(10%), 229 (7%); nmr 1.12 (s, 3 H, C-4 CH_3), no resonance for the C-3 proton. The compound showed a single component on analysis by tlc and glc (on four systems noted above).

The less polar major component (19.0 mg) on tlc showed a mass spectrum which was very similar to that of [$3\alpha,4\beta$-$^2H_2$]-4α-methylcholest-5-en-3β-ol (V) with additional ions at 399 (90%) and 366 (3%). The nmr spectrum showed the presence of signals 4.95 (m), 5.62 (m), and 8.43 in addition to the resonances seen in the spectrum of III. The spectrum showed no absorbance at 3.71 (C-3 H) or at 3.90 seen in the spectrum of the less polar component obtained as a by-product in the synthesis of IV.

Registry No.—III, 15073-00-4; IV, 1251-98-5; V, 52259-51-5; VI, 52259-52-6; VIII, 2041-92-1; X, 2239-49-8.

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Studies in Mass Spectrometry. A Comparison of the Electron Impact and Chemical Ionization Fragmentations of 8,9-Dehydro-2-adamantanol and 2-*exo*-Protoadamantenol

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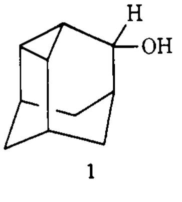
Electron impact (electron energies of 70, 20, and 14.2 eV) and chemical ionization (methane, isobutane, hydrogen, nitrogen, and nitric oxide–nitrogen mixtures as reagent gases) spectra were obtained for 8,9-dehydro-2-adamantanol (1) and 2-*exo*-protoadamantenol (2). Within the limits of experimental reproducibility, the mass spectrometric behavior of the two alcohols was identical when the site of ionization was the alcohol functional group. Only under conditions of electrophilic addition ionization were significant differences observed between 1 and 2.

Significant attention has been devoted to comparisons of the behavior of cyclopropylcarbinyl and homoallyl derivatives in solvolytic reactions.[1] Although it has been contended that "most of the [solvolytic] reactions of allylcarbinyl derivatives may be explained on the basis of the formation of a cyclopropylcarbinyl cation," [2] considerable controversy exists concerning the detailed structures of the intermediate species involved in these reactions.[1,3]

In light of these studies, it is striking that no detailed comparison of the mass spectrometric behavior of any cyclopropylcarbinyl and homoallyl derivatives has appeared. We now wish to report our results concerning the behavior of 8,9-dehydro-2-adamantanol (1) and 2-*exo*-protoadamantenol (2) in the mass spectrometer employing both electron impact and chemical ionization techniques.



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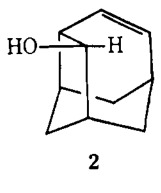

2

Table I
Partial Electron Impact Spectra of 1 and 2

	% ionization[a,b] ($100 I_i / \sum_{sample} I_i$)						
	70 eV		20 eV		14.2 eV		
m/e	1	2	1	2	1	2	Comment
43	0.9	1.0	0.9	0.8	0.8	0.6	
54	2.6	2.4	3.5	3.1	3.0	1.8	
57	1.6	1.9	1.7	1.6	1.5	1.1	
72	3.2	4.4	6.8	6.3	9.4	8.9	
77	4.3	3.4	0.8	1.0			
78	4.9	4.9	5.3	5.4	4.9	4.9	
79	12.4	14.2	12.4	14.4	6.8	6.7	C_6H_7
80	6.9	9.7	11.4	11.2	11.9	10.8	
91	5.0	4.2	3.3	3.4	2.0	2.0	C_7H_7
92	1.1	1.1	1.0	1.1	0.7	0.7	
93	1.6	1.7	1.8	1.9	1.3	1.4	
104	1.8	2.5	3.1	2.9	3.9	3.3	M − (H_2O + C_2H_4)
108	1.2	1.5	2.3	2.1	2.8	2.5	
117	4.0	5.0	6.9	6.2	6.1	5.6	M − (OH + CH_4)
132	1.4	2.1	2.6	2.3	4.0	3.1	M − (H_2O)
133	0.3	0.7	0.9	0.7	1.3	0.8	M − (OH) and ^{13}C of M − (H_2O)
150	7.6	10.0	12.3	14.2	21.2	28.4	M

[a] The ion intensities reported are uncorrected for ^{13}C isotope. [b] The reproducibility of the per cent ionizations reported is ±15% of the reported value.

Results and Discussion

Electron Impact Spectra. The partial electron impact mass spectra of 1 and 2 measured at 70, 20, and 14.2 eV are reported in Table I. The most striking conclusion resulting from a comparison of these data is that there is little difference in the electron impact fragmentations of 1 and 2 over this range of energies. Indeed, any differences in the ionic abundances of 1 and 2 reported in Table I are within the limits of experimental reproducibility. The absence of significant differences in the electron impact spectra of **1** and **2** is compatible with a common structure for the decomposing molecular ions produced by direct ionization with electrons of these energies.

The electron impact mass spectra of a number of 2-substituted adamantanes have previously been reported,[4-7] and the major fragment ions obtained from the structurally similar alcohol (**1**) are consistent with these results. However, in contrast to the reported 70-eV electron impact spectrum of 2-adamantanol (**3**),[5] **1** shows a much more intense molecular ion and a much less abundant $(M - H_2O)\cdot^+$ ion. Thus, relative to **3**, the presence of the cyclopropyl moiety in **1** stabilizes the molecular ion and inhibits the loss of water from it upon electron impact.

Further examination of Table I shows that as the electron energy is decreased from 70 to 14.2 eV a decrease in the overall amount of fragmentation of the molecular ions of both **1** and **2** occurs. However, even at the lowest energy of 14.2 eV, sufficient differences are not present in the abundances of the fragment ions of **1** and **2** to reveal any significant differences in the structures of the decomposing molecular ions of **1** and **2**. Thus, differentiation of **1** and **2** by electron impact mass spectrometry is essentially impossible.

Chemical Ionization Spectra. Chemical ionization mass spectrometry[8,9] is a form of mass spectrometry in which the sample is ionized as the result of an ion–molecule reaction between the sample and the ions of some reactant species. The ions of the reactant species are formed by a combination of electron impact ionization and ion–molecule reactions in a high-pressure mass spectrometer source. The reactions in the mass spectrometer source of these reactant ions with the sample, which is present only in trace amounts, produce the chemical ionization mass spectrum of the sample. The chemical ionization mass spectra of substances are usually markedly different from the spectra produced by electron impact ionization and thus the chemical ionization mass spectrum of a compound will often reflect different aspects of its structure than will the electron impact spectrum. Moreover, by varying the nature of the reactant ions, chemical ionization experiments can be carried out which specifically effect proton or hydride transfer, massive particle addition, or charge exchange.

Proton Transfer Chemical Ionization Spectra. If the reagent gas employed in chemical ionization produces reactant ions which act as Brønsted acids in the gas phase, then the resulting sample spectrum will be due to $(M + H)^+$ and any of its fragment ions. Of course, as the proton affinity of a species decreases, the strength of its conjugate Brønsted acid increases. Consequently, in chemical ionization the H_3^+ reactant ion in hydrogen is a stronger Brønsted acid than the CH_5^+ and $C_2H_5^+$ reactant ions formed in methane, which in turn are stronger protonating reagents than the $t\text{-}C_4H_9^+$ reactant ion in isobutane.[10] Thus, by varying the acid strength of the reactant ion, it is possible to vary the exothermicity of the proton transfer reaction and hence the resulting fragmentation.

Table II
Protonation Chemical Ionization Spectra of 1 and 2

	% ionization[a, b] $(100I_i/\Sigma_{\text{sample}} I_i)$						
	H_2		CH_4		$i\text{-}C_4H_{10}$		
m/e	1	2	1	2	1	2	Comment
67	2.4	2.5	1.0	1.0	1.4		
69			1.0	1.1	3.1		
71	0.9	1.1	0.8	1.0	2.1		
79	4.7	4.6	1.2	1.0	1.1	1.3	C_6H_7
81	2.2	2.5	0.6	0.6	0.9		
91	12.8	15.0	9.6	13.0	5.6	7.5	C_7H_7
92	1.1	1.2	0.8	1.2			
93	2.2	2.1	1.1	1.0	2.1		
95	1.5	1.9	0.5	0.6	2.2		
105	2.2	2.0					
107	1.8	2.5					
113					5.1	2.4	
121	2.6	3.2	1.6	1.8			
131	2.6	2.4	1.0	1.0			
132	0.4	0.6	0.5	0.3			
133	38.0	34.6	57.8	53.7	62.1	73.4	M − OH
134	3.6	3.8	6.7	5.6	7.2	8.9	
135			1.2	1.7			
149	10.7	10.3	9.2	8.2	1.1	2.4	M − H
150	2.1	1.5	2.7	2.7	0.9	1.1	M
151	0.8	1.1	2.5	4.0	0.9	1.6	M + H
179				0.2			$M + C_2H_5$
191				0.04			$M + C_3H_5$

[a] The ion intensities reported are uncorrected for ^{13}C isotope. [b] The reproducibility of the per cent ionization reported is ±15% of the reported value.

The chemical ionization spectra of **1** and **2**, which were obtained with hydrogen, methane, and isobutane as reagent gases, are summarized in Table II. As expected, the extent of fragmentation of **1** and **2** decreases as the acid strength of the reagent ions decreases; *i.e.*, the greatest fragmentation occurs with hydrogen and the least with isobutane. With hydrogen as the reagent gas, the extent of decomposition of the $(M + H - H_2O)^+$ ions is extensive, but there are essentially no differences present in the relative abundances of the fragment ions of *m/e* less than 133 in the hydrogen spectra of **1** and **2**. This suggests that with hydrogen as reagent gas the decomposing ions of *m/e* 133 from **1** and **2** have the same structure. Furthermore, although the methane chemical ionization spectra of **1** and **2** show significantly less decomposition of the ions with *m/e* 133 than is the case with hydrogen, the relative abundances of the low-mass fragment ions in the methane spectra of **1** and **2** are essentially identical. Thus, it also appears with methane as reagent gas that the decomposing ions of *m/e* 133 from **1** and **2** have the same structure. However, speculation on the structures of these fragment ions is unwarranted in the absence of precise mass measurements and studies with labeled compounds.

The most intense ion in the isobutane chemical ionization spectra of **1** and **2** is the $(M - OH)^+$ ion. Although this ion is obviously formed by the removal of the hydroxyl group from the alcohols, it is not clear whether the *m/e* 133 ion results from a proton transfer reaction followed by dissociation

$$C_{10}H_{13}OH + t\text{-}C_4H_9^+ \longrightarrow C_{10}H_{13}OH_2^+ + C_4H_8$$

$$C_{10}H_{13}OH_2^+ \longrightarrow C_{10}H_{13}^+ + H_2O$$

or an abstraction reaction.

$$C_{10}H_{13}OH + t\text{-}C_4H_9^+ \longrightarrow C_{10}H_{13}^+ + t\text{-}C_4H_9OH$$

The extent of fragmentation of the $(M - OH)^+$ ions in the isobutane chemical ionization spectra of **1** and **2** is significantly less than that observed with hydrogen or methane as reagents. The small differences in the isobutane spectra of **1** and **2** may be real and may indicate differences in the structures of the decomposing $(M - OH)^+$ ions. However, the differences in the isobutane chemical ionization spectra of **1** and **2** are not sufficiently great to warrant confident interpretation.

Table III
Partial N_2 and N_2–NO Chemical Ionization Spectra of 1 and 2

	% ionization[a,b] ($100 I_i/\Sigma_{sample} I_i$)				
	N_2		N_2/7.3% NO		
m/e	1	2	1	2	Comment
72	1.4	1.3			
77	1.3	1.2	0.2		
78	4.8	4.2	0.4	0.4	
79	21.4	24.5	3.1	2.5	C_6H_7
80	6.5	7.0	1.0	1.0	
91	6.9	7.3	3.7	1.7	C_7H_7
92	1.5	1.8	0.4	0.3	
93	3.0	3.0	0.9	0.8	
104	1.2	1.2	0.1	0.1	$M - (H_2O + C_2H_4)$
108	0.7	0.8	0.4	0.4	
117	3.9	3.5	0.6	0.6	$M - (OH + CH_4)$
132	1.4	1.4	0.5	0.4	$M - H_2O$
133	14.0	13.3	26.0	8.8	$M - OH$
150	2.6	3.5	17.4	19.2	M
162			1.2	1.2	$M + NO - H_2O$
180			22.8	42.4	$M + NO$

[a] The ion intensities reported are uncorrected for ^{13}C isotope. [b] The reproducibility of the per cent ionizations reported is ±15% of the reported value.

Table IV
Metastable Transitions Observed in the N_2–5% NO Chemical Ionization Spectra of 1 and 2

1

$(M + NO)^+ \longrightarrow (M + NO - H_2O)^+$
$(M + NO)^+ \longrightarrow M\cdot^+$
$(M + NO)^+ \longrightarrow (M - OH)^+$
$(M + NO)^+ \longrightarrow m/e\ 91$
$(M + NO - H_2O)^+ \longrightarrow m/e\ 91$

2

$(M + NO)^+ \longrightarrow (M + NO - H_2O)^+$
$(M + NO)^+ \longrightarrow M\cdot^+$
$(M - OH)^+ \longrightarrow m/e\ 117$
$M\cdot^+ \longrightarrow m/e\ 117$

Isobutane chemical ionization spectra of several aliphatic alcohols have been reported.[11] For secondary alcohols there were observed, in addition to $(M - OH)^+$, $(M - H)^+$, and $(M + H)^+$ ions, two ions, $(M + 39)^+$ and $(M + 57)^+$, which have been attributed to the association of the $C_3H_3^+$ and $C_4H_9^+$ ions of the isobutane plasma with the molecule.[11] Although $(M + 39)^+$ and $(M + 57)^+$ ions are present in the isobutane chemical ionization spectrum of an alcohol of similar structure, namely 3,[12] and the addition of t-$C_4H_9^+$ to olefins to form $(M + 57)^+$ ions has been reported,[13] $(M + 39)^+$ and $(M + 57)^+$ ions were not observed in the isobutane chemical ionization spectra of 1 or 2. This suggests that either the basicities of 1 and 2 are sufficiently increased relative to 3 so that the t-$C_4H_9^+$ ion acts only as a Brønsted acid with 1 and 2 to form $(M + H)^+$ ions, some of which then decompose, or the "unsaturation" present in 1 and 2 increases the stability of the $(M - OH)^+$ ions sufficiently so that the decomposition of the $(M + 57)^+$ ions is essentially complete.

Although it is apparent that the chemical ionization spectra of 1 and 2 are different from the electron impact spectra and emphasize *different* aspects of the two alcohols, it is obvious that the chemical ionization spectra could not be employed to confidently differentiate 1 and 2.

Charge Exchange Spectra. If the reagent gas employed in chemical ionization does not contain hydrogen, then proton transfer reactions cannot occur. When nonhydrogen-containing gases (*e.g.*, the rare gases, nitrogen, oxygen, carbon monoxide, and nitric oxide) are used in chemical ionization experiments, the principal ion–molecule reaction which occurs is charge exchange.[14] Thus, the radical molecular ion of the sample results from an electron transfer reaction (where $G\cdot^+$ is the reactant ion).

$$M + G\cdot^+ \longrightarrow M\cdot^+ + G$$

At pressures of about 1 Torr, the mass spectrum of nitrogen consists of three major ionic species (N_2^+, N_3^+, and N_4^+), all of which are rather high-energy ions that react by charge exchange and produce significant amounts of fragment ions of the sample. The nitrogen charge exchange spectra of 1 and 2 are summarized in Table III. Once again, the striking similarities in the behavior of 1 and 2 are immediately apparent. As is typical,[14] these charge exchange spectra are much more closely related to the electron impact spectra of 1 and 2 than to the chemical ionization spectra of these alcohols. However, it is to be noted that whereas upon electron impact 1 and 2 prefer dehydration to loss of hydroxyl, $(M - H_2O)\cdot^+/(M - OH)^+ \sim 4$–11, this behavior is reversed under charge exchange: $(M - H_2O)\cdot^+/(M - OH)^+ \sim 0.1$.

Recently, mixtures of 1–10 mol % of nitric oxide in nitrogen have been employed as charge exchange chemical ionization reagents.[15,16] Mixtures of greater than 5 mol % of nitric oxide in nitrogen produce mostly NO^+ ions. Previously, it has been shown that chemical ionization with pure nitric oxide also produces NO^+ in high abundance which can function as (a) an electron acceptor to provide $M\cdot^+$ radical ions, (b) a hydride abstracting agent to give $(M - H)^+$ ions, or (c) an electrophile to produce $(M + NO)^+$ ions.[17]

The chemical ionization spectra of 1 and 2 produced with a 7.3 mol % mixture of nitric oxide in nitrogen are summarized in Table III. Inspection of Table III shows that there are *considerable differences in the nitric oxide–nitrogen* chemical ionization spectra of 1 and 2 and that under these conditions 1 and 2 can clearly be distinguished. Thus, $(M + NO)^+$ is the dominant ion in the spectrum of 2 and $(M + NO)^+:M^+:(M - OH)^+ \simeq 5:2:1$, whereas in 1 the ion distributions are quite different and $(M + NO)^+:M^+:(M - OH)^+ \simeq 0.9:0.7:1$. That the amount of fragmentation in 1 and 2 is less in nitric oxide–nitrogen than in nitrogen reflects the fact that the recombination energy of nitric oxide is considerably less than that of nitrogen.[14]

The differences in behavior of 1 and 2 with nitric oxide–nitrogen chemical ionization are graphically illustrated in Figures 1 and 2, in which the contributions of the four major ions [$(M + NO)^+$, $M\cdot^+$, $(M - OH)^+$, and *m/e* 79 (perhaps protonated benzene)] in the spectra of 1 and 2 relative to the total sample ionization are plotted as a function of the mole per cent of nitric oxide in the nitric oxide–nitrogen mixtures. Striking differences for 1 and 2 are evident in the curves for the $(M + NO)^+$ and $(M - OH)^+$ ions. At least some of the $(M - OH)^+$ ions formed from 1 result from the decomposition of the $(M + NO)^+$ adduct, since a metastable transition is observed for this process (see Table IV). However, no metastable transition was observed for this process in 2. The curves for the variation in concentration of the $M\cdot^+$ ions with increasing nitric oxide concentration are similar for 1 and 2 and metastable transitions for $(M + NO)^+$ ions decomposing to $M\cdot^+$ ions are present for both 1 and 2. The marked decrease in the nitric oxide–

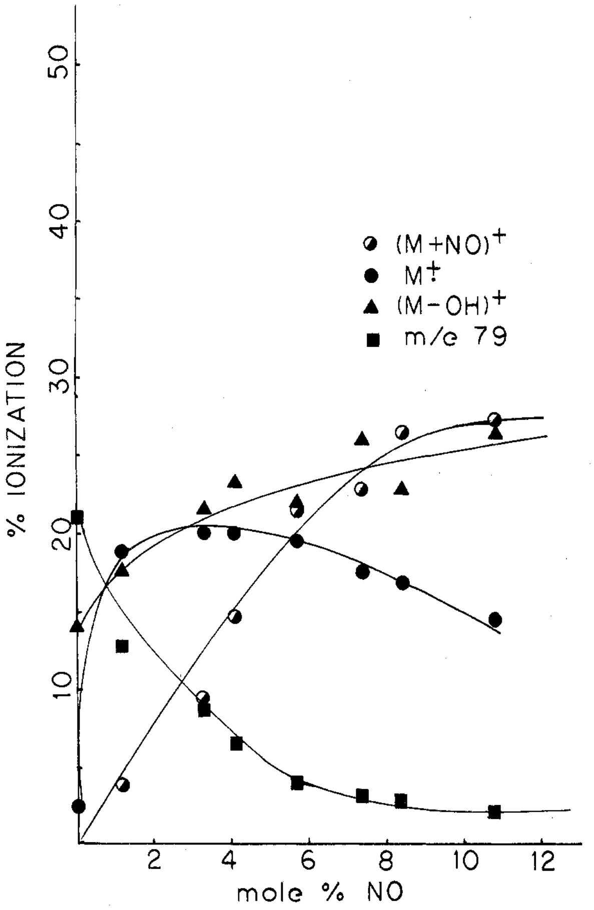

Figure 1. Behavior of several ions in the nitric oxide–nitrogen chemical ionization spectra of 1 as a function of the amount of nitric oxide present.

nitrogen spectra in 1 and 2 of the relative abundance of the major fragment ion in the nitrogen charge exchange spectra, *i.e.*, *m/e* 79, suggests that this ion is not produced to a significant extent by reactions of NO^+. The small amounts of *m/e* 79 that are still present at high concentrations of nitric oxide may result from a slow reaction of NO^+ or they may result from reactions of the small amounts of N_2^+, N_3^+, or N_4^+ ions that are present in the reagent gas.

Hunt and Ryan have reported that the nitric oxide chemical ionization spectra of secondary alcohols show abundant $(M - 1)^+$, $(M - 17)^+$, and $(M - 2 + 30)^+$ ions.[17] It was proposed that the $(M - 2 + 30)^+$ ion is formed by oxidation of the alcohol and subsequent attachment of NO^+ to the resulting ketone.[17] However, reaction of NO^+ with 1 and 2 yields $(M + 30)^+$ ions and no $(M - 2 + 30)^+$ ions. Thus, it appears that the addition of NO^+ to 1 and 2 does not involve exclusive reaction at the alcohol substituent, but rather extensive electrophilic attack occurs at the cyclopropyl or olefinic moieties of 1 and 2. Such behavior is not unprecedented, as the addition of NO^+ to olefins and olefinic alcohols to produce $(M + 30)^+$ ions has recently been observed,[18] and the nitric oxide chemical ionization spectrum of cholesterol also shows an abundant $(M + 30)^+$ ion.[14]

The major reactions of NO^+ with alcohols 1 and 2 can be summarized as follows:

$$M + NO^+ \longrightarrow$$

$$(M + NO^+)^* \longrightarrow \begin{cases} (M + NO)^+ & \text{(a)} \\ M^+ + NO & \text{(b)} \\ (M - OH)^+ + HNO_2 & \text{(c)} \end{cases}$$

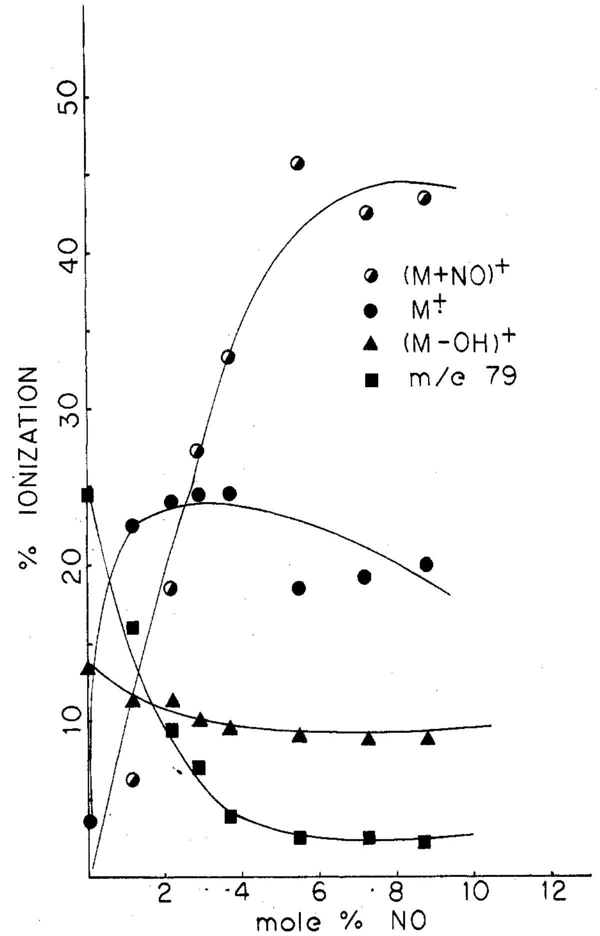

Figure 2. Behavior of several ions in the nitric oxide–nitrogen chemical ionization spectra of 2 as a function of the amount of nitric oxide present.

Electrophilic attack to produce $(M + NO)^+$ is necessarily an exothermic reaction. The relative amounts of addition and reaction, *i.e.*, a *vs.* b + c, depend upon the stability of the addition ion and the stabilities of the possible reaction ion products. Thus, if reactions b and c are endothermic, then electrophilic addition is expected to predominate. If reactions b and c are strongly exothermic, then the products of these reactions should predominate and relatively little electrophilic addition should be observed. If the reactions are approximately thermoneutral, then small differences in the heats of formation of the reactants and products may produce significant changes in the ionic product distribution. Since the ratio $(M + NO)^+/M^{\cdot+}$ is substantially larger for 2 than for 1, it would appear that charge exchange to 2 is less exothermic than charge exchange to 1, and, consequently, that the ionization potential of 1 is slightly lower than the ionization potential of 2.

Experimental Section

All electron impact spectra were obtained with a Du Pont CEC 21-110B mass spectrometer. The source block temperature was 100–120°, the repeller voltage 0 V, and the accelerating voltage 8 kV. The low-voltage electron energy was calibrated against the appearance potential of the CH_3^+ ion in methane.[19] At ionization energies much below 14.0 eV the total beam current was so small that reproducible spectra could not be obtained with the electron multiplier detector being used.

The chemical ionization experiments were carried out with a Du Pont CEC 21-110B mass spectrometer that had been modified for high-pressure operation.[14,20] The experimental conditions employed were: source block temperature 100–120°, accelerating voltage 6 kV, electron energy 400–600 eV, repeller field strength 0 V/cm, and source pressure 0.7–1.0 Torr. The technique for the mixing of reagent gases for chemical ionization experiments has been described.[15]

All samples were introduced into the source region of the mass spectrometer by direct insertion probe. An all glass probe (manufactured by Mass Spectrometer Accessories, College Station, Tex.), which has a separate heating and control system, was used in all experiments. Probe temperatures necessary for sample vaporization were 35–45°.

8,9-Dehydro-2-adamantanol (1) was prepared by the sodium borohydride reduction of 8,9-dehydro-2-adamantanone (**4**) as described by Baldwin and Foglesong.[21] However, an improved procedure for the synthesis of **4** was employed.[22]

2-*exo*-Protoadamantenol (2). To 10 ml of an 80% aqueous acetone solution which was 0.05 *M* in perchloric acid was added 100 mg of **1**. The solution was stirred at reflux for 18 hr and then diluted with 20 ml of water, neutralized with saturated sodium bicarbonate solution, and extracted with ether (3 × 30 ml). The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate, and the solvent was evaporated at reduced pressure. Glpc analysis (10 ft × 0.25 in. FFAP column, 190°, 60 ml/min of He) of the residue indicated a single component and pmr analysis (integration of the olefinic proton signals *vs.* chloroform as an internal standard) showed that the olefinic product was obtained in nearly quantitative yield. Pure **2** was isolated by glpc (above conditions) to give a white solid: mp 188–189°; pmr ($CDCl_3$) δ 6.45–5.9 (m, 2 H, olefinic protons), 3.71 [(br s, $W_{1/2}$ = 3.2 Hz, CH(OH)], 2.7–1.2 (m, 13 H); ir (CCl_4) 3630, 3350, 3035, 2920, 2865, 2850, 1460, 1430, 1365, 1210, 1175, 1150, 1100, 1060, 1050, 1030, 1015, 1000, 975, 945, 920, 900, and 700 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.82; H, 9.27.

The skeletal framework of **2** and the skeletal position and stereochemistry of the hydroxyl substituent in **2** were established by conversion of **2** to the known alcohol,[23] **2-*exo*-protoadamantanol (5).** A solution of 40 mg of **2** in 25 ml of ethanol was stirred with 100 mg of 5% palladium on charcoal under an atmosphere of hydrogen for 24 hr. The reaction mixture was then diluted with 100 ml of pentane and filtered to remove the catalyst. The catalyst was washed with pentane (2 × 20 ml) and the combined organic extracts were washed with several portions of water and then dried over anhydrous magnesium sulfate.

Evaporation of the solvent at reduced pressure provided an oily residue which glpc analysis (5 ft × 0.25 in. FFAP column, 175°, 60 ml/min of He) showed contained a single component. Isolation of this compound by glpc (above conditions) gave pure **5**, which was identified by comparison of its ir spectrum with that of an authentic sample.[23]

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Registry No.—**1**, 20815-30-9; **2**, 52217-09-1.

References and Notes

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Reductive Arylation of Aromatic Hydrocarbons. I. Naphthalene and Anthracene[1]

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Reductive phenylation of anthracene and naphthalene *via* treatment of the hydrocarbons with metals (sodium or potassium) in liquid ammonia and then with halobenzenes furnished 9-phenyl-9,10-dihydroanthracene and isomeric 1-phenyldihydronaphthalenes and 2-phenyldihydronaphthalenes in good yields. With lithium metal only the reduction of the hydrocarbon is obtained. A benzyne mechanism is proposed.

Metal–ammonia reduction and reductive alkylation of hydrocarbons have been widely used.[2] The structures of the dihydroaromatic products obtained by metal–ammonia reductions correlate to a remarkable degree with predictions of Hückel molecular orbital theory,[3] and several hydrocarbons such as naphthalene,[4] anthracene,[2b] phenanthrene,[5] chrysene,[6] cycloheptatriene,[7] fluoranthene,[8] biphenyl,[9] and terphenyl[10] have been reduced to the anions and then alkylated. The reductive methylations of anthracene, benz[*a*]anthracene, and dibenz[*a*,*h*]anthracene occur with regiospecificity to furnish the *cis*-dialkyldihydro derivatives.[11]

However, as far as we know, no attempt was made to perform a reductive *arylation* of these hydrocarbons. The recently discovered reaction of phenyl radical with hydrocarbons such as indene, fluorene, 1,3-pentadiene, and anethole[12] by the $S_{RN}1$ mechanism[13] to furnish the aryl-substituted hydrocarbons prompted us to investigate the possibility of phenylating aromatic hydrocarbons under reductive conditions, and we performed some reactions to try the