mass spectra. The cycloalkanones **4**, cyclohexanecarboxaldehyde (**3c**), and 5-hexene-2-one (**5b**) were obtained commercially. 4-Penten-2-one (**5a**) was available as a major impurity in 3-penten-2-one obtained from the Aldrich Chemical Co. Authentic samples of cyclobutanecarboxaldehyde (**3a**) and cyclopentanecarboxaldehyde (**3b**) were obtained from the reactions of cyclopentene and cyclohexene with oxygen atoms. Spiro epoxides **2** were prepared by reaction of the olefins with *m*-chloroperbenzoic acid. 6-Hepten-2-one (**5c**) was made by the acetoacetic ester synthesis.[9]

Trace amounts of 2-methylenetetrahydrofuran and 2-methylenetetrahydropyran were detected from the reactions of **1a** and **1b**, respectively. These enol ethers were independently synthesized by dehydrohalogenation reactions.[10]

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Registry No.—**1a**, 1120-56-5; **1b**, 1528-30-9; **1c**, 1192-37-6; **2a**, 157-48-2; **2b**, 185-60-4; **2c**, 185-70-6; **3a**, 2987-17-9; **3b**, 872-53-7; **3c**, 2043-61-0; **4a**, 120-92-3; **4b**, 108-94-1; **4c**, 502-42-1; **5a**, 13891-87-7; **5b**, 109-49-9; **5c**, 21889-88-3.

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Position of Nucleophilic Attack on Propargylic ↔ Allenylic Cations. An Ab Initio Molecular Orbital Calculation

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In an earlier communication,[1] we reported on the mechanism of addition of HCl to 1,2,3-pentatriene in ethanol-water (95% v/v). The first and rate-determining step is a proton transfer to the terminal carbon atom. In the second step, a chloride ion is attached to the intermediate cation to give 20% allenylic chloride (1,2 adduct) and 80% propargylic chloride (1,4 adduct). In sulfolane–CH_2Cl_2 (80:20 v/v), this ratio is 50:50.

$$CH_3{-}C^4H{=}C^3{=}C^2{=}C^1H_2 + H^+ \xrightarrow{\text{slow}} [CH_3{-}C_\alpha{}^4H\underset{\cdots}{-}C^3\underset{\cdots}{=}C_\beta{}^2{-}C^1H_3]^+$$

$$[CH_3{-}C_\alpha{}^4H\underset{\cdots}{-}C^3\underset{\cdots}{=}C_\beta{}^2{-}C^1H_3]^+ + Cl^- \rightarrow CH_3CH{=}C{=}CClCH_3 + CH_3CHClC{\equiv}CCH_3$$

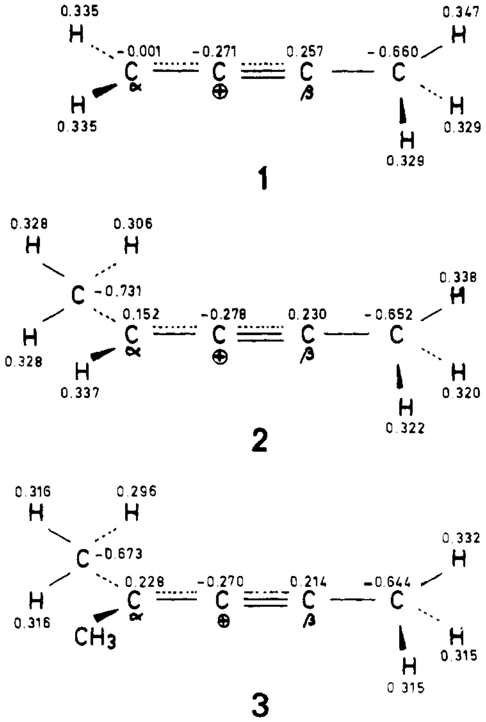

Figure 1. Net atomic charges from ab initio wave functions.

Similar intermediate carbocations are generated by S_N1 solvolysis of allenylic or propargylic halides or tosylates in aqueous solvents.[2–8] In these solvolysis reactions attack on the cation by solvent occurs exclusively at C_α to give propargylic products, unless attack at C_α is sterically hindered. The high preference for attack at C_α rather than at C_β is not expected on the basis of ^1H[9] and ^{13}C NMR[10] measurements on the relevant cations. These measurements suggest that the positive charge is present not exclusively on the propargylic position but, to a certain extent, also on the allenylic position.

In order to better understand the behavior of these cations as well as the possible influence of methyl substituents, we calculated ab initio charge distributions and molecular electrostatic potentials for cations **1–3**. A (C 6s,3p/H 3s) basis set of Gaussian-type functions contracted to a split-valence [3s,2p/2s] set was adopted.[11] Geometries of the cations were taken from ref 12–14. Gross atomic populations were calculated from the wave functions by means of Mulliken's population analysis.[15]

$$\left[\underset{\textbf{1}}{C_\alpha{}^4H_2\underset{\cdots}{-}C^3\underset{\cdots}{=}C_\beta{}^2{-}C^1H_3}\right]^+$$

$$\left[\underset{\textbf{2}}{CH_3{-}C_\alpha{}^4H\underset{\cdots}{=}C^3\underset{\cdots}{=}C_\beta{}^2{-}C^1H_3}\right]^+$$

$$\left[\underset{\textbf{3}}{(CH_3)_2C_\alpha{}^4\underset{\cdots}{-}C^3\underset{\cdots}{=}C_\beta{}^2{-}C^1H_3}\right]^+$$

The corresponding net atomic charges (in units of proton charge) are given in Figure 1. It appears that cations **1** and **2** have a higher positive charge on C_β than on C_α. However, the atomic charges on C_β and C_α are not the only determining factors for nucleophilic attack. One should also include the charge distributed over the hydrogen atoms. Therefore, we have calculated the total charge on each side of the central carbon atom C^3. (The charge on C^3 is approximately equal for the three cations.) The results are given in Table I, where q_{prop} is the total charge on the atoms to the left of C^3 and q_{all} is the total charge on the right-hand side (cf. Figure 1).

In all cations, $q_{prop} > q_{all}$, i.e. most of the positive charge is associated with the propargylic center. Moreover, the ratio

Table I. Sum of the Net Atomic Charges on Each Side of the Central Carbon Atom (in Units of Proton Charge)[a]

Cation	Registry no.	q_{prop}[a]	q_{all}[a]	q_{prop}/q_{all}	$q_{prop} - q_{all}$
1	64235-83-2	0.669	0.602	1.1	0.067
2	64235-82-1	0.720	0.558	1.3	0.162
3	53474-96-7	0.738	0.532	1.4	0.206

[a] Abbreviations prop and all refer to the left- and right-hand sides in Figure 1, respectively.

Table II. Potentials at Positions A, B, C, and D

	Potential, au					
	C_α attack		C_β attack		$\alpha - \beta$ difference, kacl mol^{-1}	
Cation	A	B	C	D	A − C	B − D
1	0.187	0.186	0.180	0.175	4.4	6.9
2	0.183	0.183	0.168	0.164	9.4	11.9
3	0.180	0.180	0.160	0.156	12.5	15.0

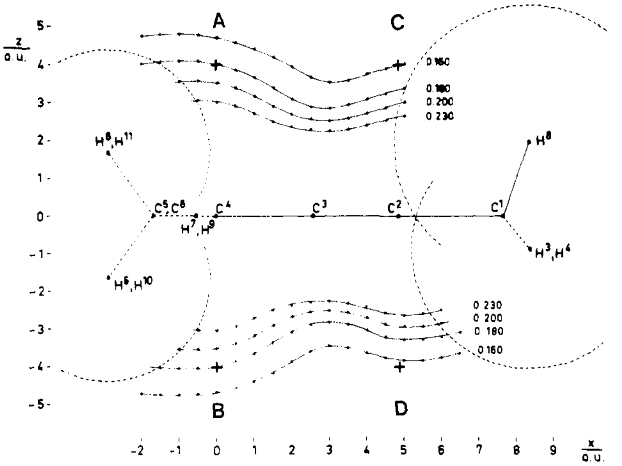

Figure 2. Contour lines of equal potential in the *xz* plane of cation 3.

q_{prop}/q_{all} increases when going from cation 1 to 3. It is worth noting that Olah[10] concluded from his ^{13}C NMR data on cation 3 the same ratio of 1.4. Thus, the ^{13}C NMR chemical shifts better fit the charges calculated for groups than for separate carbon atoms. This is in line with results by Fliszár,[16] who concluded that for alkanes the ^{13}C NMR shifts and calculated net charges only correlate well if part of the charge on the hydrogens is added to the carbon charge. From the increase in q_{prop}/q_{all} from cation 1 → 3, we conclude that methyl substitution at the propargylic position increases the preference for nucleophilic attack at that position.

The consideration of atomic or group charges tells us little about the difference in activation energy between attack at C_α and C_β. Ideally we should calculate the interaction energy in the R^+Cl^- system as a function of its geometry, e.g., by the ab initio SCF method. However, in view of the size of our systems, such a complete calculation was out of the question. Instead, we calculated the electrostatic potential V around the cation R^+.[17]

A first-order approximation of the energy of a chloride ion in the field of a cation can be obtained by multiplying V by the charge of Cl^-, i.e., −e. Since we are dealing with cations, the electrostatic potential is positive everywhere. Chloride will preferentially attack the centers with the higher positive potential. The potential field was calculated from the cation ab initio wave functions for two perpendicular planes through C^1–C^4. In the main molecular plane the potentials are appreciably smaller than in the one perpendicular to it. Therefore, we only consider the potential field in the latter plane. Contours of equal potential in this plane around cation 3 are shown in Figure 2. The potential becomes progressively higher as we approach the atomic centers. However, as soon as the charge clouds of Cl^- and the cation begin to overlap significantly, exchange forces will prevent a further approach of Cl^- toward the cation. We estimate that for this reason a region with a radius of 1.90 Å[18] around the hydrogens is not accessible (see circles in Figure 2) and likewise a region with a radius of ~1.80 Å around the carbons (based upon the C–Cl bond length) is not accessible also. The potentials are shown only outside these excluded regions. Inspection of Figure 2 shows that the potential is much higher at a given distance from C^4 or C^2 than from C^3, in agreement with the fact that C^4 and C^2 are the more positively charged carbons. In order to estimate the preference for attack at $C_\alpha{}^4$ as compared to attack at $C_\beta{}^2$, we consider the value of the potential at a distance of 4.0 au (2.12 Å) above and below C^4 and C^2 (points A, B, C, and D in Figure 2; Table II). We expect that 4.0 au is about the equilibrium distance to which Cl^- can approach an undisturbed cation. The results predict the preferred attack at C_α, i.e., formation of a propargylic product. The preference increases when going from cation 1 to 3, just as expected from the group charges.

To our knowledge, so far the electrostatic potential method has not been applied to studies of nucleophilic attack on cations. Therefore, it seems necessary to provide some justification for its use under these circumstances. Notably, one ignores exchange repulsion between the charge clouds of R^+ and Cl^-, as well as polarization and charge-transfer effects. We have therefore performed an SCF ab initio calculation on the system (cation 1 + Cl^-), with Cl^- at the A and the C position. The final SCF eigenvectors of R^+ (1) and Cl^- were used as starting vectors in the SCF calculation on R^+Cl^- (R^+ = 1). In this way, the energy in the first SCF iteration yields a first-order interaction energy. The results are shown in Table III. They show that the true first-order interaction energy (coulomb + exchange energy) is less than the potential energy (−eV), which means that at a distance of 4.0 au from the carbon atom Cl^- already experiences repulsive exchange forces. At position A, the exchange energy term (0.115 hartree) is lower than at position C (0.152 hartree). Hence, the more positive propargylic center will be approached more easily than the allenylic center. Moreover, the difference between the SCF and the first-order interaction energy, i.e., the polarization and charge-transfer effects, is more favorable for chloride attack near A than near C (Table III).

We conclude that the trend in the values of the potential energy (−eV) is enhanced in the more refined SCF calculation. Thus, although in the potential energy method the energy difference between positions A and C is much too small, this method does qualitatively give useful information.

Table III. SCF Ab Initio Calculation on the (Cl^- + Cation 1) System, with Cl^- at Position A or C

	Energy, hartree		A −C difference, kcal mol^{-1}
	Position A	Position C	
Potential energy (−eV)	−0.187	−0.180	− 4.4
Coulomb + exchange energy[a]	−0.072	−0.028	−27.6
Exchange energy[b]	0.115	0.152	
SCF interaction energy[c]	−0.230	−0.169	−38.3
Polarization and charge-transfer effects[d]	−0.158	−0.141	

[a] First-order interaction energy defined as E (first iteration) $- E_{\text{cation}} - E_{\text{Cl}^-}$, with $E_{\text{cation 1}} = -153.606\,838$ hartrees and $E_{\text{Cl}^-} = -458.922\,869$ hartrees.[19] [b] Difference between (coulomb + exchange energy) and potential energy. [c] Defined as $E_{\text{R+Cl}^-}{}^{\text{SCF}} - E_{\text{cation}} - E_{\text{Cl}^-}$. In addition to the first-order energy, this includes polarization and charge-transfer effects. [d] Difference between SCF interaction energy and (coulomb + exchange energy).

We are left with the question of why in sulfolane our HCl addition occurs in equal amounts at the α and β positions, instead of predominantly at C_α. To answer this question we first remark that our calculations are "gas phase calculations." For solutions their predictive value is restricted at best to weakly solvating solvents. Furthermore, the predictive value of electrostatic arguments such as we use is restricted to reactions with an early transition state.

To a certain extent both conditions are met in our chloride ion addition reaction in 95% aqueous ethanol. Water and alcohol are relatively hard solvents.[20] These hard solvents have only a minor solvating effect on our cations.[21] An early transition state is plausible because the chloride addition is a fast step, subsequent to the slow proton transfer.

Sulfolane will have an appreciably stronger solvating effect on the cation,[22] and our quantum chemical predictions are less applicable. For example, the propargylic position (C_α) could be the more strongly solvated position and therefore more screened for attack by chloride; the ratio of propargylic to allenylic attack will be lower than predicted. Moreover, the chloride attack might be slower in sulfolane than in aqueous alcohol and correspondingly the transition state somewhat more product-like. Probably, the energies of our propargylic and allenylic products are approximately equal. For example, from calculations on $H_2C{=}C{=}CHCl$ and $HC{\equiv}C{-}CH_2Cl$,[23] we find an energy difference of only 0.2 kcal/mol, the former molecule in fact being the slightly more stable one. Thus, if the transition state is more product-like, the product ratio will shift to 1:1.

Finally, we return to the literature data on solvolysis reactions of allenylic and propargylic halides and tosylates. These reactions are of the S_N1 type; their slow step can be considered to be the reverse of our Cl^--addition step. Since, as we just mentioned, the halides have approximately equal energies, our theoretical predictions are in line with a more rapid solvolysis of propargylic than of allenylic halides. As for Cl^- addition, the condition is that the solvent must have a low solvating power for cations. All these solvolysis reactions were performed in relatively hard aqueous solutions, and indeed all follow the predicted behavior of a faster rate for the propargylic compared with the allenylic isomer.[6] In the second step of these solvolysis reactions, a solvent molecule attacks either the α or the β position. Our calculations predict preferred attack at the α position, and indeed, experimentally, propargylic products are preferentially formed, except when attack at C_α is sterically highly hindered. Actually, in these systems, the ratio of propargylic to allenylic products is even higher than in our pentatriene system because of the presence of different substituents and the use of more aqueous solvents.

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The Spiropentyl to 3-Methylenecyclobutyl Cation Rearrangement Avoids CH^+-Trimethylenemethane or the 1-Bicyclo[1.1.1]pentyl Cation

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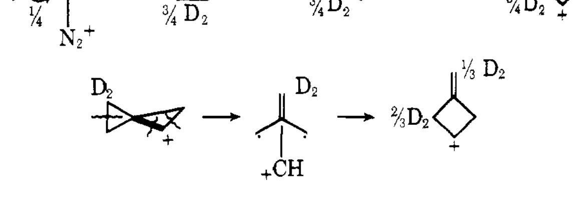
In view of successful efforts to characterize CH^+ complexes of $4n$ cyclic π systems and homologues,[1] the reported deuterium distribution in the 3-methylenecyclobutanol product from deamination of *anti*-4,4-dideuteriospiropentylamine[2] occasioned speculation in our laboratory that CH^+-trimethylenemethane (CH^+-TMM) might be involved. Applequist



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