3576–3581.

(14) All ^{1}H NMR spectra were obtained on a Varian Associates, Model A56/60, NMR spectrometer. Chemical shifts are referenced to the $(CH_3)_4Si$ resonance of a $(CH_3)_4Si/CF_2ClH$ capillary: H-1, $\delta \sim 5.6$ (m); H-2,4, ~ 2.8 (m); H-3, ~ 2.1 (m); $^+OH_2$, 8.78 (d, $J = 3$ Hz).

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(16) The limiting rate constant k was calculated^{17a} from the $\nu_{1/2}$ (<10 Hz) of the average methylene resonance of $C_4H_7{}^+$ at -61 °C. Substitution of this k into the Eyring equation^{17b} gave $\Delta G^{\ddagger} > 10$ kcal/mol.

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Contribution No. 5775
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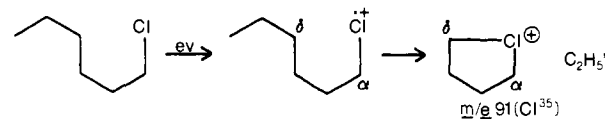*California Institute of Technology*
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Figure 1.

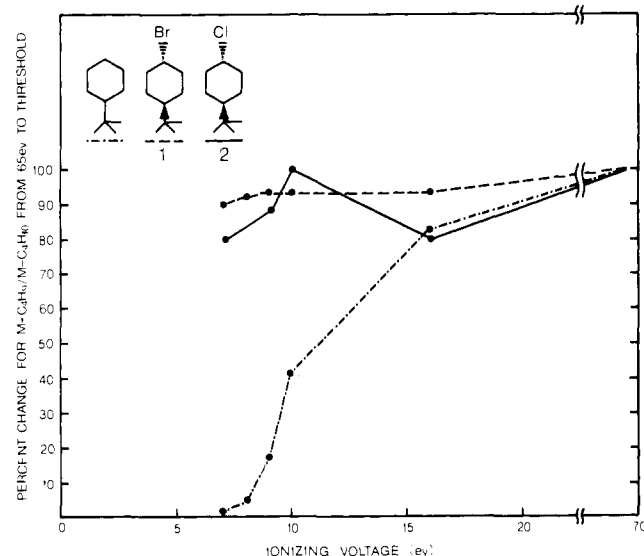**Figure 2.** The lines represent the designated molecules as shown and were calculated by setting the $M - C_4H_9/M - C_4H_{10}$ ratio at 70 eV (Table I) (the electron voltages were measured directly from the ion source terminals and are uncalibrated) equal to 100% and comparing the lower electronvolt values with it. The numbers are the averages of many independent determinations with average deviation of about $\pm 10\%$ (absolute) for **1** and **2** at the lowest electronvolt values and $\pm 30\%$ (absolute) for *tert*-butylcyclohexane. The precision increased at higher electron voltages. Measurements were made on a Du Pont 21-490 mass spectrometer at a source temperature of 130 °C.

Homolytic Substitution at Saturated Carbon: Mass Spectrometry and Free-Radical Chemistry

Sir:

Homolytic substitution at saturated carbon is a much sought after process in free-radical chemistry.[1,2] We wish to point out the following: (1) a long observed and well-investigated fragmentation of simple aliphatic halides in mass spectrometers is an unrecognized[3,4] example of this sought free-radical reaction; (2) stereochemical evidence for this fragmentation, reported here, is consistent with favored inversion of configuration at the homolytic substitution site; (3) a thermochemical explanation, in line with Ingold and Roberts' ideas,[3] can account for the observation of this reaction in mass spectrometers.

(1) In 1962 McLafferty hypothesized that hydrocarbon loss in the mass spectra of certain long-chain aliphatic halides takes place as pictured in Figure 1 for *n*-hexyl chloride.[5] Deuterium labeling of the α and δ positions demonstrates that these methylene groupings are both retained and as well occupy equivalent positions in the product *m/e* 91 ion.[6,7] The variation of relative intensity of the *m/e* 91 ion with electron beam energy[8] and the observation of a strong metastable peak for the formation of this ion[9] are consistent with a low energy of activation rearrangement mechanism.[10] Photoelectron spectroscopy of aliphatic halides shows the lowest energy ionization to involve promotion of a nonbonding electron from halogen.[11,12] This evidence identifies the reaction in Figure 1 as homolytic intramolecular displacement (S_Hi)[3] of ethyl radical from the δ carbon by chlorine radical cation.

(2) Because the stereochemistry of a homolytic displacement step is of great interest[3,4] we have prepared[13] the cis and trans isomers of 4-*tert*-butylcyclohexyl bromide (**1**) and 4-*tert*-butylcyclohexyl chloride (**2**). These materials, with a desirable fixed steric relationship between the δ-alkyl grouping and the potentially displacing halogen radical cation, show, as seen in Table I, enhanced loss of the pendant *tert*-butyl group in the trans over the cis isomers. This stereoselectivity which expresses itself in both the percent of total ionization for loss of *tert*-butyl radical, $\%\Sigma_{50}(M - C_4H_9)^+$, and as increased competitiveness with rearrangement loss of isobutane,[14] ($M - C_4H_9{}^+/M - C_4H_{10})^+$ (Table I), is consistent with assisted

Table I.^{a,b} Stereoselectivity (Trans/Cis) for Loss of the 4-*tert*-Butyl Group

	Br trans/cis	Cl trans/cis
$\%\Sigma_{50}(M-C_4H_9)^+$	79/21	73/27
$(M-C_4H_9)^+/(M-C_4H_{10})^+$	90/10	84/16

^{a} Data were taken on a Hitachi RMU-6 mass spectrometer at 70 eV and ~ 130 °C source temperature. Independent experiments were carried out on a Du Pont-21-490 mass spectrometer and gave results within experimental error of these above. ^{b} See text. Numbers are expressed as ratio of trans to cis for percent total ionization above *m/e* 50 ($\%\Sigma_{50}$) with average deviation of $\pm 5\%$ and ratio of loss of *tert*-butyl to isobutane $((M - C_4H_9)^+/(M - C_4H_{10})^+\cdot)$ with average deviation of $\pm 10\%$.

back-side displacement of alkyl radical by the halogen cation radical through the boat conformation of the intact molecular ions of *trans*-**1** and -**2**.[15]

Such a process of assisted displacement should show the characteristics of a rearrangement reaction and would be accessible to the lowest energy molecular ions in contrast to simple cleavage loss of the *tert*-butyl group. The experimental data in Figure 2 provide a test of this notion by presenting a comparison of the $(M - C_4H_9)^+/(M - C_4H_{10})^+\cdot$ ratio for

trans-**1** and -**2** and for presumably unassisted *tert*-butylcyclohexane[16] as a function of ionizing voltage. With heavy precedent,[10] this assistance mechanism should increase the competitive rate for loss of C_4H_9 in *trans*-**1** and -**2** but not in *tert*-butylcyclohexane as the ionizing energy is lowered. This is precisely what is found (Figure 2).

(3) The unusual observation of homolytic substitution at carbon may be reasonably ascribed to the nature of the substituting group. Consider the following competition. When neutral bromine radical approaches a hydrocarbon chain, S_H2 reaction at hydrogen or carbon leads, respectively, to an alkyl radical and hydrogen bromide or alkyl bromide. The 18-kcal mol^{-1} difference in bond strength[17] favoring hydrogen bromide, if reflected in the competitive transition states, will powerfully direct substitution at hydrogen as is always observed.[3] On the other hand S_H2 reaction by alkylated bromine radical ($RBr^+\cdot$) on hydrogen will produce alkyl radical and the hydridoalkylhalonium ion, while attack at carbon produces alkyl radical and dialkylhalonium ion. Kinetic evidence[18] and analogy to carbenium ion stabilities suggest that the dialkylhalonium ion is considerably more stable than the hydridoalkylhalonium ion, thus favoring S_H2 reaction at carbon. Although, in the intramolecular cases herein, the dialkylhalonium ion product of the S_Hi reaction at carbon has the recognized special stability of the five-membered ring,[7] this is not prerequisite to homolytic displacement at carbon as demonstrated by recent ion cyclotron resonance results showing that $RBr^+\cdot$ will displace bromine radical from RBr to form acyclic dialkylbromonium ions.[19,20]

The observation in electron impact mass spectrometers of homolytic displacement at carbon[5] may now be added to the Barton[21] and Hofmann–Loeffler–Freitag[22] reactions as demonstration that mass spectrometry should be a subject of increasing awareness to the field of free-radical chemistry.[11]

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Alkali Metal Enolates and Cryptands. A Novel Type of Strong Base

Sir:

In the course of our investigations, we have found that alkali metal enolates in the presence of cryptands (Figure 1) exhibited exceptionally strong basicity at room temperature.

Proton abstraction takes place within a few minutes not only from organic acids usually ionized by standard bases, but also from very weak acids such as triphenylmethane and diphenylmethane. Diethyl ether is attacked by the activated enolate and cyclohexyl chloride is quantitatively transformed into cyclohexene.

Lithium, sodium, and potassium enolates of cyclohexanone[1] were respectively prepared in diethyl ether and in THF by the usual procedures.[2] All reactions were carried out under nitrogen with 0.5 M solutions of each enolate. One equivalent of cryptand was added to the enolate solution.[3] The solution must be free of ketone and free of the basic reagent used in its preparation; this important feature must be carefully controlled since the presence in the medium of another base could perturb the results.

When triphenylmethane ($pK_a = 31.5$) was added to any of the enolate–cryptand solutions, the red color of the carbanion appeared instantaneously (in the absence of cryptand, no reaction occurs). The same observations were made using diphenylmethane ($pK_a = 33$) instead of triphenylmethane. Toluene ($pK_a \simeq 37$) is not ionized by the same procedure.