generality of this reaction is apparent from the results summarized in Table I.

The reactions were carried out by the dropwise addition of the π-allylnickel bromide complex (1 mmol) in THF (10 ml) to the quinone (2–4 mmol) in THF (10 ml) under argon at −50°. After addition was complete the reaction was stirred at −50° for 2 hr, allowed to slowly warm to 25°, and stirred at this temperature for 4 hr. The crude product was isolated by partition between ether and water. The ether phase was dried over anhydrous magnesium sulfate and concentrated, and the crude product was purified by preparative layer chromatography on silica gel, developing with 1:1 pentane–ether mixtures.[2]

The type of product obtained is dependent upon substrate. *p*-Benzoquinone reacts to produce allyl-substituted *hydroquinones*, while all other quinones studied produce allyl-substituted *quinones*. A major side product in all reactions is the hydroquinone arising from simple reduction of the substrate. This reduction is most extensive with *p*-benzoquinone, but is observed to a lesser degree with the other substrates. Quinones having methyl groups adjacent to an unsubstituted position (*e.g.*, 2-methylbenzoquinone) suffer attack at the *methylated* position as well as the unsubstituted position (Scheme I). This can be eliminated, or at least greatly reduced, by using a twofold excess of quinone. No attack at the methylated position is observed when adjacent positions both bear methyl groups (*e.g.*, 2,3-dimethylbenzoquinone). Duroquinone (tetramethylbenzoquinone) is recovered unchanged from the reaction. Quinones with several unsubstituted positions are alkylated nonspecifically. However, *only monoalkylation* products are observed.

Although the mechanism of this substitution has not yet been clarified, the results can be rationalized by Scheme I. In this scheme initial π-allylnickel bromide–quinone complex formation occurs at low temperatures. Upon warming, 1,4 addition to the quinone results. The site of allyl attack depends upon the nature of the initial complex, which, in turn, depends upon reactant ratios.[3] The 1,4 adducts then decompose or hydrolyze to produce the observed products. However, other likely mechanisms cannot be dismissed at this time.

The synthetic utility of this procedure is demonstrated by the synthesis of coenzyme Q_1 (**6**) in one step from 2,3-dimethoxy-5-methylbenzoquinone in 40% yield.[4] Similarly, plastoquinone-1 (**4**) was prepared in 61% yield. This procedure avoids the disadvantages of polyalkylation, chromanol formation, side-chain cyclization, and difficult product isolation previously encountered in the synthesis of these compounds.[6] Since a major side product, the hydroquinone, is easily reoxidized in high yield to the starting quinone, little loss of that starting material is experienced. The requisite π-allylnickel bromide complexes are easily prepared in one operation in ~90% yield by the reaction of the allylic bromide with nickel carbonyl.[5] Complexes with polyisoprenoid allyl groups (π-geranyl, π-farnesyl) or allyl groups containing functionality (COOEt, OCH_3) can be prepared,[5] allowing in principle the synthesis of naturally occurring or unusually functionalized isoprenoid quinones not readily available by present methods.

Investigations are continuing into the scope, synthetic utility, and mechanism of this promising alkylation reaction.

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(2) The scale of this reaction can be increased without experimental difficulty.

(3) The recent isolation and preliminary characterization of complexes (π-allylnickel $Cl)_2$(quinone) and (π-allylnickel $Cl)_2$(quinone$)_3$ strengthen this hypothesis. See M. R. Gal'ding and N. A. Buzina, *Dokl. Akad. Nauk SSSR*, **197**, 586 (1971). We are presently investigating these complexes as intermediates in the above reaction.

(4) While this work was in progress K. Sato, S. Inoue, and R. Yamaguchi, *J. Org. Chem.*, **37**, 1889 (1972), reported the synthesis of coenzyme Q_1 in an overall yield of ~20% over eight steps from the quinone, using the well-known[5] reaction between π-allylnickel halides and aromatic halides as the key step.

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Energy-Dependent Ring Opening of Cycloalkane Parent Ions[1]

Sir:

In recent communication[2] convincing evidence was presented for retention of the ring (cyclic) structure in the $C_3H_6^+$ ion produced by electron-impact ionization of cyclopropane. This evidence was based on the observation that $C_3H_6^+$ ions from cyclopropane reacted with NH_3 in the following manner

$$\text{c-}C_3H_6^+ + NH_3 \longrightarrow CH_2NH_2^+ + C_2H_5 \qquad (1)$$

$\Delta H = -27$ kcal/mol[3]

$$\longrightarrow CH_2NH_3^+ + C_2H_4 \qquad (2)$$

$\Delta H = -16$ kcal/mol

These processes were not observed with $C_3H_6^+$ ions formed by ionization of propylene. Distinct variations both in the rate and modes of reaction of $C_3H_6^+$ ions formed by ionization of cyclopropane, when compared to propylene, were also noted in a previous mass spec-

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(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971).

(3) Thermodynamic data given in this communication have been taken from (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26** (1969); (b) H. E. O'Neal and S. W. Benson, "Thermochemistry of Free Radicals," to be published; (c) F. P. Lossing, private communication.

Table I. $C_nD_{2n}^+ + NH_3 \rightarrow$ Products

C_nD_{2n}	IP, eV (ref 3)	Photon energy, eV	Product ion distribution, %			$k_{total} \times 10^{10}$ cm^3/(molecule sec)^b
			NH_3D^+	$CD_2H_2N^+$	$CD_2H_3N^+$	
Cyclopropane-d_6	9.93	10.6	15.0	62.5	22.5	9.4 ± 0.4
Cyclopropane-d_6	9.93	11.6–11.8	43.0	39.0	18.0	9.3 ± 0.3
Propylene-d_6	9.72	10.0	100.0	0.0	0.0	9.4 ± 0.4
Methylcyclopropane-d_8^{a}	9.46	10.0	55.4	32.9	1.4	nd
Cyclobutane-d_8	10.06	10.6	90.3	9.7	0.0	nd
1-Butene-d_8, isobutene-d_8	9.58	10.0	100.0	0.0	0.0	nd
cis-2-Butene-d_8	9.10	10.0	99.1	$\leq$0.9	$\leq$0.9	nd

[a] Other product ions in the mass range 45–50 account for 10% of the product ions. [b] Thermal kinetic energy, 300°K. nd = not determined.

trometric study.[4] On the surface these observations seem in contradiction to the conclusions of an earlier investigation[5] in which it was found that $C_3H_6^+$ ions produced by γ irradiation of cyclopropane react (at least in part) in the following manner with cyclohexane-d_{12}

$$C_3H_6^+ + c\text{-}C_6D_{12} \longrightarrow CH_2DCHDCH_3 + C_6D_{10}^+ \qquad (3)$$

The formation of $CH_2DCHDCH_3$ as a neutral product in those experiments was taken as evidence that c-$C_3H_6^+$ isomerizes to $CH_3CHCH_2^+$ prior to or during reaction 3.

In this communication we wish to report mass spectrometric[6] results which indicate that (i) ring opening does occur in cyclopropane and that (ii) the fraction of parent ions which isomerize in this fashion reflects the internal energy content of the cyclic ion.

We first established that $C_3D_6^+$ ions formed *via* photoionization of propylene-d_6 at 10 or 11.6-11.8 eV react exclusively with NH_3 by deuteron transfer

$$C_3D_6^+ + NH_3 \rightarrow C_3D_5 + NH_3D^+ \quad \Delta H = -29 \text{ kcal/mol} \quad (4)$$

at essentially every collision ($k = 9.4 \pm 0.4 \times 10^{-10}$ cm^3/(molecule sec)). Reaction 4 was apparently overlooked in the icr study.[2] In agreement with the previous report, $C_3D_6^+$ ions formed *via* photoionization of c-C_3D_6 were found to undergo reactions 1 and 2 (Table I). However, an additional energy-dependent fraction of these $C_3D_6^+$ ions reacts by deuteron transfer to NH_3 (reaction 4). Considering the radiolysis data and the fact that propylene ions react exclusively *via* reaction 4, the drastic increase in $k_4/(k_1 + k_2)$ from 0.18 to 0.75 (see Table I) observed in cyclopropane–NH_3 mixtures induced by a modest increase in photon energy (10.6 to 11.6-11.8 eV) can be attributed to increased probability for ring opening in the cyclopropane ions at higher energies. We should emphasize that our experiments involving cycloalkane-additive mixtures were carried out with samples in which the mole per cent of, for example, NH_3 was varied from 0.1 to approximately 98% and the reaction chamber pressure was varied from 0.01 to approximately 10 mTorr. It follows that the number of collisions involving $C_3H_6^+$ ions and cyclopropane does not effect $k_4/(k_1 + k_2)$ at reduced pressures; therefore, the residual energy content of the reactant ion apparently does not alter the observed branching ratios. Through suitable combinations of sample composition and pressure range we were able to follow the reaction to completion and minimize complicating secondary reactions; therefore the branching ratios and rate coefficients given in Table I reflect the behavior found for at least 98% of the reactant ions at a given energy. Further reactions of $CH_2NH_2^+$ and $CH_2NH_3^+$, as well as their partially deuterated analogs, with NH_3 to yield proton- (deuteron-) transfer products were noted at higher pressures. It is of interest that Gross and McLafferty also noted that the fraction of $C_3H_6^+$ ions which react according to eq 1 and 2 decreased markedly with increasing electron energy. This was interpreted in terms of a $C_3H_6^+$–NH_3 collision complex which "decays relatively more rapidly to starting materials than to products (reactions 1 and 2) at higher internal energy." However, our data (Table I) show that the decrease in $k_1 + k_2$ is entirely compensated for by an increased probability for deuteron transfer. When the contribution from this channel, which was apparently not detected in the previous study,[2] is added to that for reactions 1 and 2, the total rate coefficient for disappearance of $C_3D_6^+$ is found to be independent of internal energy over the range covered in this study ($k_{total} = 9.4 \pm 0.4 \times 10^{-10}$ cm^3/(molecule sec)). Unfortunately, since absolute rate coefficients were not reported in ref 2, one cannot establish the extent of ring opening at the lowest electron energy (~11.1 eV) used in the icr study. However, the decrease in the relative cross section of reactions 1 and 2 reported in Table I of ref 2 provides a measure of the degree of ring opening as a function of electron energy. Judging from the pronounced decrease in the fraction of $C_3D_6^+$ ions which undergo reaction 4 as the photon energy is reduced, it would appear that only those $C_3D_6^+$ ions formed by ionization of c-C_3D_6 at energies near the ionization threshold (9.93 eV) may react *exclusively via* reactions 1 and 2. The apparent negligible probability for deuteron transfer from the cyclic $C_3D_6^+$ ion to NH_3 is rather unexpected considering the exothermicity of such a reaction channel ($\Delta H_{rxn} = -14$ kcal/mol).

The conclusions derived from the $C_3D_6^+$–NH_3 experiments were confirmed by additional experiments involving photoionization of c-C_3D_6–CH_3OH and CD_3CDCD_2–CH_3OH mixtures at 10.6 eV. Here again the exothermic deuteron-transfer reaction

$$CD_3CDCD_2^+ + CH_3OH \longrightarrow CH_3OHD^+ + C_3D_5 \qquad \Delta H \cong -4 \text{ kcal/mol} \quad (5)$$

occurs at essentially every collision ($k = 1.0 \pm 0.4 \times 10^{-9}$ cm^3/(molecule sec)) with propylene ions as reactants. In contrast, in c-C_3D_6–CH_3OH mixtures only 16% of the $C_3D_6^+$ ions transfer a deuteron (with the same rate coefficient as propylene ions), while the re-

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(5) P. Ausloos and S. G. Lias, *ibid.*, 43, 127 (1965).

(6) (a) L. W. Sieck, S. K. Searles, and P. Ausloos, *J. Amer. Chem. Soc.*, 91, 7627 (1969); (b) L. W. Sieck and S. K. Searles, *ibid.*, 92, 2937 (1970).

maining are unreactive toward CH_3OH ($k < 10^{-11}$ cm^3/(molecule sec)). Considering that the deuteron-transfer reaction involving the cyclic ion

$$\text{c-}C_3D_6^+ + CH_3OH \rightarrow CH_3OHD^+ + \text{c-}C_3D_5 \qquad \Delta H = +7 \text{ kcal/mol} \quad (6)$$

is endothermic, this observation confirms our view that approximately 15–16% of the $\text{c-}C_3D_6^+$ ions undergo ring opening at 10.6 eV.

The $C_4D_8^+$ results (Table I) can be interpreted in the same manner as the C_3D_6 data. Here again we find that $C_4D_8^+$ ions formed *via* photoionization of the various butene isomers react with NH_3 nearly exclusively by deuteron transfer. On the other hand, more than 30% of the $C_4D_8^+$ ions formed in the 10-eV photoionization of methylcyclopropane react in a manner analogous to reaction 1.

$$C_4D_8^+ + NH_3 \longrightarrow CD_2NH_2^+ + C_3D_6H \qquad (7)$$

If one assumes, by analogy with the cyclopropane system, that the $C_4D_8^+$ ions participating in a reaction such as (7) have maintained their cyclic structure, then $\Delta H_{\text{rxn}} = -13$ to -18 kcal/mol. The energetically less favorable reaction

$$C_4D_8^+ + NH_3 \longrightarrow CD_2NH_3^+ + C_3D_6 \qquad \Delta H \cong -7 \text{ kcal/mol} \quad (8)$$

occurs with a much lower probability.

In cyclobutane, only 10% of the $C_4D_8^+$ ions obtained *via* photoionization at 10.6 eV undergo reactions 1 and 2. The relative probability is reduced to less than 5% at 11.6–11.8 eV. This result is in accord with those of a recent photoionization study[7] carried out in a static system in which it was shown that at least 95% of the cyclobutane parent ions isomerize to the $i\text{-}C_4H_8^+$, $2\text{-}C_4H_8^+$, and $1\text{-}C_4H_8^+$ structures at 11.6–11.8 eV.

We can tentatively conclude from the data presented here that the fraction of $C_3H_6^+$ and $C_4H_8^+$ ions which transfer a proton to NH_3 or to other proton acceptors can be considered as an accurate measure of the fraction of ions which exhibit an acyclic structure under the particular conditions (pressure, temperature, etc.) of the experiment.

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Lithium Tri-*sec*-butylborohydride. A New Reagent for the Reduction of Cyclic and Bicyclic Ketones with Super Stereoselectivity. A Remarkably Simple and Practical Procedure for the Conversion of Ketones to Alcohols in Exceptionally High Stereochemical Purity

Sir:

Addition of 1 mol equiv of tri-*sec*-butylborane to a tetrahydrofuran (THF) solution of lithium trimethoxyaluminohydride (LTMA) at room temperature results in a facile and rapid displacement of aluminum methoxide, producing the new reagent, lithium tri-*sec*-butylborohydride, in quantitative yield. This highly hindered lithium trialkylborohydride, first reagent of its kind to be reported, is an active reducing agent and exhibits essentially enzyme-like stereoselectivity in the reduction of cyclic and bicyclic ketones. Thus even ketones with an alkyl group relatively remote from the reaction center, such as 3-methyl- and 4-*tert*-butylcyclohexanone, are reduced in ≥95% stereoselectivity, producing the less stable epimer. This appears to be the first nucleophilic reagent capable of reducing such cyclic ketones with such high stereoselectivity.[1] Hindered ketones, such as 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone, camphor, etc., are reduced rapidly and quantitatively with this new reagent with over 99.5% stereoselectivity to the corresponding less stable isomers. Thus, the lithium trimethoxyaluminohydride–tri-*sec*-butylborane combination provides a new simple practical procedure for the conversion of ketones to alcohols with the highest stereospecificity realized.

We recently reported that lithium perhydro-9b-boraphenalylhydride (PBPH), prepared from *cis,cis,-trans*-perhydro-9b-boraphenalene and lithium hydride, reduces cyclic and bicyclic ketones with high stereoselectivity, rapidly and quantitatively.[2] Since then this new reagent and related trialkylborohydrides have been used extensively for the stereoselective reduction of ketones to the alcohol function, including two major applications in the synthesis of prostaglandins, where the use of all other previously known reagents had failed.[3–5]

It appeared possible that a more hindered trialkylborohydride might improve the stereoselectivity. Unfortunately, we encountered a major synthetic difficulty. The more hindered trialkylboranes failed to react at any appreciable rate with lithium hydride in THF. Thus, the reactions of triethyl-, tri-*n*-butyl-, and triisobutylboranes proceeded rapidly and quantitatively with lithium hydride in refluxing THF, whereas the corresponding reaction with tri-*sec*-butylborane proceeded only 10% in 24 hr (eq 1). (Sodium hydride

$$\text{LiH} + \textit{sec-}\text{Bu}_3\text{B} \xrightarrow[\substack{\text{reflux} \\ \text{24 hr}}]{\text{THF}} \underset{10\%}{\text{Li-}\textit{sec-}\text{Bu}_3\text{BH}} \qquad (1)$$

failed to react under these conditions.) Yet preliminary results indicated that the stereoselectivity achieved by lithium tri-*sec*-butylborohydride was much better than that achieved by the other three trialkylborohydrides.

We recently observed that the addition of a molar amount of triethylborane to a THF solution of LTMA results in an instantaneous vigorous exothermic reaction forming a gel.[6] Analysis of the reaction mixture revealed that a displacement reaction had taken place to form the corresponding lithium triethylborohydride and a polymeric gel of aluminum methoxide.[7] Accordingly, we examined this reaction with a repre-

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