effects of different degrees of hydrogen bonding, and other subtle structural differences between the local silicon environments of silica gel and silicate–water glass, these values are in reasonable qualitative agreement with the values found by ^{29}Si CP/MAS for silica gel. Thus, the −109.3-ppm shift is assigned to the silicon atoms bound to four other OSi< moieties at the silica gel surface, the −99.8-ppm resonance is assigned to the surface silicon atoms attached to three OSi< moieties and one OH group, and the −90.6-ppm resonance is assigned to surface silicon atoms bonded to two OSi< groups and two hydroxyl groups.

Corroboration of these assignments is obtained from the cross polarization relaxation data summarized in Figure 2. This figure shows the dependence of the amplitude of each of the three ^{29}Si NMR signals as functions of the cross polarization contact time under Hartmann–Hahn conditions in a single-contact experiment.[13] The initial rise on the left side of each plot is due to the growth of ^{29}Si magnetization due to cross polarization by protons (with a characteristic time T_{SiH}), and the later decline is a manisfestation of relaxation of the spin-locked ^{1}H magnetization (characterized by the ^{1}H spin–lattice relaxation time in the rotating frame, $T_{1\rho\mathrm{H}}$). The data were analyzed by a least-squares treatment based on a previously reported theory for the case in which the abundance of protons is much greater than that of the nuclide being cross polarized (4.7% natural abundance for ^{29}Si).[18] The results are summarized in Table I.

From Table I, we see that the proton $T_{1\rho}$ values measured from the three resonance peaks are essentially the same, within experimental error.[19] The more interesting parameter is the ^{1}H–^{29}Si cross polarization relaxation parameter, T_{SiH}. By far the largest value of T_{SiH} is for the peak at −109.3 ppm, which we have assigned to Si*(OSi<)$_4$; the Si* atom in this environment is removed by at least four bonds from the nearest hydroxyl proton.[20] The peaks assigned to (HO)$_2$Si*(OSi<)$_2$ and HOSi*(OSi<)$_3$ structures (at −90.6 and −99.8 ppm, respectively) have similar T_{SiH} values (2.3 and 2.9 ms) and correspond to silicon positions removed by two bonds from the nearest hydroxyl proton. The shorter of these two T_{SiH} values is assigned to the Si moiety with two hydroxyl groups attached, the longer with only one attached hydroxyl group. Thus, the assignments based upon chemical shift analogies agree with what one would derive from the cross polarization relaxation times.

In conclusion, the three peaks observed in the ^{29}Si CP/MAS spectra of silica gel can be assigned to particular silicon environments at the surface. This makes possible a variety of interesting studies of the influence of preparation methods on the structure of silica gel and of the nature of adsorption and covalent attachment of silica gel surfaces. Such studies are under way.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work under Grant No. CHE74-23980 and to Dr. V. J. Bartuska for invaluable instrumental assistance. We also gratefully acknowledge use of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. 78-18581, in obtaining ^{29}Si spectra of related liquid samples.

---

(18) M. Mehring, "High Resolution NMR Spectroscopy in Solids", Springer-Verlag, New York, 1976, p 138.

(19) In the least-squares and analysis for the Si*(OSi<)$_4$ data, the analysis was constrained by assuming that $T_{1\rho\mathrm{H}}$ must be a weighted average of $T_{1\rho\mathrm{H}}$ values for (HO)$_2$Si*(OSi<)$_2$ and HOSi*(OSi<)$_3$ because presumably these moieties represent the types of protons available for cross polarizing Si*(OSi<)$_4$; an average of 21 ms was used.

(20) There may be some contribution from silicon nuclei imbedded more deeply in the silica structure (at least five bonds from hydroxyl hydrogen), which would cause significant deviation from a single-exponential behavior.

Gary E. Maciel,* Dean W. Sindorf

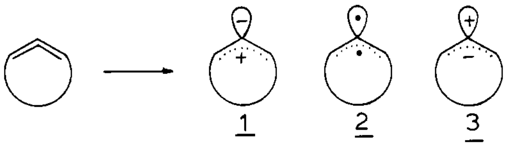
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Received August 8, 1980

Chirality as a Probe for the Structure of 1,2-Cycloheptadiene and 1,2-Cyclohexadiene

Sir:

An allene incorporated in a carbocyclic ring of nine or more carbons is relatively unstrained.[1] However, if the ring size is decreased, the linear perpendicular allene will be twisted and bent until at some point the energy gained by π bonding in the two double bonds should be insufficient to offset the increased strain. At that point the allene moiety would be expected to prefer a bent, planar structure with electrons distributed as in **1**, **2**, or **3**.[2] For unsubstituted 1,2-dienes, the concensus seems to be that eight- and seven-membered rings are sufficiently large to accommodate the strain of the twisted diene and therefore should prefer two double bonds, albeit certainly distorted and strained.[1] On the other hand, opinions on the preferred structure of singlet 1,2-cyclohexadiene are mixed. On the basis of extensive studies of its chemistry, Bottini[3] and co-workers prefer initial formation of a bent, twisted allene which rapidly isomerizes to the diradical, which is the active agent in both 2 + 2 and 2 + 4 cycloadditions.[3,4] They also contend that the species with electrons distributed as in **3** is responsible for some of the chemistry of this diene.[3] In contrast, Moore and Ward[5] and, more recently, Greenberg and Liebman[1] prefer **8** for the structure of 1,2-cyclohexadiene, a contention that has found support in an INDO–MO study by Dillon and Underwood.[2]



At this time we report experimental results that lead us to conclude that the species initially generated from dehydrohalogenation of both 1-bromocycloheptene[6-8] and 1-bromocyclohexene[3,4,9-12] are nonplanar and are therefore best represented as bent allenes. Our results also require that these are the species that are responsible for 2 + 4 cycloaddition to 1,3-diphenylbenzo[*c*]furan[7,9,10] and further suggest that, at around 80 °C, conversion of the nonplanar form of 1,2-cyclohexadiene to a symmetrical isomer (presumably **8**)[2] competes with its reaction with the allene trap. The latter probably is not the case for 1,2-cycloheptadiene.

Our strategy for probing this problem was based on the chirality that is inherent in the allene structures **6** and **7** but is absent in planar allene forms such as **8** and **9**. Starting materials for chirality studies were optically active 1-bromo-6-deuteriocyclohexene (**4**) and 1-bromo-7-deuteriocycloheptene (**5**), which were synthesized as shown in Schemes II and III (absolute configurations are unknown). Activity was introduced by reduction of the enones with lithium aluminum hydride–quinine complex.[13]

Base-induced elimination of HBr from **4** and **5** with potassium *tert*-butoxide in tetrahydrofuran[7,8] gave the desired intermediates. Enantiomeric enrichment was expected if nonplanar allenes **6** and **7** were initially formed because elimination of HBr and DBr, which

---

(1) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 126–30.

(2) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *92*, 779–87.

(3) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Tetrahedron* **1972**, *28*, 4883–904.

(4) Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* **1975**, *31*, 1997–2001.

(5) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469–74.

(6) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc.* **1961**, 143–4. *J. Chem. Soc.* **1962**, 2298–304.

(7) Wittig, G; Meske-Schuller, J. *Justus Liebigs Ann. Chem.* **1968**, *711*, 76–81.

(8) Bottini, A. T.; Frost, K. A., II; Anderson, B. R.; Dev, V. *Tetrahedron* **1973**, *29* (14), 1975–81.

(9) Wittig, G.; Fritze, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846.

(10) Wittig, F.; Fritze, P. *Justus Liebigs Ann. Chem.* **1968**, *711*, 82–7.

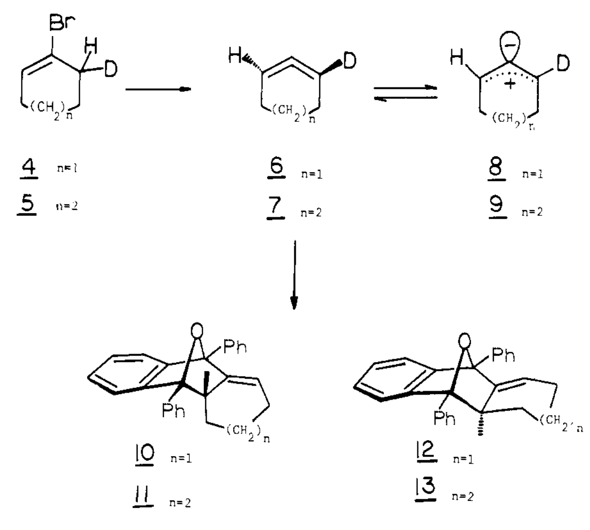
(11) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Tetrahedron Lett.* **1970**, 4753–6, 4757–60.

(12) Bottini, A. T.; Cabral, L. J.; Dev, V. *Tetrahedron Lett.* **1977**, 615–8.

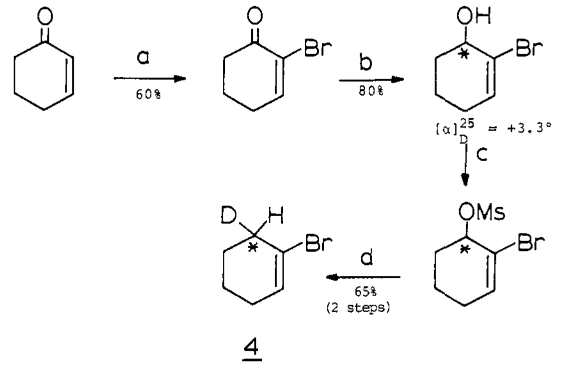
(13) Wynberg, H.; Marsman, B. *J. Org. Chem.* **1980**, *45*, 158–61.

0002-7863/80/1502-7607$01.00/0 © 1980 American Chemical Society

Scheme I

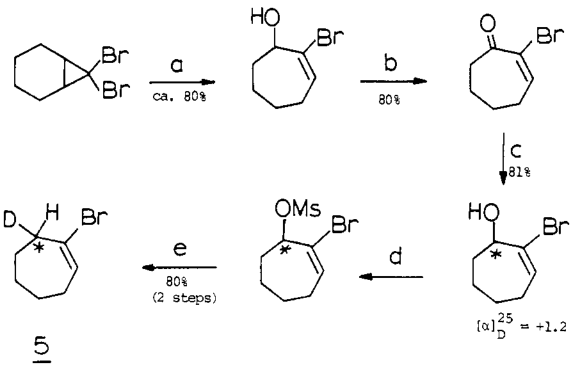


Scheme II[a]



[a] (a) Bromine, collidine.[19] (b) Quinine, $LiAlH_4$. (c) MsCl, NEt_3. (d) $LiAlD_4$.

Scheme III[a]



[a] (a) $AgClO_4$, acetone/water (9:1). (b) PCC. (c) Quinine, $LiAlH_4$. (d) MsCl, NEt_3. (e) $LiAlD_4$.

would give different enantiomers,[14] should occur at different rates. The intermediates were trapped with 1,3-diphenylbenzo[*c*]furan[7,9,10] to give **10**, **11**, **12**, and **13**.[15] All four adducts are chiral and should therefore show activity if the intermediates were active.[16]

Table I. Optical Activities of Adducts[a]

temp, °C	specific rotation $[\alpha]^{25}_{D}$, deg			solvent and time
	12 minor adduct	10 major adduct	11 major adduct	
53	+1.6 ± 0.11	−0.3 ± 0.09	+0.94 ± 0.06	THF, 20 h,[b] 2 h[c]
80	+0.3 ± 0.2	0.0 ± 0.11		diglyme, 6 h[b]
100	0.0 ± 0.06	0.0 ± 0.06	+0.69 ± 0.06	diglyme, 1 h,[b] 15 min[c]
140			+0.35 ± 0.1	diglyme, 10 min[c]

[a] For all reactions the same concentrations of all starting materials were used. [b] For 1-bromo-6-deuteriocyclohexene. [c] For 1-bromo-7-deuteriocycloheptene.

Optical activities of the four adducts (carefully chromatographed but not recrystallized) are given in Table I. From the results at 53 °C it is clear that both the initially formed and reacting intermediates from both **4** and **5** must be chiral and therefore cannot be adequately represented by intermediates with electrons distributed as in **1**, **2**, or **3** but are consistent with structures **6** and **7**. The effect of temperature on optical activity is also instructive. In the case of 1-bromocycloheptene, the optical activity drops off with an increase in temperature at a rate that is consistent with a simple temperature effect[17] on k_H/k_D. However, in the case of 1-bromocyclohexene, the loss of activity is much too rapid to be explained by this simple effect. We therefore suggest that in the range of 80 °C isomerization of **6** to **8** is competitive with trapping by 1,3-diphenylbenzo[*c*]furan; the unimolecular racemization is expected to be more sensitive to temperature than the competitive bimolecular Diels–Alder reaction. At this time we do not feel that such a racemization mechanism is required for 1,2-cycloheptadiene.[18]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.[20]

Supplementary Material Available: Accompanying Experimental Section with syntheses of compounds (4 pages). Ordering information is given on any current masthead page.

Metin Balci, W. M. Jones*
Department of Chemistry
University of Florida
Gainesville, Florida 32611

Received May 27, 1980

---

[14] This would be true only if the elimination is concerted. To our knowledge the mechanism of elimination from small-ring 1-halocycloalkenes has not been studied. However, it was a priori unlikely that it would be E1cb and this is confirmed by the results reported here. It may also be noted that concerted elimination *must* be cis; trans is sterically impossible.

[15] No cycloalkyne adducts were observed.

[16] Activity in the adduct is in reality a result of asymmetric induction in that an enantiomer of the allene should attack one face of the diene faster than the other.

[17] Shiner, V. J.; Smith, M. L. *J. Am. Chem. Soc.* **1961**, *83*, 593–8.

[18] Determination of the effect of changing the concentration of the diene on the activity of the adduct could, in principle, provide a less equivocal test for competitive unimolecular racemization and bimolecular cycloaddition. Unfortunately, to date, experimental difficulties have precluded applying this test to either **4** or **5**.

[19] Bouvell, F. G.; Wellman, K. M. *J. Org. Chem.* **1963**, *28*, 2544.

[20] We also acknowledge with gratitude the suggestion of Professor Ronald Breslow that chirality could be a way to probe the cycloheptatrienylidene–cycloheptatetraene question. The work reported here was an outgrowth of the latter which will be reported at a later time.

Macrocyclic Inclusion Complexes. Synthesis, Complexation, and X-ray Crystal Structures of Binuclear Cation Complexes of Dipyridine Crown Ethers[1]

Sir:

Over the past decade, a myriad of novel synthetic macrocyclic ligands have been designed to complex metal cations. Generally

---

[1] Presented in part at the "Symposium on Macrocyclic Ligands", held at the Institute of Inorganic Chemistry at the University of Basel, Switzerland, July 2–4, 1980.

0002-7863/80/1502-7608$01.00/0 © 1980 American Chemical Society