found 209.1525 ($C_{13}H_{21}O_2$, M^+ – Br); ^{1}H NMR 1.06–1.88 (m, 14 H), 2.09 (s, 3 H), 2.23 (m, 1 H), 2.48 (m, 1 H), 5.17 (dd, J = 8.5, 5.0 Hz, 1 H), 6.19 (dd, J = 9.0, 5.8).

(*Z*)-2-Bromo-2-cyclotridecen-1-yl Acetate (6a). Commercial *trans*-cyclododecene was used in the reaction sequence described above to prepare (*E*)-2-bromo-2-cyclotridecen-1-yl acetate (**6a**): colorless oil; EI–MS found 237.1857 ($C_{15}H_{25}O_2$, M^+ – Br); ^{1}H NMR 1.12–1.53 (m, 15 H), 1.57–1.78 (m, 2 H), 1.81–1.99 (m, 1 H), 2.06 (s, 3 H), 2.09–2.25 (m, 1 H), 2.28–2.47 (m, 1 H), 5.25 (dd, J = 4.0, 10.2 Hz, 1 H), 6.10 (dd, J = 9.4, 5.4 Hz, 1 H).

Acknowledgment. We thank Dr. Robert J. Highet for valuable discussions.

Registry No. 1, 14310-05-5; 2, 100206-51-7; 3, 100296-00-2; 4, 100206-52-8; 5, 100206-53-9; 6, 100206-54-0; AgOAc, 563-63-3; 7,7-dibromobicyclo[4.1.0]heptane, 2415-79-4; 8,8-dibromobicyclo[5.1.0]octane, 7124-41-6; 9,9-dibromobicyclo[6.1.0]nonane, 1196-95-8; 10,10-dibromobicyclo[7.1.0]decane, 36262-23-4; 11,11-dibromobicyclo[8.1.0]undecane, 64480-09-7; 13,13-dibromobicyclo[10.1.0]tridecane, 17301-57-4; cyclononenone, 100206-56-2; cyclononanol, 24469-56-5; cyclononene, 3618-11-9; cyclodecenone, 100206-55-1; cyclodecanol, 1724-39-6; cyclodecene, 3618-12-0; *trans*-cyclododecene, 1486-75-5.

(12) Highet, R. J. *J. Org. Magn. Reson.* **1984**, *22*, 136.
(13) (a) Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133. (b) Ermer, O.; Lifson, S. *Ibid.* **1973**, *95*, 4121. (c) Allinger, N. L.; Sprague, J. T. *Ibid.* **1972**, *94*, 5734.

Reinterpretation of Two Degradations of (–)-Albene

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The natural product (–)-albene, a tricyclic $C_{12}H_{18}$ olefin first isolated in 1962 from *Petasites albus*,[1] was recognized in 1972 to be one of four stereoisomers of 2,6-dimethyltricyclo[5.2.1.0^{2,6}]dec-3-ene.[2] An attempt to differentiate among these four possibilities through two degradative reaction sequences led to the conclusion that (–)-albene should be represented by structure I.[2]

Direct achiral comparisons by proton NMR and infrared spectroscopy demonstrated that *endo*-camphane (XII) derived from (–)-albene through the reactions outlined in Scheme I was structurally identical with authentic *endo*-camphane prepared from (+)-camphene.[2]

The chiral ketone albanone, formulated as V in Scheme I, was converted in three steps to a ketonitrile (Scheme II). The product was assigned structure IX, for it exhibited an ORD curve with negative Cotton effect at 286 nm, while authentic (1*S*)-(+)-camphenilone derived from (+)-camphene showed a positive and somewhat more intense Cotton effect at 280 nm,[2,3] indicative of a minor image relationship between the norcamphor units in the two compounds. Thus the 1*R* absolute stereochemistry was inferred for IX, and (–)-albene was assigned structure I, with absolute stereochemistry implied.[2]

An initial reservation about the photochemical decarbonylation of Scheme I was allayed through a stereorational synthesis of albanone;[4] it and the two degradations were taken as reliable grounds for assigning both relative and absolute stereochemistry for (–)-albene[5] until 1977 when Kreiser and his collaborators[6–10] demonstrated that albene must have endo methyl groups, a conclusion abundantly supported by others through three stereochemically unambiguous total syntheses of *dl*-albene.[11–13] The degradations of Schemes I and II must then be reconsidered and reformulated for a proper understanding.

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