to assign stereochemistry in **5a** by chemical means.

It is interesting to speculate about the origin of the apparent stereoselectivity in this reaction. For a concerted process, two possibilities are allowed based on the configuration of the intermediate alkoxyallylic cation and the mode of cycloaddition: extended (exo) or compact (endo). These possibilities are illustrated in Figure 1. Inspection of molecular models suggests that **7** represents the best transition state structure for the reaction. The incipient five-membered ring in **8** is in a boatlike conformation, resulting in a severe transannular interaction between hydrogens on the methylene group next to the furan ring and on the angular ethyl group. While the high stereoselectivity supports a concerted process, a stepwise mechanism has not been ruled out. Moreover, the configurational stability of the heavily substituted allylic cations, the probable intermediates in the work, is open to some question, leading to further uncertainties regarding the specific course of the reaction.[12] Experiments designed to deal with these uncertainties are in progress.[13]

In summary, we have found that certain 2-alkoxyallylic sulfones serve as efficient precursors to 2-alkoxyallylic cations or their functional equivalents. These intermediates undergo intramolecular 4 + 3 cycloaddition with furans in high yield. Quaternary centers are formed with impressive ease. The cycloadducts are formed stereoselectively and bear alkyl and oxygen functionality in locations shared by various guiane and pseudoguiane sesquiterpenes. This methodology may therefore be of use in the total synthesis of these and other natural products. Further progress will be reported in due course.[14,15]

Acknowledgment. We are grateful to the National Science Foundation for partial support of the NMR (Grant PCM-8115599) and MS (Grant PCM-8117116) facilities at the University of Missouri. Thanks to Professor Elmer O. Schlemper for acquisition of the X-ray data and to Dr. Hanna Gracz and Dale Sanson for high-field NMR data.

Supplementary Material Available: Tables of positional parameters, thermal parameters, interatomic distances, interatomic angles, and dihedral angles for non-hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

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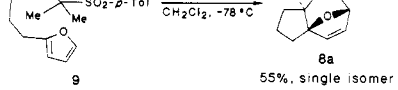
(13) We have recently found that treatment of **9** as a mixture of isomers with $TiCl_4$ results in the formation of **5a** in 55% yield as the only cycloaddition adduct. However, we have not yet succeeded in separating the isomers of **9**.



(14) All new compounds exhibited acceptable ^1H NMR and IR spectra as well as satisfactory combustion or HRMS data. All yields are for chromatographically purified materials.

(15) This work was presented in part at the 196th National Meeting of the American Chemical Society, Los Angeles, CA; ORGN 158.

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Another Challenge to the Validity of the Use of Cyclizable Probes as Evidence for Single-Electron Transfer in Nucleophilic Aliphatic Substitution. The Reaction of $LiAlH_4$ with Alkyl Iodides

Summary: It has been found that a recent report challenging the use of cyclizable radical probes as evidence for single-electron transfer in the reaction of $LiAlH_4$ with alkyl iodides is itself based on an invalid model system.

Sir: We[1] and others[2] have used cyclizable radical probes in a number of studies to obtain evidence for the intermediacy of radicals in nucleophilic aliphatic substitution. The mechanism that we proposed in 1984 for this reaction is shown in Scheme I.[1d,4,5]

Recently Newcomb et al.[6,7] have reported that the lack of cyclization of **1b** (Scheme I) on reaction with $LiAlH_4$ "indicates that SET from the reducing agent to the halide to give a free radical is not an important process" and that "these reductions are best explained as conventional nucleophilic displacements of halide by hydride." The reason given for the lack of cyclization product (**7**, **8**) is that radical **6b**, because of its stability, does not participate in rapid halogen exchange with **1b** to produce **9b**, therefore eliminating what he claims to be the only route to cyclized product. It was concluded that when halogen atom exchange ($\mathbf{6} \xrightarrow{1} \mathbf{9}$) does not take place, cyclized product is not produced, and hence when other probes used by ourselves and others resulted in cyclization, all cyclized product was a result of reduction of **9**. It was also suggested that the initial radical (**3**) originates from impurities,[5] hence eliminating our suggestion that $LiAlH_4$ is the one-electron donor that initiates the process ($\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{3}$). Three years prior to the Newcomb report, we had already reported that the formation of **8** via the process $\mathbf{6} \xrightarrow{1} \mathbf{9} \rightarrow \mathbf{8}$ is important in the reaction of $LiAlH_4$ with alkyl iodides but that some of **8** is also formed directly from **6**.[1d,7] More recently, we have provided even more convincing evidence to support this point.[1i] It is important to note that we have never reported the formation of cyclized product when $LiAlH_4$ is allowed to react with an unhindered primary alkyl iodide probe in THF, but only with a hindered one (neopentyl type). Therefore, the lack of formation of cyclized product in the reaction of $LiAlH_4$ with **1b** in THF was not a surprise to us.

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(2) (a) Chung, S. J. *J. Org. Chem.* **1980**, *45*, 3513. (b) Singh, P. R.; Nigam, A.; Kurona, J. M. *Tetrahedron Lett.* **1980**, *21*, 4753. (c) Lee, K. W.; Flippo, J. *Organometallics* **1983**, *2*, 906. (d) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098.

(3) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Tetrahedron Lett.* **1981**, *22*, 3729.

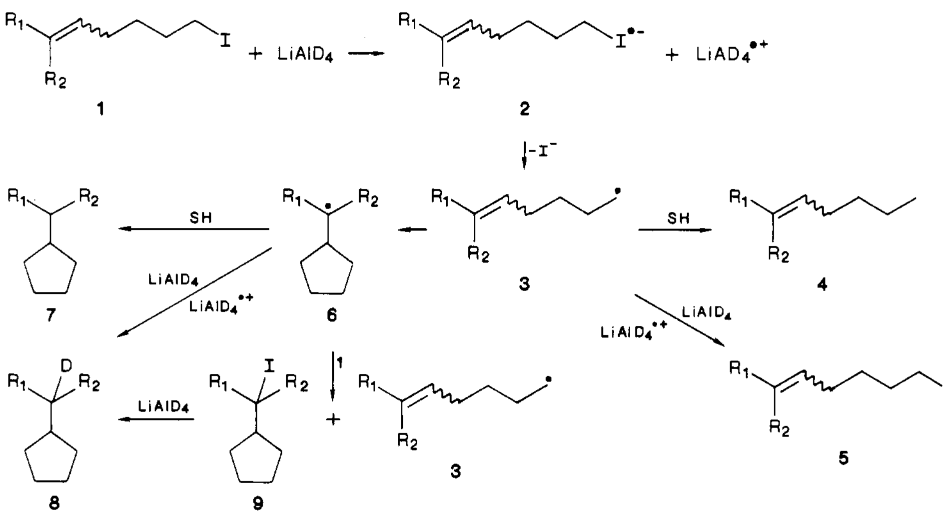
(4) The mechanism reported in 1984[1d] was for a sterically hindered primary alkyl iodide and for secondary alkyl iodides. The same mechanistic pathway is described in Scheme I except that a non-sterically hindered primary alkyl iodide is used for the purpose of this discussion.

(5) It has been suggest by a referee that conversion of $\mathbf{6} \rightarrow \mathbf{8}$ and $\mathbf{3} \rightarrow \mathbf{5}$ might take place by reaction of **6** and **3** with $LiAlH_4$ rather than $LiAlH_4^{\bullet+}$ in a radical chain hydrogen atom abstraction process. We agree and present evidence to support this suggestion.

(6) Park, Seung-Un; Chung, Sung Kee; Newcomb, M. *J. Org. Chem.* **1987**, *52*, 3275.

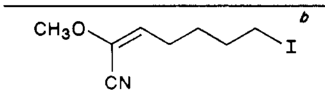
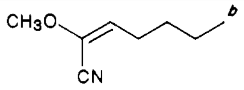
(7) A summary of Newcomb's position was published after submission of this manuscript. Newcomb, Martin; Curran, Dennis P. *Acc. Chem. Res.* **1988**, *21*, 206.

Scheme I. Mechanism of $LiAlH_4$ ($LiAlD_4$) Reduction of Alkyl Iodides[6]



a, $R_1 = R_2 = H$; **b**, $R_1 = OCH_3$, $R_2 = CN$, **c**, $R_1 = CH_3$, $R_2 = C_6H_5$

Table I. Reaction of 7-Iodo-2-methoxy-2-heptenenitrile (Z/E = 38/62) (1b) with $LiAlH_4$ (0.05 M)[a,b]

	 [b]				 [b]			recovered starting material[b]		
exp	*Z*, %	*E*, %	solvent	time, h	*Z*, %	*E*, %	yield, %	*Z*, %	*E*, %	% recovered
1	38.1	61.9	THF	3	16.0	84.0	94.0	0	0	0
2	38.1	61.9	Et_2O	24	5.4	94.6	7.4	11.9	88.1	61.2
3	38.9	61.1	benzene	24	0	0	0	39.0	61.0	99.0
4	38.5	61.9	THF[c]	3	17.5 (92.2% D)	82.5 (94.6% D)	95.1			
5	38.9	61.1	Et_2O[c]	6	18.2 (91.5% D)	81.8 (95.7% D)	3.3	27.4	72.6	87
6	38.5	61.5	THF[d]	2	2.0	98.0	93.0	0	0	0
7	38.3	61.7	THF[e]	0.17	8.7	91.3	86.0			
8	38.5	61.5	THF[f]	3	30.4	69.6	32.0	38.5	61.5	66.1

[a] All reactions were carried out at room temperature. [b] Percent *Z/E* in reactants and products were normalized: 100% = % *Z* + % *E*. [c] Reaction was carried out with $LiAlD_4$ and 10 mol equiv of 1,4-cyclohexadiene. [d] Reaction was carried out in the presence of a sun lamp (25 cm). [e] Reaction was carried out with 5 equiv of LAH. [f] Reaction was carried out in the presence of 1 equiv of *p*-dinitrobenzene.

In this report we plan to show (1) that probe **1b** studied by Newcomb *does* show evidence of a radical intermediate even though no cyclized product was found, (2) why **1b** was not a good choice for this study, and (3) that the results of a study with use of a *valid* probe to test the exclusivity of halogen atom exchange as the sole route to cyclized product do indicate the presence of radical intermediates initiated by a SET process.

(1) Evidence for a Radical Intermediate in the Reduction of 1b by $LiAlH_4$. Halide **1b** was allowed to react with $LiAlH_4$ in THF, ether, and benzene (Table I, experiments 1–3) and with $LiAlD_4$ in the presence of the hydrogen atom donor radical trap, 1,4-cyclohexadiene (experiments 4, 5). Table I shows that the reduction took place in high yield in THF; however, the reaction is much slower in ether and does not proceed at all in benzene. In THF (experiment 4) the deuterium incorporation of the product (**5b**) was only 92–95%, indicating that at least 5–8% of the alkyl halide produced a radical intermediate that was trapped by the hydrogen atom donor. While a similar observation (experiment 5) was made in ether, the reaction was very slow. As we have shown, 100% deuterium incorporation is observed in those cases where a two-electron-transfer process is expected such as in the reduction of an alkyl tosylate by $LiAlD_4$.

(2) Evidence That 1b Is Not a Valid Probe. When we repeated the earlier work on **1b**, we found that the *Z/E* ratio of the product (16/84) was substantially changed from that of the reactant (38/62), indicating that the double bond was somehow participating in the reaction (experiment 1).[8] This is not unexpected since not only is the cyano group capable of reduction by LAH, but also the α,β unsaturated nitrile would be expected to have a considerably lower reduction potential than a compound such as **1a** that does not have a cyano group. In addition (as we show in section 3), when the cyano group is not present such double bond isomerization does not take place.

(3) Studies Involving a Valid Probe That Mimics 1b. In order to determine the uniqueness of **1b** as an invalid probe, we prepared 8-iodo-3-methyl-3-octene (**1c**), thus replacing the methoxy and cyano groups with methyl and ethyl groups. Methyl and ethyl groups do not affect the reduction potential of the double bond as would be expected for the methoxy and cyano groups nor is it possible for $LiAlH_4$ or AlH_3 (produced as a byproduct) to react with the methyl and ethyl groups in contrast to the methoxy and cyano groups. The reactions with this probe (**1c**) were carried out in diethyl ether under exactly the same conditions of concentration, temperature, etc. as used in the studies involving **1b**. This probe mimics **1b** in the sense that **6** $\xrightarrow{1}$ **9** would not be favorable since it involves the conversion of a stable tertiary radical to a much less stable primary radical. Experiments 1–5 (Table II) show

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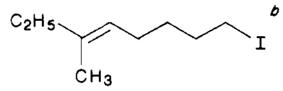
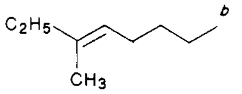
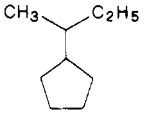
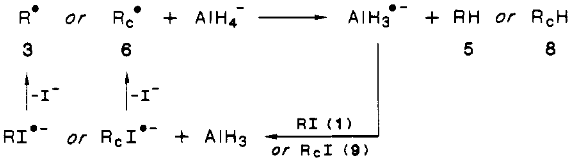
[8] The *E/Z* ratio is based on the NMR designation of the methoxy hydrogens (*E*, 3.70 ppm; *Z*, 3.60 ppm). Newcomb has previously shown[5] that the more stable isomer is the one with the methoxy group *E* to the remainder of the chain.

Table II. Reaction of 8-Iodo-3-methyl-3-octene (1c) (0.05 M) with $LiAlH_4$ (0.05 M)[a]

	 [b]					 [b]				
exp	Z, %	E, %[b]	reagent	solvent	RX time, h	Z, %	E, %		total yield,[c] %	
1	40.9	59.1	LAH	Et_2O	24	41.5	58.5	9.6	97.5	
2	40.5	59.5	LAD	Et_2O	24	40.7 (94.2% D)	59.3 (94.7% D)	18.4 (89.4% D)	97.0	n3
3	41.2	58.8	LAH	THF	3	40.9	59.1	0	98.1	
4	41.0	59.0	LAD	THF	3	40.1 (99.3% D)	59.9 (99.4% D)	0	98.1	
5	41.0	59.0	5 LAD	THF	3	40.5	59.5	0	98.1	

[a] Reductions were carried out at room temperature under laboratory light. [b] Normalized: 100% = % Z + % E. [c] Yields were determined by GLC.

Scheme II. Hydrogen Atom Radical Chain Process

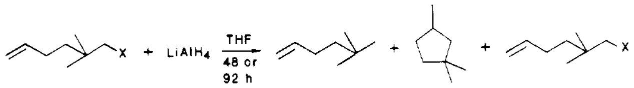


that the Z/E ratio of the product of **1c** (41/59) does not change from that of the reactant, indicating that the double bond is not affected by these groups. Importantly, when **1c** was reduced with $LiAlH_4$ in ether, cyclized product (**7c**) was formed in 9.6% yield, and when **1c** was reduced with $LiAlD_4$, cyclized product (**8c**) was formed in 18.4% yield with 89.4% deuterium incorporation.[9]

When halide **1c** (0.05 mmol) in 4 mL of dry benzene was treated with hexaphenylditin (0.005 mmol) in the presence of a sun lamp, 96.2% of starting material was recovered, and no cyclized iodide was detected after 24 h. Also the same reaction with 0.01 mmol of hexaphenylditin in 4 mL of dry ether under reflux produced 38% of the cyclized reduction product **7c**; cyclized iodide **9c** was not detected. Since cyclized iodide **9c** is not expected as an intermediate in the reaction of $LiAlH_4$ with **1c**, then the cyclized product **7c** must come from the radical **6c**. Additional convincing evidence comes from the reduction of **1c** by $LiAlD_4$ in ether. Not only is there significant protium content in the cyclized product (11%) but also in the straight chain product (5%). All of these data are clearly not compatible with Newcomb's interpretation but are compatible with the mechanism shown in Scheme I.

We would also like to report that in addition to the halogen atom radical chain process **3** → **6** $\xrightarrow{1}$ **9**, which accounts for some but not all of the cyclized products (**7**, **8**), we have found evidence to support a hydrogen atom radical chain process to account for the conversion of **3** → **5**, **6** → **8**, and **9** → **8** by reaction of radicals $R^\bullet$ (**3**) and $R_c^\bullet$ (**6**) with $LiAlH_4$ (Scheme II). Support for the hydrogen atom radical chain process is based on (1) the increased amount of **5** formed (3.3% to 9.4% to 15.2%) as the ratio of $LiAlH_4$:1 is increased from 0.1:1 to 1:1 to 5:1, showing that radical **3** is quenched with $LiAlH_4$ at a faster rate in competition with reaction with SH, $LiAlH_4^{\bullet+}$, and the cyclization of **3** → **6**, and (2) the results of an entrainment experiment (Table III), which shows that although the chloride **11** does not react with $LiAlH_4$ in THF for 48 or 92 h, 28% reaction of chloride **11** does take place over the same period of time in the presence of an equivalent amount of iodide (**10**). It has been shown that **11** is not converted to **10** by reaction with LiI. Both of these studies are consistent with the mechanism suggested in Scheme II.

Table III. Reaction of 10 and 11 with $LiAlH_4$ in 0.5:0.5:1 Ratio



	% yield		
X = I (**10**)	9.4	90.1	0
X = Cl (**11**)	0	0	100
X = I + Cl (50%:50%)	8.9	52.3	36 (Cl)[a]

[a] 14% of the 50% of the chloride or 28% of the total chloride did react.

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[9] **Note added in proof.** In similar studies two additional mimics of **1b**, 4-iodo-3,3-dimethyl-1-butene and 7-iodo-2,6,6-trimethyl-2-heptene, were found to cyclize on reaction with $LiAlH_4$ to form the cyclized product in 35% and 42% yield, respectively.

A New and General Synthesis of α-Silyl Carbonyl Compounds by Si–H Insertion from Transition Metal Catalyzed Reactions of Diazo Esters and Diazo Ketones

Summary: α-Silyl esters and α-silyl ketones are formed in high yield by $Rh_2(OAc)_4$- or $Cu(acac)_2$-catalyzed decomposition of diazo esters and diazo ketones in the presence of organosilanes.

Sir: Although α-silyl carbonyl compounds are widely recognized for their utility in organic synthesis,[1] there are few general methods available for their preparation. The most widely investigated procedures involve enolate anion displacement of chloride from chlorosilanes.[2] However, only amide enolates undergo predominant C-silylation under ordinary conditions.[3] With ester and lactone eno-

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