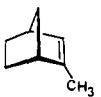

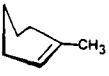
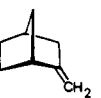



proportions of 95 and 4%. Ketone **6** probably arose by cleavage of a dioxetane precursor rather than by decomposition of the allylic hydroperoxide.¹² However, the first-formed hydroperoxide **7** underwent further reaction with singlet oxygen, but at a rate about five times slower than the initial one.¹³ After half the olefin had been consumed, 85–90% of the product consisted of **7**.

Although these reactions are smooth, their rates are governed by steric factors as comparison with the rates for 1-methylcyclopent-1-ene (**8**), 1-methylcyclohex-1-ene (**9**), and methylenecyclopentane (**10**) reveals. 2-Methylnorborn-2-ene reacts some 15 times more slowly than its flexible analog **8** and even more slowly than the cyclohexene **9**.^{14,17} In contrast, both 2-methylenenorbornane (**2**) and its nonbridged analog **10** exhibit

Table I. Relative Reactivities of Acceptors

Acceptor	Rel Rate ^a
1 	3.2
8 	115.0 ^b
9 	9.5 ^b
2 	1.0
10 	2.3

^a Calculated from acceptor disappearance (error $\pm 20\%$). ^b From ref 4a.

(12) (a) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); (b) P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970); (c) C. S. Foote and R. W. Denny, *ibid.*, **93**, 5162 (1971).

(13) The photooxidation of Δ^2 -cholesten-3 β -yl acetate follows the same course (W. Eisfeld, Ph.D. Thesis, University of Göttingen, 1965).

(14) The large difference in rate between **8** and **9** undoubtedly springs from differences in bond-angle strain (ref 15 and 16).

(15) E. W. Garbisch, S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

(16) R. Maurel and J. Tellier, *Bull. Soc. Chim. Fr.*, 4191 (1968).

(17) In comparing rates, allowance was made for the number of abstractable allylic hydrogens available.

similar rates which are half as fast as that of 2-methylnorborn-2-ene (**1**) (see Table I).

The interpretation of these findings leads to the following conclusions about the transition state (TS). (1) Access of singlet oxygen to either side of 2-methylnorborn-2-ene (**1**) is hampered relative to the reference olefin **8**, with hindrance being greater on the endo side as the composition of the kinetic product (exo:endo ratio of 66:1) clearly shows. (2) A corollary of point 1 is that the TS resembles the reactant (**1**) in that little double bond character develops between C-2 and the methyl carbon. (3) Although it is the relative steric environment about the double bond which steers the incoming singlet oxygen, nevertheless the steric exigencies are less severe than those experienced for typical one-step cyclic additions such as hydroboration or epoxidation¹⁸ where the exo:endo ratio is 200:1. Accordingly, the singlet oxygen-ene reaction passes through a "loose" cyclic transition state in which steric factors present in the reactant are determinative.¹⁹

Similar considerations should apply to 2-methylenenorbornane, but await confirmation by labeling studies.

Acknowledgments. We are indebted to the Swiss National Science Foundation for support of this project (No. 2.595.71).

(18) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(19) For an interesting parallel see: A. Nickon, V. T. Chuang, P. J. L. Daniels, R. W. Denny, J. B. DiGiorgio, J. Tsunetsugu, H. G. Vilhuber, and E. Werstiuk, *J. Amer. Chem. Soc.*, **94**, 5517 (1972).

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Reductive Dehalogenation of Alkyl Halides with Lithium Aluminum Hydride. A Reappraisal of the Scope of the Reaction

Sir:

Complex metal hydrides possess considerable versatility as selective reagents for the reduction of a wide variety of organic molecules.¹ In the particular case of the reductive dehalogenation of alkyl halides, lithium aluminum hydride (LiAlH_4) is commonly used for reactive substrates,² whereas recourse is made to organotin hydrides to effect reduction of substrates conventionally regarded as inert.³

A wealth of literature attests to the fact that LiAlH_4 behaves as a nucleophile and displaces or replaces halide in either an $\text{S}_\text{N}2$ or an $\text{S}_\text{N}1$ process depending on the substrate.⁴ We now present evidence to show that

(1) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956.

(2) L. F. Fieser and M. Fieser "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 587.

(3) A. K. Sawyer, Ed., "Organotin Compounds," Vol. 1, Marcel Dekker, New York, N. Y., 1971.

(4) (a) L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949); (b) E. L. Eliel, *ibid.*, **71**, 3970 (1949); (c) E. R. Alexander, *ibid.*, **72**, 3796 (1950); (d) D. J. Malter, H. J. Wotiz, and C. A. Hollingsworth, *ibid.*, **78**, 1311 (1956); (e) E. J. Corey, M. G. Howell, A. Borton, R. L. Young, and R. A. Sneen, *ibid.*, **78**, 5036 (1956); (f) G. K. Helmkamp and B. Rickborn, *J. Org. Chem.*, **22**, 429 (1957); (g) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **84**, 4876 (1962); (h) M. S. Newman, J. R. Le Blanc, H. A. Karnes, and G. Axelrod, *ibid.*, **86**, 868 (1964); (i) R. A. Appleton, J. C. Fairlie, and R. McCrindle, *Chem. Commun.*, 690 (1967); (j) L. A. Paquette and P. C. Storm, *J. Org. Chem.*, **35**, 3390 (1970).

LiAlH_4 reacts smoothly with supposedly inert compounds such as vinyl, bridgehead, and cyclopropyl halides to give their parent hydrocarbons in high yield.

We recently reported that vinyl halides as exemplified by the C-3 halo derivatives of 2-phenylbicyclo[3.2.1]oct-2-ene are hydrogenolyzed with LiAlH_4 .⁵ This appears to be a generality, as heating 3-bromobicyclo[3.2.1]oct-2-ene with LiAlH_4 in dimethoxyethane (DME) for 100 hr gave bicyclo[3.2.1]oct-2-ene in >80% yield.⁶ Similar treatment of 2-bromo-2-methylstyrene for 24 hr resulted in an 81% conversion to 2-methylstyrene.⁸

Bridgehead halides were also found to be remarkably susceptible to reduction. 1-Bromoadamantane (**1**) on exposure to LiAlH_4 in boiling ether for 18 hr gave adamantane as the sole product in 80% yield. It could be argued that **1** represents the frontier at which bridgehead carbenium ion can achieve measurable stability,⁹ and that hydride anion displaces bromide in the corresponding contact ion pair **2** which is in equilibrium with its covalent partner **1**. Nevertheless, that exemplar of inertness, namely 1-bromotriptycene,¹⁰ on reaction with LiAlH_4 in DME for 48 hr was also converted to the parent hydrocarbon in equally high yield.

Lastly we come to cyclopropyl halides. These compounds under $\text{S}_{\text{N}}1$ conditions often open to allylic derivatives¹¹ while $\text{S}_{\text{N}}2$ processes are geometrically prohibited.¹² Here again we find that LiAlH_4 easily effects substitution of halide by hydrogen without rupture of the ring. 7,7-Dibromobicyclo[4.1.0]heptane (**3**) on treatment with LiAlH_4 gave the anti and syn monobromo (**4** and **5**) derivatives together with the fully reduced hydrocarbon **6** (Table I). Treatment of either **4** or **5** with additional LiAlH_4 furnished **6**.

Table I. LiAlH_4 Reduction of Some Cyclopropyl Halides **3**, **7**, and **11**

Reactant	Product ratio, %			Anti/syn ratio	Overall yield, %	Reaction time, hr
	Anti	Syn	Parent			
3	4	5	6			
	23.2	70.0	6.8	0.33	73.0	18 ^b
7	8	9	10			
	58.5	29.2	12.2	2.0	82.5	27 ^c
11	12	13	14			
	45.8	22.9	7.0	2.0	80.0	45 ^b
	8	9	7 + 10			
	13.3	8.6	2.4	1.6		

^a In all reductions a fourfold molar excess of LiAlH_4 was used.

^b In ether as solvent. ^c THF, as unreactive in ether.

(5) C. W. Jefford, A. Sweeney, and F. Delay, *Helv. Chim. Acta*, **55**, 2214 (1972).

(6) Reduction of phenyl halides has been reported using LiAlH_4 in tetrahydrofuran (ref 7).

(7) (a) G. J. Karabatsos and R. L. Shone, *J. Org. Chem.*, **33**, 619 (1968); (b) P. Olavi, I. Virtanen, and P. Jaakola, *Tetrahedron Lett.*, 1223 (1969); (c) H. C. Brown and S. Krishnamurty, *J. Org. Chem.*, **34**, 3918 (1969).

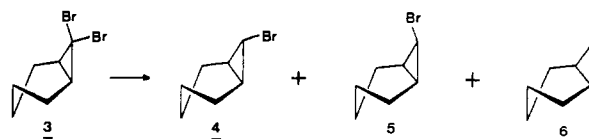
(8) We thank A. Sweeney for running this experiment.

(9) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

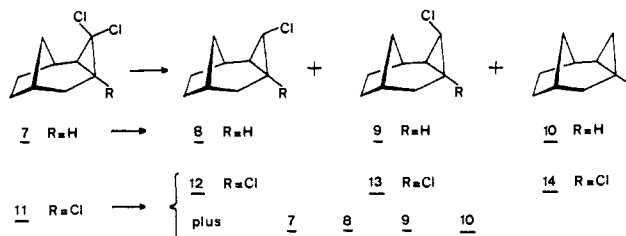
(10) C. W. Jefford, R. McCreddie, P. Müller, and B. Siegfried, *J. Chem. Educ.*, **48**, 708 (1971).

(11) (a) C. W. Jefford, *Chimia*, **24**, 357 (1970); (b) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968).

(12) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).



Interestingly enough, the structurally related, but rigid molecule, 3,3-dichlorotricyclo[4.2.1.0^{2,4}]nonane (**7**) underwent the same reductive course to give the anti and syn monochloro derivatives **8** and **9**, but with preponderant formation of the less encumbered isomer **8**.



Confirmation of the ease of reduction of both cyclopropyl and bridgehead halides together with an indication of their relative reactivities was provided by the behavior of the trichloro derivative **11**.¹³ The action of LiAlH_4 in ether on **11** gave all seven expected products (**12–14** and **7–10**) (see Table I).¹⁵ Inspection of the table reveals that geminal chlorine is far more reducible than the bridgehead chlorine. Moreover, the inverse anti-syn ratios exhibited by the bicyclic and tricyclic compounds (**3** vs. **7** and **11**) indicate that steric accessibility of LiAlH_4 to the geminal dihalo grouping is not solely responsible for the configurational outcome at the reduced carbon.

What is the significance of these results? Firstly, LiAlH_4 strikingly parallels the macroscopic chemical behavior of organotin hydrides.^{16,18} Thus, for reductions like those cited here, organotin hydrides offer no advantage, whereas their cost is high and their use bothersome.¹⁹ A corollary is that organotin hydride reductions of alkyl halides without radical initiator may not necessarily involve radical intermediates as has so often been inferred.^{18a}

Secondly, the mechanistic role of LiAlH_4 itself is questionable. It undoubtedly reacts as a nucleophile, but how? For the moment, we consider two possi-

(13) Compounds **7** and **11** were prepared by the addition of dichlorocarbene to bicyclo[3.2.1]oct-2-ene and its 3-chloro derivative. For the general method see ref 14. Details of these syntheses will be published shortly (work of F. Delay).

(14) (a) C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. Le Gras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971); (b) C. W. Jefford, S. Mahajan, R. T. Medary, W. Wojnarowski, B. Waegell, and K. C. Ramey, *Chem. Commun.*, 310 (1967).

(15) Compounds **4–6**, **8–10**, and **12–14** were isolated by preparative gas-liquid chromatography and the structures assigned from consideration of their nmr spectra. Anti epimers were easily distinguished from their syn forms by the magnitude of the cis and trans vicinal proton coupling constants.

(16) (a) Organotin hydrides reduce vinyl bromides in high yield, whereas bridgehead halides react poorly to give yields of usually less than 10% of the parent hydrocarbon (ref 17).

(17) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 764 (1964).

(18) (a) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); (b) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); (c) S. J. Cristol, R. M. Segueira, and C. H. DePuy, *J. Amer. Chem. Soc.*, **87**, 4007 (1965); (d) W. E. Barnett and R. F. Koebel, *Chem. Commun.*, 875 (1969).

(19) Tri-*n*-butyltin hydride (TBTH) is some 14 times more expensive than LiAlH_4 from which it is usually prepared (*cf.* Alfa Catalog, 1971). Moreover, disposal of the tin residues after reaction is not easy (see G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 369 (1957)).

bilities: (i) either hydride attacks the halogen atom directly to yield the appropriate carbanion which then can capture environmental hydrogen, or (ii) less plausibly, the Lewis acid properties of LiAlH_4 engender the formation of what is tantamount to an incipient carbenium ion which is then attacked as soon as it is formed by hydride in a front-side manner.²⁰

Experiments are under way to decide between these mechanisms. From the synthetic standpoint, it can be predicted that LiAlH_4 will, with the correct choice of solvent, effect reductive dehalogenation of any alkyl halide regardless of functional type.

Acknowledgments. We are indebted to K. Mislow and P. Schleyer for pertinent comments and a referee for helpful suggestions. We thank U. Burger and F. Kloeti for obtaining the nmr and mass spectral data.

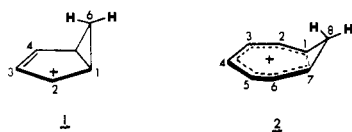
(20) A similar mechanism has been proposed to account for the stereospecific reduction of *gem*-bromofluorocyclopropanes (H. Yamana, T. Yagi, K. Teramura, and T. Ando, *Chem. Commun.*, 380 (1971)).

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Homotropylium-4-d Ion. On the Energy Barrier to a Non-Least-Motion Circumambulatory Rearrangement¹

Sir:

Orbital symmetry allowed² degenerate rearrangements, in which a cyclopropane ring suprafacially circumambulates the periphery of a cyclic polyene³ or polyenylium ion,⁴ should show alternating stereochemical behavior. In the cation series, the migrating group should invert configuration in $1,n$ rearrangements ($n = 4, 8, 12 \dots$) and retain it in $1,m$ rearrangements ($m = 2, 6, 10, 14 \dots$). The $1,n$ rearrangements, which use a "least-motion" pathway with relatively little distortion of normal atomic coordinates, should be stereochemically facile, and a number of examples in the bicyclo[3.1.0]hex-3-enyl system ($n = 4$),⁴ including the parent ion **1**,^{4f} are known. The "allowed" migration in **1** preserves the original endo and exo nature of the 6-hydrogens at each step and occurs with $\Delta F^\ddagger = 15$ kcal/mol.^{4f}



(1) We thank the National Institute of General Medical Sciences for a grant (No. GM 16962-02) in partial support of this work.

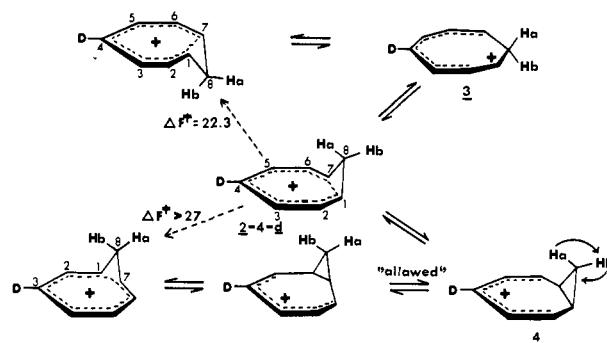
(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, pp 124-140.

(3) (a) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966); *Rec. Chem. Progr.*, **27**, 139 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); (c) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(4) (a) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968); (b) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968); (c) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970); (d) V. H. Koptuyug, L. I. Kuzubova, I. S. Isaev, and V. I. Manatyuk, *ibid.*, 389 (1969); (e) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); (f) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

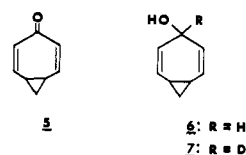
The next higher vinyllog, homotropylium ion (**2**),⁵⁻⁷ is a $1,m$ system, rearrangement of which by a suprafacial "allowed" pathway would require an interchange of the 8-endo and 8-exo hydrogens at each step. Winstein, *et al.*,^{5,8} already have noted that **2-8-endo-d** upon storage at $32-37^\circ$ is converted with $\Delta F^\ddagger = 22.3$ kcal/mol to an equimolar mixture of **2-8-endo-d** and **2-8-exo-d**. Although this equilibration was ascribed⁵ to a conformational ring inversion passing through the planar, classical cyclooctatrienyl cation **3**, it is evident that the "allowed" circumambulatory reaction would provide an alternative account of the observation (Scheme I, ΔF^\ddagger values in kilocalories per mole). A

Scheme I



ring-labeling experiment is required to distinguish the rearrangement (endo-exo interchange coupled with label scrambling) from the conformational inversion (endo-exo interchange only). The present paper reports the preparation of homotropylium-4-d ion and the minimum value $\Delta F^\ddagger > 27$ kcal/mol for its rearrangement.

4,5-Homotropone (**5**)⁹ is reduced in high yield to the dienol **6** at 0° with diisobutylaluminum hydride¹⁰ or to the corresponding 4-deuterio analog **7** with diisobutyl-



aluminum deuteride.¹¹ The dienol, upon extraction from CD_2Cl_2 with $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ at -120° ¹² or upon treatment with concentrated H_2SO_4 at -78° and slow warming to room temperature, gives stable preparations of homotropylium ion (**2** from **6** and **2-4-d** from **7**). The nuclear magnetic resonance (nmr) spectrum of **2** so obtained is the same as that previously

(5) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

(6) (a) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); (b) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).

(7) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

(8) For a similar observation on 8-chlorohomotropylium ion, see G. Boche, W. Hechtel, H. Huber, and R. Huisgen, *J. Amer. Chem. Soc.*, **89**, 3344 (1967).

(9) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969).

(10) Attempted reductions with LiAlH_4 give products resulting largely from saturation of the olefinic bonds. Comparable experiences have been reported by K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).

(11) Prepared from diisobutylaluminum chloride and LiD [cf. G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **618**, 267 (1958)].

(12) We thank Dr. Pierre Vogel for instruction in this procedure.