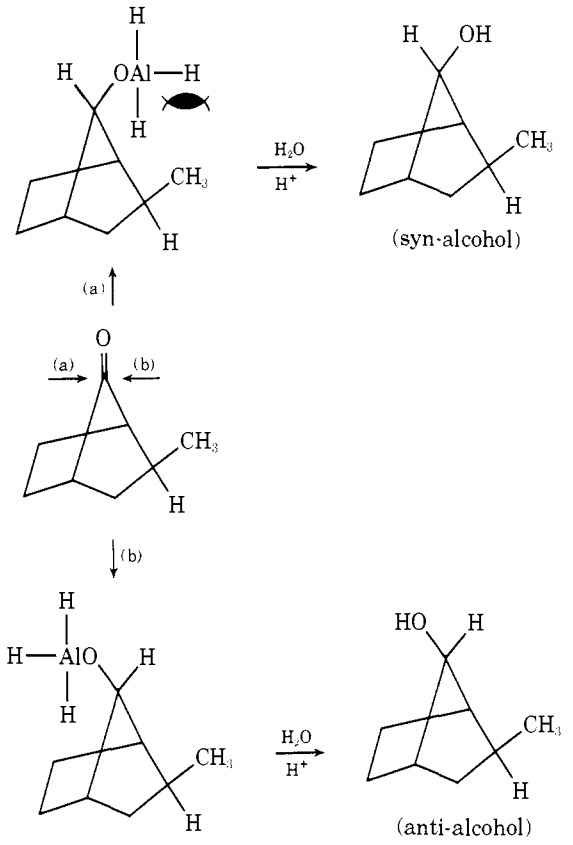

to the syn-alcohol. In order to test perturbations on the carbonyl group other than the steric effect exerted by the 2-*exo*-methyl group, the reaction of $LiAlH_4$ with the 2-*endo*-methyl compound III was studied. If only the steric effect of the 2-*exo*-methyl group is significant, then the reaction of $LiAlH_4$ with III to produce both the syn- and anti-alcohol should proceed at the same rate as the reaction of $LiAlH_4$ with I and at twice the rate compared to the formation of the *syn*-2-*exo*-methyl alcohol.

Table I shows that reaction of $LiAlH_4$ with II produces only the syn-alcohol as a result of anti attack with respect to the 2-*exo*-methyl group. This shows that the 2-*exo*-methyl group exerts a significant steric effect with respect to attack at the 7-keto group since no anti-alcohol is observed. When I and II were admixed in equimolar portions with an insufficient amount of $LiAlH_4$, the alcohol products of I and II were produced in a 2:1 ratio indicating no noticeable product development control. Reaction of I and III in equimolar portions with an insufficient amount of $LiAlH_4$ produced the corresponding alcohols in 1:1 ratio showing that the 2-methyl group has no effect on the rate of reaction of the 7-keto group except when it is in the exo position. Admixture of II and III in equimolar ratio produced the corresponding alcohols in a 1:2 ratio and admixture of I, II, and III in equimolar ratio produced the corresponding alcohols in a 2:1:2 ratio when allowed to react with an insufficient amount of $LiAlH_4$, supporting the conclusion that anti attack on II takes place at the same rate as attack from either side of the carbonyl on I and III and indicating that the 2-*exo*-methyl group, although exerting a signicant steric effect, does not affect the formation of the syn-alcohol of II. Further experiments in THF, at different stoichiometries and experiments using AlH_3 as the reducing agent, simply provide further evidence for the above conclusions.

The synthesis of I was accomplished by using the procedure of Gassman and Pape.[9] Compounds II and III were prepared by following the method outlined by Lightner and Jackman.[10]

The reductions of I, II, and III were carried out under identical conditions. According to GLC and ^{13}C NMR, I and II gave only one reduction product, whereas III gave both the syn- and anti-alcohols. By comparing GLC and ^{13}C NMR, it was substantiated that the lone reduction product of II was the syn-alcohol. The syn-alcohol IV was allowed to equilibrate under Meerwein-Ponndorf conditions. The anti-alcohol V was formed almost exclusively except for a trace of the syn-alcohol. Also ketone II produced only the anti-alcohol V when allowed to react with aluminum isopropoxide and isopropyl alcohol thus establishing the anti-alcohol V as the thermodynamic isomer.

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Alkane Elimination in Mass Spectrometry. A Counterpart to the McLafferty Rearrangement

Sir:

We report a primary fragmentation of simple ketones, alcohols, and amines which can be the most facile reaction at low energy. In spite of the detailed attention[1] accorded the primary fragmentations of these functional groups over the past 20 years, this process has, in a situation reminiscent of the emperor's clothes,[2] not been commented upon.[3] The reaction is alkane elimination from the molecular ion.

Consider the mass spectrum[1a] of diisopropyl ketone which shows, as the fourth most abundant fragment ion, a peak at *m/e* 70 ($C_4H_6O^{\cdot+}$ [4]). The origin of this ion directly and exclusively[5] from the molecular ion of the ketone is shown by the accelerating voltage scan[6,7] of Figure 1a. The metastable peak confirms the transition (1).

$$C_3H_7COC_3H_7^{\cdot+} \rightarrow C_3H_6CO^{\cdot+} + C_3H_8 \qquad (1)$$

A scan of the mass-analyzed ion kinetic energy (MIKE) spectrum[8] of the molecular ion of diisopropyl ketone, shown in Figure 1b, confirms that on the time scale of this experiment, alkane elimination is the major primary fragmentation (>95%). The MIKE spectrum taken at higher collision gas pressures shows the well-known α-cleavage reaction leading to acylium ion formation. (The base peak in the mass spectrum is also due to this reaction.) Alkane elimination competes poorly with alkyl radical loss in these higher

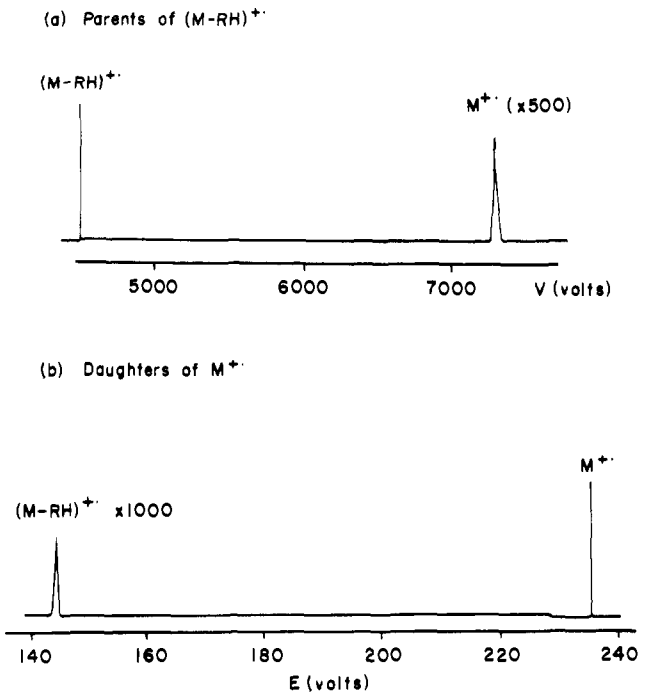

Figure 1. Ion kinetic energy spectra of diisopropyl ketone. (a) Accelerating voltage (V) scan showing all reactant ions leading to the propane elimination product. (Hitachi RMH-2). (b) Electric sector (E) scan showing all product ions formed from the molecular ion (MIKES).

energy ions. This situation, in which a rearrangement fragmentation is dominant from low energy ions and a simple cleavage from high energy ions, is common in mass spectrometry[9] and implies a crossing of the two rate constant ($k(\epsilon)$) curves. Further confirmation of the low energy required for alkane elimination was obtained by running the charge exchange mass spectrum[10] with reagent ions of low recombination energy. Figure 2 compares regions of these spectra with the conventional electron impact spectrum.

Alkane elimination from diisopropyl ketone occurs by loss of an α-hydrogen, i.e., by a 1,2-elimination. This was shown by preparation[12] of a mixture of the d_0, d_1, and d_2 C_2 and C_4 labeled analogues and selection[13] within the MIKE spectrometer, of the pure d_1 and d_2 compounds. The extent of 1,2-reaction was 100% within the estimated accuracy of 5%.[14]

A significant peak corresponding to alkane molecule loss is present in the mass spectra[1a] of many simple ketones which cannot undergo McLafferty rearrangement through either alkyl chain. It has been confirmed in acetone, 3-pentanone, 2-methyl-3-pentanone, and 2,2,4-trimethyl-3-pentanone from the ion kinetic energy spectra of the molecular ions. In 2-methyl-3-hexanone propane loss occurs in competition with ethylene loss (McLafferty rearrangement). When enolic ions are generated, for example, as McLafferty rearrangement products, then alkane elimination is not observed. However, further work is needed in order to establish whether the reaction occurs from a keto or enol form of the molecular ion.

The process has also been observed in alcohols and amines. Isopropyl alcohol exhibits the loss of methane. Ethane loss has been observed in *sec*-butyl alcohol, 3-pentanol, *sec*-butylamine, and 3-aminopentane. The loss of a propane molecule occurs in 2,4-dimethyl-3-pentanol. *sec*-Butylamine is particularly interesting since the metastable molecular ion undergoes competitive loss of a molecule of ethane and an ethyl radical leading to peaks of similar intensity.

In conclusion the present rearrangement reaction, like its

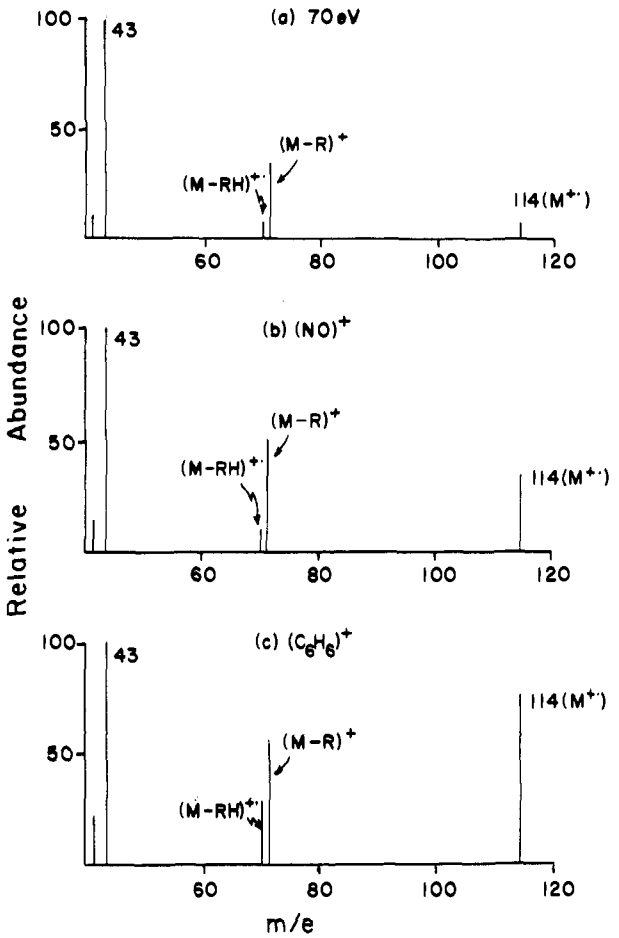

Figure 2. Electron impact (a) and charge exchange ionization of diisopropyl ketone using the ionizing agents NO^+ (b) and $(C_6H_6)^+$ (c).

well-known counterpart, the McLafferty rearrangement,[16] occurs in several classes of compounds and in a number of cases represents the lowest energy fragmentation pathway for molecular ions. It seems remarkable that the 1,5-hydrogen rearrangement (alkene loss) has become the most studied of all mass spectrometric reactions while the 1,3-hydrogen rearrangement (alkane loss) occurs in the same classes of compounds but has not previously been discerned.

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The Photochemical Induced Cyclization of Allyl Grignard Reagents

Sir:

The interconversion of allyl carbanions to cyclopropyl carbanions has been a topic of increasing interest since the formulation of the selection rules by Woodward and Hoffmann.[1] Most of the studies on allyl carbanions have dealt with their thermal transformations, while their photochemical behavior has received only marginal attention.[2,3]

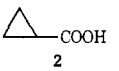
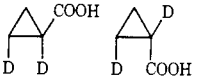
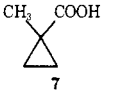
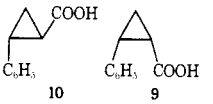
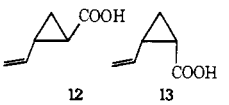
This communication describes the first light-induced cyclization of allylmagnesium halides to cyclopropylmagnesium halides. Allylmagnesium halides have been chosen as model systems for allyl carbanions, since these compounds are known to exist in solution as aggregates of tight anion–cation pairs.[4-6]

Allylmagnesium bromide (**1**) was prepared by dropwise addition of allyl bromide to a large excess of magnesium turnings in peroxide-free, dry ether. After completion of the reaction, the volatile components were evaporated under high vacuum, and the solid residue was redissolved in a new portion of dry ether. The irradiation of the allyl Grignard was carried out in a quartz apparatus for 24 h at 0–5 °C with an external SP 500 Philips high-pressure mercury arc lamp. The irradiated mixture was treated with solid carbon dioxide and hydrolyzed carefully. The acidic reaction products were extracted with base and then separated by either column chromatography (silica gel, Merck 70–230 mesh, methanol–ethyl acetate–benzene 10:10:80), or preparative VPC (10% Carbowax on Chromosorb 30/60, 6 m, ⅜ in., 200 °C). The carboxylic acid mixture was found to contain 45% cyclopropanecarboxylic acid (**2**) as the major photoproduct,[7] 30% of a higher molecular weight compound $C_7H_{10}O_2$,[8] 25% vinylacetic acid, and minor amounts of biallyl and polymeric materials as well. Product **2** was identified by comparison with an authentic sample.

Similarly, irradiation of *cis*-2,3-dideuterioallylmagnesium bromide (**3**) yielded, after carbonation, a 1:1 mixture of *trans*- and *cis*-1,2-dideuteriocyclopropanecarboxylic acid, (**4**) and (**5**), and a mixture of carboxylic acids, $C_7H_7D_3O_2$,[8] each labeled with three deuterium atoms.

β-Methylallylmagnesium chloride (**6**), cinnamylmagnesium bromide (**8**), and γ-vinylallylmagnesium chloride (**11**) were found to undergo analogous cyclization reactions. Thus irradiation of (**6**) yielded after carbonation 1-methylcyclopropanecarboxylic acid (**7**) as the major product and trace amounts of a higher molecular weight material $C_8H_{12}O_2$,[8] while irradiation of (**8**) furnished a mixture of *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid, (**9**) and (**10**). The trans isomer **10** was found to be the predominant one; (trans/cis ratio 49:1, determined by analytical VPC). Similar results were obtained on irradiation of γ-vinylallyl Grignard (**11**). Thus, a mixture of *trans*- and *cis*-2-vinylcyclopropanecarboxylic acid (**12**) and (**13**), was obtained (trans/cis ratio 6:1). The yields of the various prod-

Table I

Irradiated allyl Grignard	Uv spectrum	Cyclic photoproducts	% yield[7]	Trans/cis ratio
$CH_2=CHCH_2MgBr$ **1**	246 (ε 4 300)[a]	 **2**	45	–
$CHD=CDCH_2MgBr$ **3**		 **4** **5**	45	1:1
$CH_2=C(CH_3)CH_2MgCl$ **6**	251 (ε 4 100)[a]	 **7**	70	–
$C_6H_5CH=CHCH_2MgBr$ **8**	252 (ε 20 000)[12]	 **10** **9**	75	49:1
$CH_2=CHCH_2=CHCH_2MgCl$ **11**		 **12** **13**	50	6:1

[a] The UV spectrum was measured in ether solutions after filtration. With addition of water, the absorption band of the Grignard reagent disappeare ' The resultant spectrum was due to the superposition absorption of the magnesium salts and the olefinic coupling products which were formed during the preparation of the Grignard reagent.