

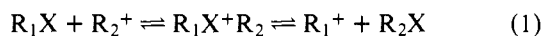
A MINDO/3 Investigation of Cyclic Chloronium Ion-Chloroalkyl Carbocation Equilibria. Comparisons with Stable Ion Solution Chemistry

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Abstract: MINDO/3 calculations of 13 tetramethylene- and pentamethylenechloronium ions and their isomeric chloroalkyl carbocations have been performed, with full geometry optimization except for primary carbocations. The relative stability orders of the halonium ions and carbocations, after branching errors are corrected, are in agreement with experiment. In all cases the halonium ions are predicted to be more stable than their respective chloroalkyl carbocation isomer. Although MINDO/3 tends to slightly overestimate the relative stability of chloronium ions, the calculations indicate, in agreement with experiment, that chloronium ions become relatively more stable than open carbocations in the gas phase. Based on reaction-coordinate calculations, some predictions on the ring-opening reactions have been made. Also, the rearrangement of six-membered to five-membered cyclic halonium ions is discussed. The importance of alkyl-group substitution at the α carbons of halonium ions and of entropy effects in the cyclization steps is emphasized.

Although ionic equilibria of the type shown in the equation



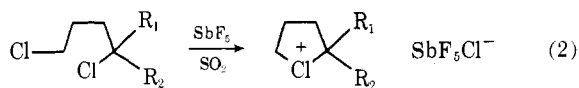
X = OH, NH₂, SH, halogen, etc.

R₁ = R₂ = H, alkyl, or aryl

have interested chemists for many years,² the widespread acquisition of instrumental and experimental techniques for the study of such processes in the gas phase has occurred principally within the past decade. The results of gas-phase studies are indeed significant as they complement studies in solution and provide, among other things, reaction energetics in the absence of solvent effects and relative stabilities of the cationic species. While a considerable amount of fruitful experimental effort has been expended in these studies,³⁻¹⁹ very little attention has been given to such reactions by theoreticians. However, experimental work done in one of our laboratories on halonium ion-haloalkyl carbocation equilibria in solution²⁰⁻²² has stimulated our interest in gas-phase model reactions and in theoretical methods which might allow us to predict reaction pathways as well as to calculate properties of intermediates.

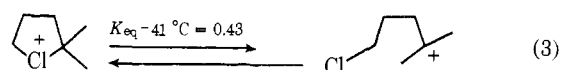
Until recently, good values for the properties of complex ground-state molecules or reactive intermediates could not be calculated because of the complexities of the calculations.²³ However, the MINDO/3 SCF MO method^{23,24} provides chemists with a means of obtaining good estimates, in many cases,²⁵ of some properties of ground-state molecules²⁴ and reactive intermediates.²⁶ Furthermore, it allows for the prediction of reaction pathways.²⁷ We have utilized this method for the study of halonium ion-haloalkyl carbocation equilibria.

Olah, Peterson, and co-workers²⁸ first showed that stable cyclic five-membered halonium ions can be prepared in solution by such reactions as the ionization of 1,4-dihaloalkanes in SbF₅-SO₂ at low temperature, eq 2. Although halonium

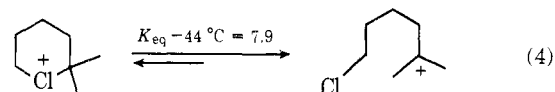


ions bearing fewer than two substituents on either carbon attached to halogen have been assumed to be static, closed ions,^{29,30} some 1,1-disubstituted three-, five-, and six-membered halonium ions have been shown to be in equilibrium with

open haloalkyl carbocations.^{29,31,32} Henrichs and Peterson³¹ have employed ¹³C NMR to evaluate the equilibrium constants for several systems, e.g., eq 3. It is evident from their work that



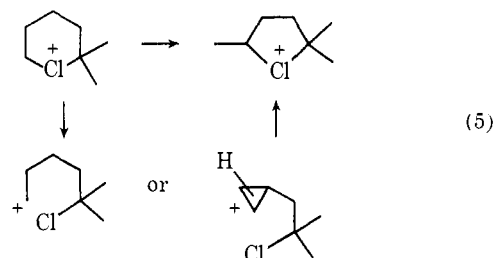
all alkyl-substituted five-membered chloronium or bromonium ions are more stable than their isomeric open haloalkyl carbocations at low temperature in nonnucleophilic media. With six-membered rings the equilibrium is shifted to the right; compare eq 3 and eq 4.³² McManus and Peterson²¹ have shown



that the halonium ion-haloalkyl carbocation equilibria are solvent dependent with halonium ion concentration increasing as the solvent polarity decreases.

Another interesting finding of the solution work is that some cyclic halonium ion ring sizes tend to be disfavored relative to other ring sizes, perhaps for multiple reasons.^{31,33} For example, a cursory comparison of the K_{eq} values for eq 3 and 4 leads one to suggest that an unusual ring stability order exists when halonium ions are compared to cycloalkanes.³⁴ However, after consideration of the effect of the chlorine on the stability of the respective carbocations, one concludes that the six-membered ring should open to a slightly more stable carbocation than that from the five-membered ring. This, of course, should be reflected in the equilibrium constant. Since enthalpy or entropy could control the magnitude of K_{eq} , the entropy effect is another factor to be considered.

When the 1,1-dimethylpentamethylenechloronium cation is prepared in sulfur dioxide solution, it rearranges to the 1,1,4-trimethyltetramethylenechloronium cation, eq 5. The



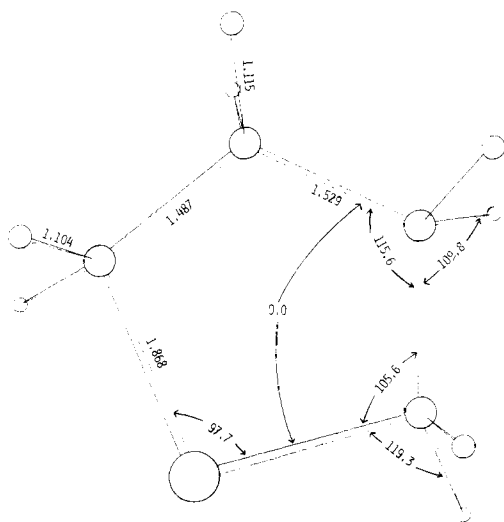


Figure 1. The MINDO/3 optimized geometry of the tetramethylenechloronium ion.

primary cation, formed by ring opening of the halonium ion in the unexpected direction, or the protonated cyclopropane, have been suggested as possible intermediates in the reaction.³¹ It would be of interest to calculate the energies involved for intermediates and transition states for rearrangement and, in fact, to determine if other routes for rearrangement are possible which have not been considered.

In this paper we evaluate the use of MINDO/3 for predicting the relative stabilities of cyclic halonium ions and their haloalkyl carbocation isomers.³⁵⁻³⁸ We have also calculated (1) the effect of alkyl group substitution on halonium ion stability, (2) the relative energies of some isomeric five- and six-membered halonium ions, and (3) the activation enthalpy for opening the unsubstituted five- and six-membered halonium ions along two reaction coordinates. The results and possible significance of these calculations are discussed.

Theoretical Section

All computations to be discussed in this work were accomplished using the MINDO/3 SCF MO method described by Dewar et al.,^{23,24} and previously employed in one of these laboratories for a variety of applications.^{27,39} The primary advantage of this method is the geometry-optimization feature based upon the Davidon-Fletcher-Powell method.⁴⁰ This geometry-optimization feature allows one to treat complex transition states and full reaction coordinates with a relatively small amount of computer time, an advantage which is not available, or if so takes prohibitive amounts of computer time, in alternative SCF MO procedures at the present time. For the calculations to be described, complete geometry optimizations were performed in all cases, the only restrictions being that the various methylene groups each have equal C-H bond lengths and equal H-C-C bond angles. This was done in an effort to prevent the open primary carbocations from rearranging by hydride shifts to the more stable secondary carbocations during the geometry-optimization procedure.

Results and Discussion

Tetramethylenechloronium Ion. The MINDO/3 optimized geometry of the tetramethylenechloronium ion is shown in Figure 1. As can be seen, this chloronium ion is predicted to be planar with C_{2v} symmetry. Its calculated enthalpy of formation is 153.83 kcal/mol. The tendency for MINDO/3 to underestimate ring puckering has been discussed;²⁴ it is possible that this ring system and others reported in this work may be too flat.

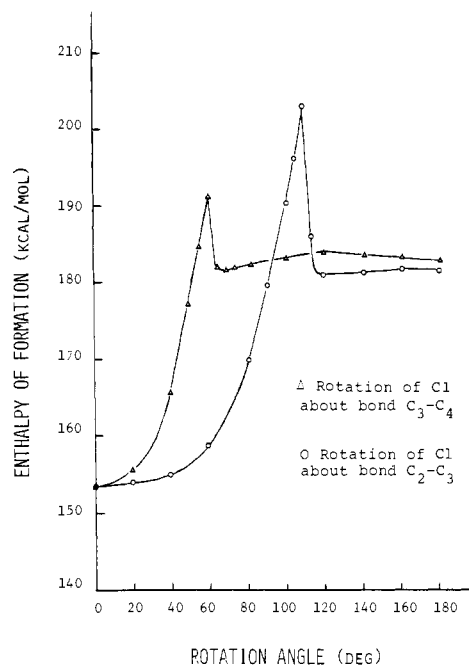


Figure 2. MINDO/3 energy surfaces for ring opening of the tetramethylenechloronium ion.

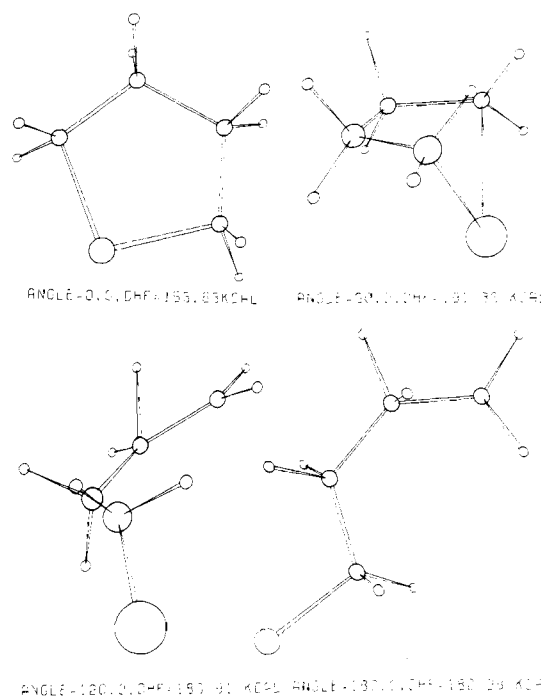


Figure 3. MINDO/3 geometries along the coordinate for rotation about the C_3 - C_4 bond.

Two reaction surfaces for ring opening of the tetramethylenechloronium ion are shown in Figure 2. MINDO/3 predicts that the lower energy pathway, with an activation enthalpy of ca. 37.5 kcal/mol, is rotation of the Cl about the C_3 - C_4 bond (Figure 2). The maximum in the potential surface (191.35 kcal/mol) occurs at an angle of 60.0° with respect to the plane containing the four carbons. At a rotation angle of 62.0° the enthalpy of formation has decreased to 181.96 kcal/mol. The C-Cl bond distances were 1.87 Å in the ground state (cyclic chloronium ion), 1.78 Å in the transition state, and 1.76 Å in the fully open carbocation (180° rotation angle). The geometry at several points along the reaction coordinate is shown in Figure 3. The other ring-opening reaction coordinate computed

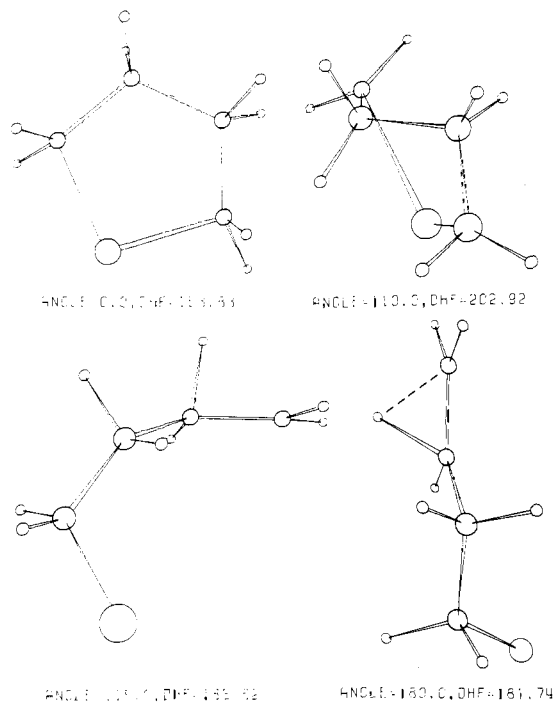


Figure 4. MINDO/3 geometries along the coordinate for rotation about the C₂-C₃ bond.

involved rotation about the C₂-C₃ bond (Figure 4). The maximum in this potential surface (202.92 kcal/mol) occurs at a rotation angle of 110.0°, and the predicted activation enthalpy was ca. 49.1 kcal/mol. The C₄-Cl bond distance at the potential maximum was 2.01 Å in this case, while it was 1.76 Å again for the fully open carbocation. Thus, for this latter reaction coordinate there is a substantially larger tendency for C₄-Cl bond stretching before the C₁-Cl bond actually breaks than is the case for the lower energy pathway. In fact, for the rotation about C₃-C₄ the C₄-Cl bond length decreases throughout the entire reaction coordinate. It should be noted that the optimized geometry of the carbocation for the latter pathway (180° rotation about C₂-C₃) is predicted to have an enthalpy of formation of 181.74 kcal/mol, which is only slightly more stable than the open cation for 62.0° rotation about C₃-C₄. A check of the reaction coordinate between the two conformations of the open carbocation (i.e., rotation about C₂-C₃ of the resulting conformer from 62° rotation about C₃-C₄) revealed that the activation enthalpy for passing from the 181.96 kcal/mol form to the 181.74 kcal/mol form was only ca. 0.7 kcal/mol. Thus it seems clear that of the ring-opening coordinates considered for the tetramethylenchloronium ion, rotation about the C₃-C₄ bond is preferred over rotation about the C₂-C₃ bond.

Pentamethylenchloronium Ion. The MINDO/3 optimized geometry of the pentamethylenchloronium ion is shown in Figure 5. This chloronium ion, in contrast to the tetramethylenchloronium ion, optimized to a puckered conformation very similar to the "chair" conformation of cyclohexane. The calculated enthalpy of formation of the pentamethylenchloronium ion is 145.18 kcal/mol. Again two reaction surfaces for ring opening were computed. As was the case for the tetramethylenchloronium ion, the barrier of rotation of Cl about the C₄-C₅ bond (Figure 5) was lower (45.9 kcal/mol, counterclockwise; 47.0 kcal/mol, clockwise) than was the case for rotation about C₃-C₄ (49.2 kcal/mol), although the difference was much less dramatic for the pentamethylenchloronium ion. The potential surface maxima occurred for a 170° counterclockwise rotation about C₄-C₅ (191.09 kcal/mol), for a 70° clockwise rotation about C₄-C₅ (192.17 kcal/mol), and

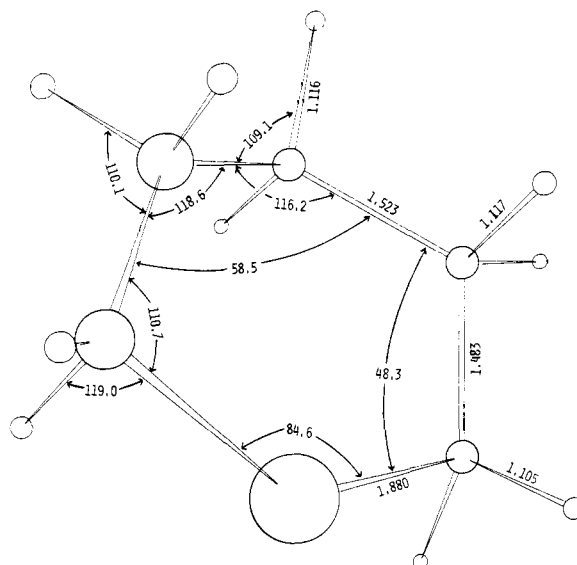
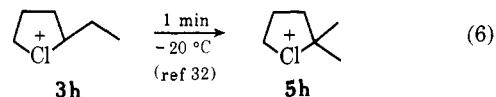


Figure 5. The MINDO/3 optimized geometry of the pentamethylenchloronium ion.

for an 80° rotation about C₃-C₄ (194.42 kcal/mol). Only for the counterclockwise rotation about C₄-C₅ did the C₅-Cl and C₁-Cl distances remain approximately constant over a large rotation range (ca. 120°) as the ion rotated through a "boat" conformation ($\Delta H_f \approx 150.6$ kcal/mol for a 120° rotation). For the other two rotational coordinates, there was a continuous lengthening of C₁-Cl with respect to C₅-Cl. At the potential maxima the computed C₅-Cl bond distances for the coordinates were 1.83 (counterclockwise about C₄-C₅), 1.83 (clockwise about C₄-C₅), and 2.08 Å (about C₃-C₄).

Effects of Alkyl Substitution. Tetramethylenchloronium Ions. Table I lists the enthalpies of formation predicted by MINDO/3 for several alkyl derivatives of the tetramethylenchloronium ion and their isomeric chloroalkyl carbocations. The "uncorrected" values in Table I represent the enthalpies of formation actually computed by MINDO/3. In every case MINDO/3 predicts that the cyclic chloronium ion is more stable than its open carbocation isomer. This, of course, is the result found in solution experiments as previously discussed.^{21,28-32} The calculated chloronium ion ΔH_f values reveal a pronounced alkyl group effect. Thus, as an alkyl group is substituted at a carbon attached to chlorine (i.e., either C₁ or C₄), the stability of the chloronium ion relative to the carbocation increases (see 3 and 4 in Table I). This alkyl group effect is observed in solution experimentally; for example, at -60°C in SbF₅-SO₂ClF the 1,1,4-trimethylenchloronium ion is 97% closed, while under the same conditions the 1,1-dimethyltetramethylenchloronium ion is only 82% closed.²¹ Gas-phase studies of three- and five-membered-ring bromonium ions⁴¹ and calorimetric studies of the heats of formation of three-membered-ring bromonium ions⁴² also show a marked alkyl group effect on cyclic halonium ion stability.

The trends in alkyl group substitution are not fully in line with experimental observations, however. Specifically, MINDO/3 predicts that the 1-ethyltetramethylenchloronium ion 3h⁴³ should be more stable than its 1,1-dimethylchloronium ion 5h isomer, contrary to experimental fact,^{31,32} eq 6. Furthermore, the isomeric open carbocations, i.e., 3c⁴³



and 5c, respectively, are calculated to be separated by only 3.1 kcal/mol (Table I), although 3c is a secondary and 5c is a

Table I. MINDO/3 Enthalpies of Formation for Some Cyclic Tetramethylenchloronium Ions and Their Isomeric Chloroalkyl Carbocations

Cation no.	Substituents	ΔH_f , kcal/mol (25 °C) ^a		ΔH_f , kcal/mol (25 °C) ^b		$\Delta\Delta H_f$, kcal/mol	Deviation from planarity of ring
		Uncorrected	Corrected ^c	Uncorrected	Corrected ^c		
1	a = b = d = e = H	153.8	160.3	181.7	188.2	27.9	0
2	a = CH ₃ , b = d = e = H	141.7	143.6	165.5	167.4	23.8	<1°
3	a = CH ₂ CH ₃ , b = d = e = H	135.6	137.5	157.4	159.3	21.8	<4°
4	a = d = CH ₃ , b = e = H	130.4	134.2	160.0	163.8	29.6	<1°
5	a = b = CH ₃ , d = e = H	140.5	127.9	154.3	141.7	13.8	<2°
6	a = b = d = CH ₃ , e = H	129.5	118.8	148.5	137.8	19.0	<3°

^a A complete geometry optimization was performed. ^b A complete geometry optimization was performed except that dihedral angle 1234 was fixed at 180°. ^c See text.

Table II. MINDO/3 Charge Distributions and Carbon–Chlorine Bond Lengths for the Tetramethylenchloronium Ions and Their Isomeric Carbocations^a

Cation no.	Substituents	C-Cl bond lengths, Å					C ₄ -Cl bond lengths, Å							
		C ₁	C ₂	C ₃	C ₄	Cl	C ₁	C ₂	C ₃	C ₄	Cl			
1	a = b = d = e = H	0.28	0.01	0.01	0.28	0.02	1.87	1.87	0.22	0.17	0.02	0.24	-0.14	1.76
2	a = CH ₃ , b = d = e = H	0.33	0.00	0.02	0.28	-0.03	1.93	1.85	0.47	-0.04	0.05	0.25	-0.12	1.76
3	a = C ₂ H ₅ , b = d = e = H	0.31	0.01	0.02	0.28	-0.04	1.94	1.85	0.44	-0.03	0.09	0.24	-0.16	1.76
4	a = d = CH ₃ , b = e = H	0.32	0.01	0.01	0.32	-0.08	1.91	1.90	0.47	-0.04	0.05	0.26	-0.17	1.79
5	a = b = CH ₃ , d = e = H	0.33	0.00	0.02	0.28	-0.08	2.00	1.84	0.43	-0.03	0.05	0.25	-0.13	1.76
6	a = b = d = CH ₃ , e = H	0.32	0.01	0.02	0.32	-0.12	1.97	1.89	0.43	-0.03	0.05	0.26	-0.18	1.79

^a The remainder of the net +1 charge is distributed among the hydrogens and alkyl substituents.

tertiary carbocation. A similar discrepancy is found on comparing MINDO/3 calculations of simple carbocations. For example, the *tert*-butyl cation is calculated⁴⁴ to be 3.7 kcal/mol more stable than the 2-butyl cation, while the experimental difference⁴⁵ is found to be 13.9 kcal/mol. We believe that the discrepancies are caused by the tendency of MINDO/3 to underestimate the stability of compact, globular molecules, as has been noted previously by Dewar and co-workers.^{24,46} In fact, if one examines the alcohol series CH₃CRR'OH, the alkyl halide series CH₃CRR'Cl, and the geminally substituted cyclopentanes c-C₅H₁₀RR', it is observed that the average errors in enthalpies of formation as predicted by MINDO/3 are (kcal/mol) -6.5 ± 0.3, -1.9 ± 1.0, +12.6 ± 2.6 for R = R' = H; R = CH₃, R' = H, R = R' = CH₃, respectively. Thus, the "corrected" values in Table I were derived by applying the above average errors to the "uncorrected" or raw values. After applying these corrections, one sees that the ordering of the stabilities of the chloronium ions and carbocations is now qualitatively in accord with experimental observations.^{31,32,41,42}

Other effects on structure are calculated when alkyl group substitution on the halonium ions is studied. For example, unlike the unsubstituted ion **1h**, substituted tetramethylenchloronium ions are slightly deformed from planarity when alkyl groups are added to C₁ and C₄, Table I. The alkyl substituents also cause a significant change in the C–Cl bond lengths and the Cl, C₁, and C₄ charge densities, Table II. As C₁ becomes substituted, and hence can better accommodate a positive charge, it is observed that the calculated C₁ positive charge density increases. This is accompanied by a shortening of the C₄–Cl bond, a lengthening of the C₁–Cl bond, and a charge density decrease on the chlorine atom. When C₁ and C₄ are substituted, e.g., ion **4h**, both C–Cl bond lengths increase slightly, and the charge at chlorine is shifted to both

α-carbon atoms. Thus, the stabilizing effect of alkyl groups is apparently explained by the present calculations.

For the open carbocations the positive charge increases markedly at C₁ with monomethyl substitution (compare **1c** and **2c**, Table II). It decreases somewhat from the maximum when two methyl groups are at C₁, e.g., ions **5c** and **6c**, Table II. A rather substantial positive charge resides on C₄ for all of the carbocations because of the presence of the electronegative chlorine function.

Special note should be made of the substantial amount of positive charge at C₂ in the carbocation **1c**. This results from the tendency of MINDO/3 to rearrange primary carbonium ions to secondary ones, or at least bridged ions.³⁷ Thus even though the two C₂–H bond lengths and the HC₂C₁ bond angles were constrained to optimize concurrently (symmetrically), there is a definite tendency toward a bridged ion; i.e., the distances between the two C₂ methylene hydrogens and C₁ optimized to 1.32 and 2.16 Å. Each C–H distance for the C₂ methylene group was 1.18 Å. The geometry optimization feature of MINDO/3 did not attempt to form bridged ions for the secondary or tertiary carbocations **2c**–**6c**. For example, the corresponding distances for the methylene hydrogens bonded to C₂ from C₁ for the 1-methyl secondary carbocation were 2.05 and 2.02 Å; within the C₂ methylene group the C–H bond distances were 1.12 Å. One notes that the charge on Cl is generally negative, but less negative for the closed chloronium ions than for the isomeric open carbocations. This is due to the accommodation of part of the positive charge by the Cl, with this being more efficient for the closed chloronium ions for which internal solvation is important.

Pentamethylenchloronium Ions. The enthalpies of formation for several alkyl derivatives of the pentamethylenchloronium ion and their isomeric carbocations are shown in Table III. Similar trends exist for the Δ in Tables I and III. Again,

Table III. MINDO/3 Enthalpies of Formation for Some Cyclic Pentamethylenechloronium Ions and Their Isomeric Chloroalkyl Carbocations

Cation no.	Substituents	ΔH_f , kcal/mol		ΔH_f , kcal/mol		$\Delta\Delta H_f$, kcal/mol
		Uncorrected	Corrected ^a	Uncorrected	Corrected ^a	
7	a = b = d = e = H	145.2	151.7	173.0	179.5	27.8
8	a = CH ₃ , b = d = e = H	134.2	136.1	155.2	157.1	21.0
9	b = CH ₃ , a = d = e = H	132.5	134.4	154.3	156.2	21.8
10	a = b = CH ₃ , d = e = H	131.9	119.3	145.5	132.9	13.6
11	b = e = CH ₃ , a = d = H	120.9	124.7	148.2	152.0	27.3
12	b = d = CH ₃ , a = e = H	122.9	126.7	149.5	153.3	26.6
13	a = d = CH ₃ , b = e = H	123.9	127.7	150.9	154.7	27.0

^a Corrected values were obtained by the same procedure as for tetramethylenechloronium ions; see text.

all of the cyclic chloronium ion derivatives are more stable than are their open carbocation isomers, with the difference decreasing with methyl substitution on the carbocation center. The only unique effect that deserves comment is that methyl substitution in the equatorial position of the six-membered ring is preferred over methyl substitution in an axial position. This is, of course, the case with methyl substitution in cyclohexane.

The Chloronium Ion-Carbocation Equilibria. As pointed out in the previous sections, the cyclic chloronium ions are predicted to be more stable than their open-chain isomeric carbocations in each instance. With one exception, i.e., structure 10, see eq 4, this trend is borne out by studies in solution.^{21,31,32} The $\Delta\Delta H$ values measured in solution, however, are considerably lower than the differences calculated here for the gas phase. For example, while the measured K_{eq} for the reaction **5h** \rightleftharpoons **5c** (see eq 3) gives a free-energy difference between **5h** and **5c** of ca. 0–2 kcal/mol in nonnucleophilic solvents,^{21,31} the difference calculated for the gas-phase equilibrium at 25 °C is considerably higher ($\Delta\Delta H = 13.9$ kcal/mol). This significant change in the measured solution and calculated gas-phase $\Delta\Delta H$ may be attributed either to an error in the calculation or to a large solvation effect. We will now evaluate the alternatives.

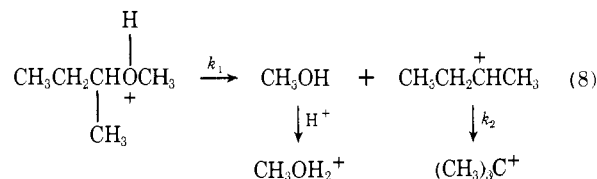
There are no gas-phase energy data on cyclic chloronium ions for direct comparisons. However, Jorgensen³⁷ has compared available gas-phase experimental data to his MINDO/3 calculations for RCIH^+ and concluded that proton affinities for simple alkyl chlorides are overestimated by ca. 7 kcal/mol. When R = methyl and ethyl, the energies of stabilization, ΔE_s , calculated by eq 7 are 53.3 and 33.0 kcal/mol, respectively,

$$\Delta E_s \equiv \Delta H_f(\text{R}^+) + \Delta H_f(\text{HCl}) - \Delta H_f(\text{RCIH}^+) \quad (7)$$

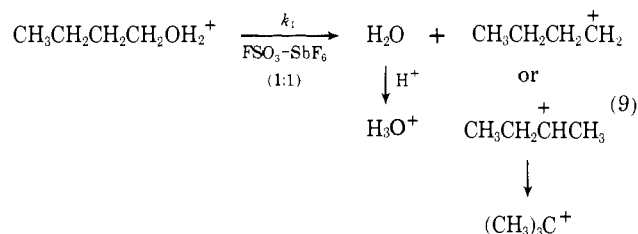
while the experimental values are 51 and 27 kcal/mol, respectively. Thus, the MINDO/3 method does tend to overestimate the calculated ΔE_s in the specific cases cited. If this trend holds for secondary and tertiary carbocations calculated by MINDO/3, that is, ΔE_s is overestimated by 2.3–6.0 kcal/mol, we can assess the gas-phase vs. solution-phase effect. Jorgensen's ΔE_s is equivalent to our $\Delta\Delta H_f$ values of Table I and III. If the **5h** \rightleftharpoons **5c** equilibrium is considered, the corrected gas-phase $\Delta\Delta H_f$ could be as low as 7.8 kcal/mol. When compared to the 0–2 kcal/mol solution values for $\Delta\Delta H$, the obvious conclusion is that the chlorine is filling the role of solvent in the gas-phase ions and hence the cyclic (carbocation-solvated) form is more stable. This is consistent with our earlier suggestion^{20,21} based on experimental findings that specific solvation is very important to carbocations, but of a lesser importance to halonium ions.



There are experimental studies which tend to substantiate the above claim and hence offer validity to the MINDO/3 calculations. For example, Olah et al.^{47,48} have carried out experiments demonstrating that ethers and alcohols readily cleave in strong-acid media. Specifically, methyl *sec*-butyl ether cleaves smoothly at –17 to –29 °C in 1:1 $\text{FSO}_3\text{H-SbF}_5$ following the reaction sequence shown in eq 8. It was stated



that $k_2 \gg k_1$ and $E_a = 8.4 \pm 3$ kcal/mol.⁴⁷ Thus ΔH between the protonated ether and the alcohol plus the 2-butyl cation is less than 8.5 \pm 3 kcal/mol. Also, the decomposition of ethers having a bond between oxygen and a tertiary carbon might occur even with a negative ΔH . In support of this claim, *tert*-butyl ether is said to cleave rapidly at –70 °C.⁴⁷ The primary alcohol reaction in eq 9 has also been studied kinetically⁴⁸ and

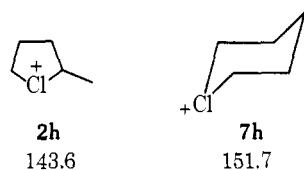


found to have $E_a = 19.98 \pm 0.79$ kcal/mol. Tertiary alcohols cleave very rapidly even at low temperature.⁴⁸ Despite the fact that the above reactions are not equilibrium processes, they nevertheless indicate that under the conditions employed, oxonium ion \rightarrow carbocation reactions are reasonably facile.

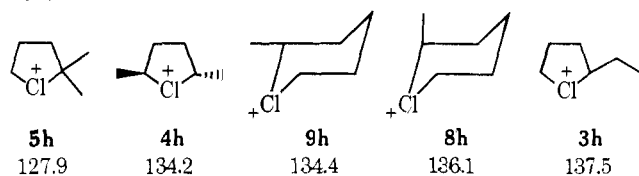
Hiraoka and Kebarle⁴ have experimentally determined the energetics of water-carbocation reactions in the gas phase. The enthalpy change determined for the reaction of water with the *tert*-butyl cation is –11.2 kcal/mol. From measured $\Delta H_f(\text{R}^+)$,⁴⁵ $\Delta H_f(\text{H}_2\text{O})$, and the proton affinity of water, enthalpy changes calculated for the reactions of water with the 2-propyl, ethyl, and methyl cations are respectively –22.8, –37, and –66 kcal/mol.⁴ Compared to the solution values determined by Olah et al.,^{47,48} it indeed appears that the water-carbocation complexes are more tightly bound in the gas phase. Thus, our MINDO/3 predictions for the minimum $\Delta\Delta H_f$ values between cyclic five-membered or six-membered chloronium ions and tertiary, secondary, and primary open δ - or ϵ -chloroalkyl carbocations, (i.e., 7.6, 15, and 21.8 kcal/mol) appear to be quite reasonable.^{49,50}

Comparison of Isomeric Chloronium Ions. The Origin of Six-Membered Ring "Instability". According to our calculations, the isomeric chloronium ions can be ranked in the following orders of stability (all ΔH_f values in kcal/mol).

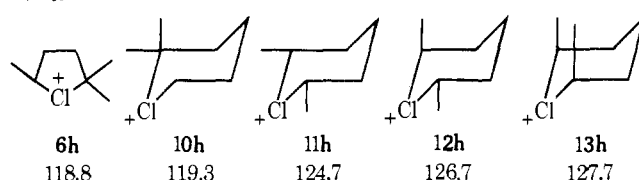
$C_5H_{10}Cl^+$:



$C_6H_{12}Cl^+$:

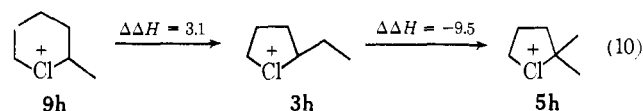


$C_7H_{14}Cl^+$:



For the most part, these orders are explained by the factors earlier discussed; that is, alkyl substitution on the α carbons promotes charge dispersal from chlorine, and equatorial substitution in the six-membered rings is favored over axial substitution.

The comparison of isomeric monosubstituted structures **3h** vs. **9h** indicates that six-membered rings are thermodynamically more stable than five-membered rings. While the rearrangement of **10h** to **6h** shown earlier in eq 5 is explainable on the basis of their relative stabilities, the rearrangement of **9h** to **5h** (eq 10) is not so readily predicted since it involves rear-



rangement of **9h** to the higher energy structure **3h**.³¹ Although **9h** relative to **3h** may have the lower ground-state enthalpy, a consideration of entropy factors may yield a satisfactory understanding.

It is well known that cyclization to form a five-membered ring is favored over a similar process to form a six-membered ring.^{51,52} The rate differences can be dramatic because of entropy effects. Therefore, while the enthalpy difference favors **9h** over **3h**, entropy and free-energy differences may favor **3h** over **9h**.

Conclusions

When branching corrections are made, the MINDO/3 SCF MO method predicts an order of stability for tetramethylenchloronium and pentamethylenchloronium ions and their open-chain chloroalkyl carbocation isomers which is qualitatively in agreement with experiment. The method tends to slightly overestimate the stability of the chloronium ion relative to the carbocation by a factor of 2.3–6.0 kcal/mol. When this factor is applied to the $\Delta\Delta H_f$ values, the chloronium ions are still the more stable in all cases in agreement with experiment. The added stability of chloronium ions relative to carbocations in the gas phase is attributed to internal solvation of the carbocation by the chlorine atom.

Some predictions have been made about ring opening and rearrangement based on these calculations. Of the reaction coordinates considered for chloronium ion ring opening, a rotation of the chlorine away from the carbocation center has a lower activation barrier than does rotation away from the chlorine of the portion of the carbon skeleton containing the carbocation. The rearrangement of six-membered ring chloronium ions to five-membered rings is suggested to occur primarily as a result of favorable entropy effects for five-membered ring formation and because of the added stability given the five-membered ring system with an extra α -alkyl substituent.⁵³

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References and Notes

- (1) (a) Auburn University; (b) The University of Alabama in Huntsville.
- (2) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969, pp 421–584; G. A. Olah and P. R. Schleyer, "Carbonium Ions", Vol. 1, Wiley-Interscience, New York, N.Y., 1968.
- (3) P. Ausloos, Ed., "Interaction between Ions and Molecules", Plenum Press, New York, N.Y., 1975; R. W. Taft in "Fast Proton Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975.
- (4) K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 360 (1977).
- (5) K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 366 (1977).
- (6) W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6125 (1976).
- (7) P. Armentrout, R. Hodges, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 3162 (1977).
- (8) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 5781 (1976); **99**, 2085, 4992 (1977).
- (9) S. K. Pollack, J. F. Wolf, B. A. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 1350 (1977).
- (10) J.-L. M. Abboud, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 6072 (1976).
- (11) R. H. Staley, M. Taagepera, W. G. Henderson, I. Koppel, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 326 (1977).
- (12) J. E. Bartmess, W. J. Hehre, R. T. McIver, Jr., and L. E. C. Overman, *J. Am. Chem. Soc.*, **99**, 1976 (1977).
- (13) J. E. Bartmess and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **99**, 4163 (1977).
- (14) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974).
- (15) J. I. Ebrahman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970).
- (16) W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4219 (1977).
- (17) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311, 318 (1976).
- (18) M. M. Ner and F. H. Field, *J. Am. Chem. Soc.*, **99**, 998 (1977).
- (19) P. Ausloos and S. G. Lias, *J. Am. Chem. Soc.*, **99**, 4198 (1977).
- (20) S. P. McManus and D. W. Ware, *Tetrahedron Lett.*, 4271 (1974).
- (21) S. P. McManus and P. E. Peterson, *Tetrahedron Lett.*, 2753 (1975).
- (22) S. P. McManus, R. D. Olinger, and P. E. Peterson, unpublished results.
- (23) M. J. S. Dewar, *Chem. Br.*, **11**, 97 (1975).
- (24) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975), and accompanying papers.
- (25) For some exceptions, see ref 24 and the following: J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975); W. J. Hehre, *ibid.*, **97**, 5308 (1975); M. J. S. Dewar, *ibid.*, **97**, 6591 (1975).
- (26) See ref 24 and subsequent papers in the series.
- (27) See ref 23 and the following: M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, **99**, 2446 (1977); C. Cone, M. J. S. Dewar, and D. Landman, *ibid.*, **99**, 372 (1977); J. M. Figueroa, P. B. Shevlin, and S. D. Worley, *ibid.*, **98**, 3820 (1976), and references therein.
- (28) G. A. Olah and P. E. Peterson, *J. Am. Chem. Soc.*, **90**, 4675 (1968); G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968); P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2840 (1970).
- (29) G. A. Olah, "Halonium Ions", Wiley-Interscience, New York, N.Y., 1975.
- (30) P. E. Peterson, *Acc. Chem. Res.*, **4**, 107 (1971).
- (31) P. M. Henrichs and P. E. Peterson, *J. Am. Chem. Soc.*, **95**, 7449 (1973); *J. Org. Chem.*, **41**, 362 (1976), and references cited therein.
- (32) G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *J. Am. Chem. Soc.*, **96**, 3565 (1974).
- (33) P. E. Peterson, *J. Org. Chem.*, **37**, 1180 (1972).
- (34) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 188–190.
- (35) A preliminary communication on a portion of this work has appeared: S. P. McManus and S. D. Worley, *Tetrahedron Lett.*, 555 (1977).

- (36) The use of MINDO/3 for acyclic halonium ions was reported during the course of our work; cf. ref 37. Dewar et al. have previously calculated energies of carbocations of various structures with reasonable success; cf. ref 23, 24, and 38.
- (37) W. L. Jorgensen, *J. Am. Chem. Soc.*, in press; **99**, 280, 4272 (1977); V. L. Jorgensen and J. E. Monroe, *Tetrahedron Lett.*, 581 (1977).
- (38) P. K. Bischof and M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 2278 (1975), but see ref 36 for corrections; M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *ibid.*, **99**, 377 (1977).
- (39) D. G. Graczyk, R. L. Julian, J. W. Taylor, and S. D. Worley, *J. Am. Chem. Soc.*, **97**, 7380 (1975); W. B. Jennings and S. D. Worley, *Tetrahedron Lett.*, 1435 (1977).
- (40) W. C. Davidson, *Comput. J.*, **10**, 406 (1968); R. Fletcher, *ibid.*, **8**, 33 (1965); R. Fletcher and M. J. D. Powell, *ibid.*, **6**, 163 (1963).
- (41) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).
- (42) J. W. Larsen and A. V. Metzner, *J. Am. Chem. Soc.*, **94**, 1614 (1972).
- (43) The **h** and **c** stand for halonium ion and carbocation, respectively.
- (44) Our calculated ΔH_f for the 2-butyl cation is 174.5 kcal/mol; ref 24 gives a higher value.
- (45) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
- (46) Steric factors are not the probable cause of these errors. For example, the calculated strain energies of ethylcyclopentane (6.81 kcal/mol) and 1,1-dimethylcyclopentane (6.86 kcal/mol) reveal no problem in the hydrocarbon models: S. P. McManus, M. R. Smith, and R. D. Olinger, unpublished results.
- (47) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).
- (48) G. A. Olah, J. Sommer, and E. Namenworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967).
- (49) Obtained by taking the lowest $\Delta\Delta H_f$ from Table I or III and subtracting 6 kcal/mol which was the maximum error between calculated and measured ΔE_s values for alkyl chlorides; see ref 37 and the discussion earlier in this section. These values are not doubly corrected since branching-error corrections do not affect the magnitude of $\Delta\Delta H_f$.
- (50) Kebarle (D. K. Sen Sharma and P. Kebarle, *J. Am. Chem. Soc.*, submitted for publication) has just completed the initial experimental studies of the gas-phase equilibria: $R_1^+ + ClR_2 \rightleftharpoons R_1Cl + R_2^+$. His results lend support to our computed $\Delta\Delta H$ values.
- (51) B. Capon and S. P. McManus, "Neighboring Group Participation", Plenum Press, New York, N.Y., 1976, pp 43-70.
- (52) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1973).
- (53) One of us has recently found (S. P. McManus and M. R. Smith, *Tetrahedron Lett.*, submitted for publication) that, in general, the errors in calculating enthalpies of formation by MINDO/3 are ca. 2 kcal/mol greater for five-membered rings than for six-membered ones, the error favoring the stabilities of the former over the latter.

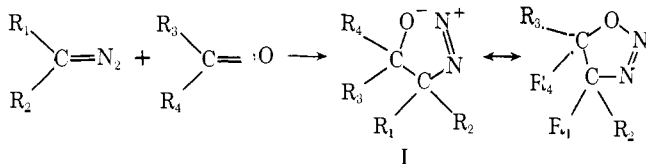
Cycloaddition of Diazoalkanes to Penta- and Hexafluoroacetones. Isolation of Δ^3 -1,3,4-Oxadiazolines and Their Decomposition via Carbonyl Ylides

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Abstract: Diaryl and arylmethyl diazomethanes add rapidly at -20°C to hexa- and pentafluoroacetone to yield Δ^3 -1,3,4-oxadiazolines (**3** and **4**, **a-h**). At 25°C and above in benzene the diaryloxadiazolines lose nitrogen to yield epoxides **5** and **6**, **a-e** and **h**, accompanied by diaryl ketones in most cases. The phenylmethyloxadiazolines **3f** and **4f**, on nitrogen elimination in benzene, gave high yields of the acetophenone enol ethers **7** and **8**. Evidence is presented that the rate-determining step in these decompositions is the concerted formation of a carbonyl ylide which does not entirely retain its configuration. Of various reagents tried, only methanol proved capable of generally intercepting this ylide, yielding as principal product the adduct consisting of the mixed ketal of the aryl ketone. The decompositions of the oxadiazolines were all kinetically of the first order, showing no appreciable polar solvent effect, and responding to the σ^+ parameters of substituents in the benzene ring with a ρ^+ of -0.50 . In formation of acetophenone enol ether, the kinetic isotope effect, $k(\text{CH}_3)/k(\text{CD}_3)$, was only 0.96, confirming that the intramolecular proton transfer occurred within the ylide after the rate-determining step.

Diazoalkanes are well known to react with carbonyl compounds, usually under mild conditions, to give oxiranes and ketenes.^{2a} Most data on this reaction have been concerned with diazomethane itself. The reaction has been interpreted as a nucleophilic attack of the diazoalkane on the carbonyl group to yield a diazonium betaine (I), or neutral Δ^2 -1,2,3-oxadiazoline as a reaction intermediate which is generally too unstable to be isolated.^{2b} We have found, however, that aromatic diazo compounds react readily with perfluoroacetones to give unexpected cycloadducts, Δ^3 -1,3,4-oxadiazolines, in high yield. Despite the extensive studies on the Δ^3 -1,3,4-thiadiazoline,^{3a,4-6} little has been reported on the chemistry of oxadiazolines,^{3b,7-9} interesting precursors of the carbonyl ylides.^{9,10} Hoffmann and Luthardt have succeeded in preparing 2-acetoxy-1,3,4-oxadiazolines by oxidation of benzoyl hydrazones with lead tetraacetate.⁸



zoline as a reaction intermediate which is generally too unstable to be isolated.^{2b} We have found, however, that aromatic diazo compounds react readily with perfluoroacetones to give unexpected cycloadducts, Δ^3 -1,3,4-oxadiazolines, in high yield. Despite the extensive studies on the Δ^3 -1,3,4-thiadiazoline,^{3a,4-6} little has been reported on the chemistry of oxadiazolines,^{3b,7-9} interesting precursors of the carbonyl ylides.^{9,10} Hoffmann and Luthardt have succeeded in preparing 2-acetoxy-1,3,4-oxadiazolines by oxidation of benzoyl hydrazones with lead tetraacetate.⁸

We report here the results of the cycloaddition reaction of aromatic diazo compounds with hexa- and pentafluoroacetones and show the details of thermal decomposition of isolated 1,3,4-oxadiazolines.

Results

1. Reaction of Aryldiazomethanes with Perfluoroacetones. Dry hexafluoro- or pentafluoroacetone (**1a** or **1b**) was bubbled into a cold pentane solution (ca. -20°C) of aryldiazomethane (**2a-g**) until the characteristic color of the diazo compound had faded. Usually reaction took place instantly. Solvent was removed by evaporation under vacuum while the solution was kept cool (-20°C). The residue (solid or liquid) was found to be almost pure cycloadduct (**3** and **4**) by NMR analysis and chemical reactions. All adducts were unstable at room temperature and decomposed smoothly with evolution of nitrogen. The structure of the cycloadducts was confirmed by chemical evidence (see later section) as well as spectral data. Typical NMR spectra of the cycloadduct taken at low temperature are illustrated in Figure 1, and the results are shown in Table I. The reaction of diazoalkanes with acetone or acetophenone was too slow and the adducts could not be detected. It is known that the reaction of diazoalkanes with ketones or