

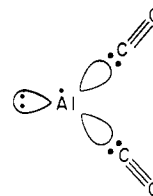
	A_{iso}	A_{dip}
Cu(CO)	2142 MHz	16 MHz
Cu(CO) ₃	71 MHz	81 MHz

These values should be compared with the atomic values $A_{\text{iso}}^0(^{63}\text{Cu}) = 6151$ MHz, the hfc constant of the ^{63}Cu atoms ($3d^{10}4s^1$) isolated in an argon matrix, and $A_{\text{dip}}^0(^{63}\text{Cu}) = 200$ MHz, a value estimated for a unit spin density in the Cu 4p orbital from the known hf splitting term, $a(j = 1/2)$, of the Ga atoms ($4s^24p^1$).¹⁵ The atomic values A_{iso}^0 and A_{dip}^0 for the carbon 2s and 2p orbitals have been computed theoretically; they are $A_{\text{iso}}^0(^{13}\text{C}) = 3780$ MHz, and $A_{\text{dip}}^0(^{13}\text{C}) = 107$ MHz.¹⁶ The observed ^{13}C hfc tensor of Cu(CO) is apparently dominated by the A_{iso} term. We thus assessed, from the observed hfc tensors, the following spin density distribution in Cu(CO): $\rho(4s)_{\text{Cu}} = +0.67$, $\rho(4p_{\sigma})_{\text{Cu}} = +0.08$, and $\rho(2s)_{\text{C}} = +0.05$. The balance of spin density (~ 0.2) is believed to be mostly at the C $2p_{\sigma}$ orbital, and perhaps some at the oxygen $2p_{\sigma}$ and Cu $3d_{\sigma}$ orbitals.

In Cu(CO)₃ the ^{13}C hfc tensor is determined essentially by the C $2p_{\pi}$ orbital part of eq 7. The ^{13}C hfc tensor should thus be approximately axially symmetric, the symmetry axis being coincident with that of the Cu hfc tensor. For a positive spin density in a p orbital, A_{dip} in eq 8 is a positive quantity, and hence $A_{\parallel} > A_{\perp}$. We shall therefore assert, for the ^{13}C hfc tensor of Cu(CO)₃, $A_{\parallel} = +6$ MHz, and $A_{\perp} = -31$ MHz. Analysis of these quantities in terms of eq 8 yields $A_{\text{iso}}(^{13}\text{C}) = -18.7$ MHz and $A_{\text{dip}}(^{13}\text{C}) = +12.3$ MHz. We thus assessed the following spin density in Cu(CO)₃: $\rho(4s)_{\text{Cu}} = +0.01$, $\rho(2s)_{\text{C}} = -0.005$, $\rho(4p_{\pi})_{\text{Cu}} = +0.41$, and $\rho(2p_{\pi})_{\text{C}} = +0.11$. The small densities in the Cu 4s and C

2s orbitals are attributed to polarizations of filled orbitals. A negative spin density in the carbon 2s orbital is particularly interesting; it can be best accounted for by polarization of electrons in the σ dative bond by the large positive spin density in the Cu $4p_{\pi}$ orbital.

Recently we have observed and analyzed ESR spectra of Al(CO)₂ generated in argon matrices.¹⁷ Its structure and bonding scheme were shown to be as follows:



The aluminum complex is thus also formed by the σ -type dative interaction between the lone-pair electrons of CO and vacant sp hybrid orbitals of the metal atom and the back-donation from the semiffilled p_{π} orbital of the metal atom. From the observed ^{27}Al and ^{13}C hfc tensors the following spin density distribution was assessed: $\rho(3s)_{\text{Al}} = +0.02$, $\rho(2s)_{\text{C}} = -0.004$, $\rho(3p_{\pi})_{\text{Al}} = +0.42$, and $\rho(2p_{\pi})_{\text{C}} = +0.09$. Similarity between the semiffilled orbitals of Cu(CO)₃ and Al(CO)₂ is striking. The observed CO stretching frequencies of these complexes are also similar (1890 and 1988 cm^{-1} for the Al complex, and 1977 and 1990 cm^{-1} for the Cu complex). Noting that the $d_{\pi} \rightarrow \pi^*$ back-donation is impossible in Al(CO)₂, we surmise that essentially all of the back-donation in Cu(CO)₃ originates from the semiffilled Cu $4p_{\pi}$ orbital.

Registry No. Cu(CO), 55979-21-0; Cu(CO)₃, 55979-19-6.

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NMR Chemical Shift and NMR Isotope Shift Evidence for the Influence of Nonbonded Interactions on Charge Distribution in α,β -Unsaturated Methoxycarbenium Ions

David A. Forsyth,^{*1a} Virginia M. Osterman,^{1a} and John R. DeMember^{1b}

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115, and the Research Laboratories, Polaroid Corporation, Cambridge, Massachusetts 02139. Received August 13, 1984

Abstract: ^{13}C NMR chemical shifts and deuterium isotope effects on chemical shifts in α,β -unsaturated methoxycarbenium ions provide evidence regarding the influence of nonbonded interactions on charge distribution. The α,β -unsaturated methoxycarbenium ions exist as *Z* and *E* isomers due to restricted rotation about the $\text{C}_1\text{-O}$ bond. A 5- to 7-ppm difference between *Z* and *E* isomers at C_3 , which are sp^2 carbons remote from the site of structural variation, indicates a difference in polarization of the π -bonded segment. Deuterium substitution in the methyl group of the 1-methoxy-2-cyclohexenyl cation induces an upfield shift at C_3 of the *Z* isomer only. This isotope shift, along with the lack of significant shift differences at C_3 in the analogous hydroxycarbenium ions, shows that the polarization is due to an interaction with the methoxy methyl group. The observations are explicable within the theory of nonbonded interactions.

Introduction

Differences in the thermodynamic stability of cis-trans geometrical isomers of alkenes, as well as conformational preferences in a variety of other systems, have been explained in terms of a combination of nonbonded (long-range) orbital interactions and steric effects.² A recent study of energy levels of terminal

methyl-substituted butadienes by electron-transmission spectroscopy provided evidence for through-space orbital interactions of methyl groups with the π system.³ We have previously sug-

(1) (a) Northeastern University. (b) Polaroid Corporation.

(2) (a) Epiotis, N. D. *J. Am. Chem. Soc.* 1973, 95, 3087-3096. (b) Epiotis, N. D.; Sarkanen, S.; Bjorkquist, L.; Yates, R. L. *Ibid.* 1974, 96, 4075-4084. (c) Epiotis, N. D.; Yates, R. L.; Bernardi, F. *Ibid.* 1975, 97, 5961-5968. (d) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Top. Curr. Chem.* 1977, 70.

Chart I

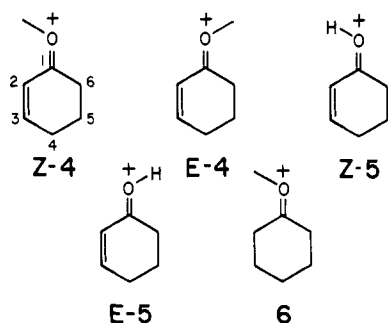
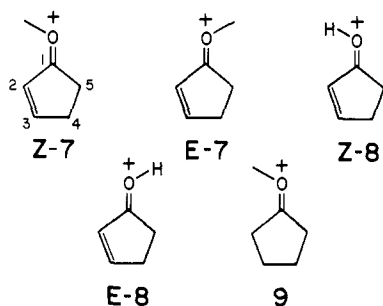
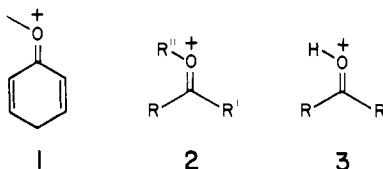


Chart II



gested that nonbonded interactions may have a substantial influence on the distribution of electrons within conjugated, charged systems.⁴ This hypothesis was inspired by the observation of some unusual ¹³C NMR chemical shifts in carbocations, especially the *p*-methoxybenzenium ion, **1**, wherein the carbons meta to the methoxy group differ by about 7 ppm. In this paper, we present evidence consisting of ¹³C chemical shifts and deuterium isotope effects on chemical shifts in α,β -unsaturated methoxycarbenium ions which further supports this hypothesis concerning the influence of nonbonded interactions on charge distribution.



Alkoxy-carbenium ions, **2**, and hydroxycarbenium ions, **3**, constitute an important class of intermediates in organic reactions. Alkoxy-carbenium ions are formed as intermediates in the acid-catalyzed hydrolysis of acetals, ketals, and orthoesters, in rearrangements of hydroperoxides, in substitution reactions of halo ethers, in reactions of electrophiles with alkoxy-substituted alkenes and arenes, and in mass spectrometric fragmentation reactions. Hydroxycarbenium ions occur as intermediates in most acid-catalyzed reactions of carbonyl compounds, via protonation of the carbonyl oxygen. Both alkoxy-carbenium ions and hydroxycarbenium ions are known to exist preferentially in a planar, bent configuration ($\angle\text{C}-\text{O}-\text{R} \neq 180^\circ$) from NMR studies of the stable cations.⁵ The ions have significant C-O double-bond character which restricts rotation about the C-O bond and allows the observation of *E-Z* geometrical isomerism. This paper deals with noteworthy differences in ¹³C chemical shifts between *E* and *Z* isomers of α,β -unsaturated alkoxy-carbenium ions.

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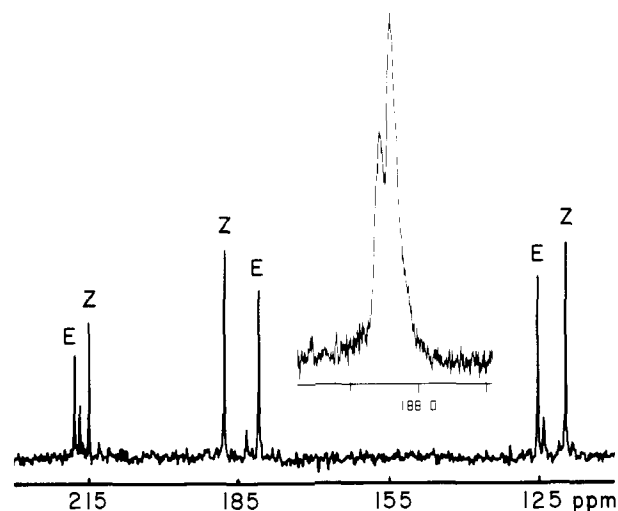
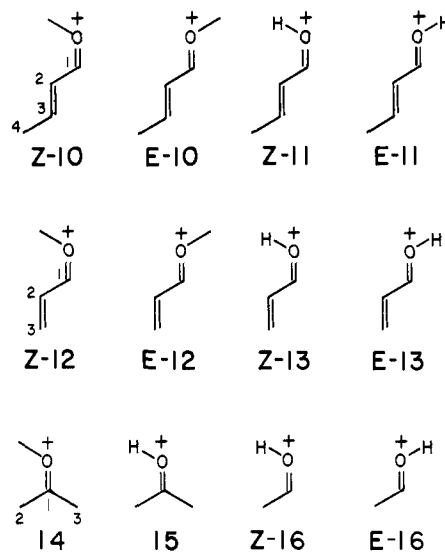


Figure 1. Downfield region of the 15.0-MHz ¹³C spectrum of the 1-methoxy-2-cyclohexenyl cation, **4**. Peaks marked Z correspond to the *Z*-**4** isomer and E to the *E*-**4** isomer. The smaller, unmarked set of three peaks is due to the 1-hydroxy-2-cyclohexenyl cation. Inset peaks show the upfield isotope shift of the C₃ peak of *Z*-**4**, from a 75.4-MHz ¹³C spectrum of a 60:40 mixture of 4-methyl-*d*₃ and unlabeled **4**.

Chart III



Results

Methoxycarbenium ions were prepared from the corresponding dimethyl acetals and ketals by ionization in a mixture of FSO₃H and SO₂ClF at -78 °C. Hydroxycarbenium ions were prepared by protonation of the parent carbonyl compounds, both in FSO₃H/SO₂ClF and in FSO₃H-SbF₅ (1:1)/SO₂ClF. For convenience in comparison, the structures are grouped in Charts I-III by ring size or open-chain character.

All of the hydroxycarbenium ions have been prepared previously.⁵⁻⁷ Our ¹³C data for the α,β -unsaturated systems are in fair agreement with the partial results found via the difficult INDOR method in the early study of Olah et al.;⁶ the INDOR method was not sensitive enough to detect separate signals for *E* and *Z* isomers. While several of the methoxycarbenium ions have been previously prepared, **4** and **7** have not been reported, and no other ¹³C data are available for the α,β -unsaturated methoxycarbenium ions.^{5,8-10}

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Table I. ^{13}C NMR Chemical Shifts^a and Equilibrium Composition^b of Methoxy- and Hydroxycarbenium Ions^c

ion	equil comp	^{13}C NMR chemical shifts						
		C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	OCH ₃
Z-4	56	215.4	120.3	188.4	28.7	20.6	33.6	64.5
E-4	44	218.3	125.9	181.6	26.9	19.5	30.6	64.2
5	<i>d</i>	217.2	124.7	183.1	27.4	20.3	33.2	
Z-5 ^e	47	217.3	124.2	189.5	28.4	20.5	32.6	
E-5 ^e	53	217.7	124.8	188.7	28.1	20.5	34.1	
6		248.7	36.7	25.7*	22.4	25.4*	40.8	67.3
Z-7	32	227.8	127.6	201.9	35.2*	36.2*		67.0
E-7	68	229.9	131.8	196.6	34.8	30.3		67.4
8	<i>d</i>	229.1	131.3	198.5	34.9*	35.9*		
Z-8 ^e	43	229.1	131.2	201.8	36.0* ^f	36.0* ^f		
E-8 ^e	57	229.7	131.7	202.3	36.0* ^f	36.6*		
9		258.0	40.0	23.4	23.4	42.1		71.0
Z-10	7	204.0	125.8	199.6	24.6			66.4
E-10	93	207.3	128.5	194.1	23.6			73.4
11	<i>d</i>	205.7	129.5	196.2	23.8			
Z-11 ^e	14	205.6	129.7	201.4	24.7			
E-11 ^e	86	204.4	129.7	201.4	24.7			
Z-12	0 ^g							
E-12	100 ^g	211.5	132.1	169.7				75.6
13	<i>d</i>	210.6	133.0	170.2				
Z-13	10	211.5	133.1	174.9				
E-13	90	210.3	133.1	174.9				
14		244.9	26.8	32.0				68.7
15		248.1	31.5	30.2				
Z-16	18	235.9	31.1					
E-16	82	236.5	29.3					

^a ^{13}C chemical shifts are in ppm (± 0.1) relative to external (capillary) tetramethylsilane. ^bPercent composition of isomeric pairs at -80°C , based on relative ^{13}C peak intensities. Compositions are averages from all positions where peak intensities can be compared. ^cIn $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$, unless otherwise indicated. ^dEquilibrium composition could not be determined owing to rapid proton exchange with acid. ^eIn $\text{SbF}_5\text{-FSO}_3\text{H}/\text{SO}_2\text{ClF}$. ^f ± 0.3 ppm (overlapping peaks). ^gReference 10 reports a 4:96 ratio of *Z* to *E* in FSO_3H at -40°C .

Table I lists the ^{13}C chemical shifts for the methoxy- and hydroxycarbenium ions. The downfield region of the spectrum for the 1-methoxy-2-cyclohexenyl cation, **4**, is shown in Figure 1. This spectrum is typical of the methoxycarbenium ion solutions, in showing peaks corresponding to the two geometrical isomers, *Z*-**4** and *E*-**4**, and to the hydroxycarbenium ion, **5**, which results from partial hydrolysis of the dimethyl ketal in the FSO_3H solution. In FSO_3H , the hydroxy proton of each hydroxycarbenium ion exchanges rapidly with the acid, but exchange is slow in $\text{FSO}_3\text{H-SbF}_5$ so that *E* and *Z* isomers were observed in this stronger acid medium. The ^{13}C resonances for hydroxycarbenium ions in $\text{FSO}_3\text{H-SbF}_5$ also appear further downfield than in FSO_3H .

In another important experiment, the isotope effects on chemical shifts due to deuteration of the methoxy methyl group were determined. The spectrum (insert, Figure 1) of the 1-methoxy-2-cyclohexenyl cation, **4**, as a 60:40 mixture of the methoxy-*d*₃ and unlabeled cations, was obtained by ionization in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ of a 60:40 mixture of the corresponding labeled and unlabeled cyclohex-2-enone dimethyl ketal. In a 75.4-MHz ^{13}C spectrum, the only measurable NMR isotope shift for the ring carbons was an upfield shift of 0.040 ± 0.005 ppm at C₃ of *Z*-**4**.

The peak assignments in Table I for the *E* and *Z* isomers of methoxycarbenium ions were based on the following criteria. (1) The data obtained from the separately prepared hydroxycarbenium ions were used to identify the peaks of the hydroxycarbenium ion in each methoxycarbenium ion spectrum. (2) The methoxycarbenium ion peaks were divided into two sets, corresponding to the major and minor isomers, based on relative peak heights. (3) The identification of isomers for cations **10** and **12** was aided by a previous study which identified the major and minor isomers through ^1H NMR data. The study reported the major isomer for both cations to have the *E* configuration about the C-O bond.^{9,10} (4) Peak multiplicities were determined in off-resonance spectra. (5) The alkene carbon peak assignments were based on the expectation of lower electron density at C₃ than C₂, which is associated with a downfield shift at C₃.⁶ (6) Identification of

the *E* and *Z* isomers for structures **4** and **7** was based on the well-known γ -substituent effect.¹¹ If the methoxy methyl group is considered to be a γ substituent relative to the α carbons, here C₂ in all cations and C₆ in **4** and C₅ in **7**, then an α carbon in the position syn to the methyl should be shielded relative to an α carbon in the anti alignment. The *Z* configuration places the γ substituent syn to C₂ in **4** and **7**. Therefore, the set of peaks that included the higher field peak of the two alkene α -carbon peaks (C₂) in each spectrum was attributed to the *Z* isomer and the other set to the *E* isomer. (7) A few of the assignments of the alkane peaks are less certain, but our peak assignments for C₆ in **4** and C₅ in **7** were aided by comparison with the ^{13}C chemical shifts for the corresponding hydroxycarbenium ions and for the saturated oxycarbenium ions, **6**, **9**, and **14-16**. These assignments also reflect the expected γ -substituent effect of the methoxy methyl group on the saturated α carbons.

Discussion

Evidence for π -Polarization by Methyl. The ^{13}C chemical shifts for the sp² carbons in the α,β -unsaturated methoxycarbenium ions **4**, **7**, and **10** show distinct differences between the *Z* and *E* isomers. In all three cases, C₁ and C₂ appear upfield and C₃ appears downfield in the *Z* isomer compared to the *E* isomer. It is noteworthy and unusual that the largest difference in shifts is at C₃, which is sterically remote from the methyl substituent.

The shift differences at C₂ and C₃ are analogous to the shift differences between ortho positions and between meta positions observed previously in the *p*-methoxybenzenium ion, **1**.⁴ In the saturated methoxycarbenium ions **6**, **9**, and **14** and at the saturated positions C₆ in **4** and C₅ in **7**, shift differences comparable to those observed at C₂ in the unsaturated ions may be found, but there are no saturated analogues for the shift differences between isomers observed at C₃. The 5- to 7-ppm difference between *Z* and *E* isomers at C₃, which are sp² carbons remote from the site of structural variation, is unequivocal evidence for a significant difference between isomers in polarization of the π -bonded segment of the molecules.

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(10) Childs, R. F.; Hagar, M. E. *Can. J. Chem.* **1980**, *58*, 1788-1794.

(11) See, for example: Breitmaier, E.; Voelter, W.; ^{13}C NMR Spectroscopy, 2nd ed.; Verlag Chemie: Weinheim, 1978; pp 74-75.

Initially it seemed reasonable to consider that the difference in polarization between unsaturated methoxycarbenium ion isomers could arise from an interaction of the π system with the in-plane, lone-pair electrons on oxygen. Electrostatic repulsion between the C_2 - C_3 π bond and the lone pair in the *E* isomers could polarize the C_2 - C_3 bond toward C_3 , resulting in an upfield shift at C_3 . However, this hypothesis can be ruled out by comparison with the unsaturated hydroxycarbenium ions **5**, **8**, **11**, and **13**, for which only minor shift differences are observed between *E* and *Z* isomers. This evidence also rules out significant differences in σ -conjugation¹² as the source of charge differences between *E* and *Z* isomers.

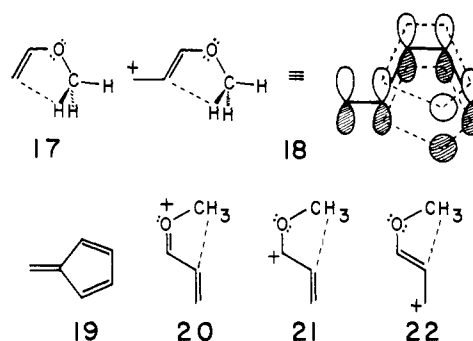
A more likely possibility is that a deshielding of C_3 occurs in the *Z* isomers from an interaction with the methyl group that polarizes the π system to place more positive charge at C_3 . We thought that this hypothesis should be testable by deuteration of the methyl group.

Deuterium substitution in the methyl group of the 1-methoxy-2-cyclohexenyl cation, **4**, induces an upfield shift of 0.040 ppm in the ¹³C NMR signal of the C_3 carbon of the *Z* isomer, and no other isotope shift was detectable for C_1 , C_2 , or C_3 of either isomer. This long-range NMR isotope shift is evidence for an interaction with the methyl group in the *Z* isomers as the source of the different polarization between isomers. It has previously been demonstrated that deuterium substitution reduces the hyperconjugative interaction of alkyl groups (isotopic perturbation of hyperconjugation).¹³ In the present situation, the postulated interaction with the methyl group must increase positive charge at C_3 . Thus, diminishing the strength of the methyl interaction by isotopic perturbation should decrease positive charge at C_3 and result in an upfield isotope shift, which is the observed result in *Z*-**4**. The lack of an isotope effect in the *E* isomer suggests that the methyl interaction is not operative in that isomer, where the distance between C_2 and the methyl is much larger.

Theoretical Basis for Polarization by Methyl. The experimental evidence makes it clear that there is a polarizing interaction between the π system and the methyl of the methoxy group that is present in the *Z* isomers but not the *E* isomers of α,β -unsaturated methoxycarbenium ions. Very similar hyperconjugative interactions between the methyl and the oxygen terminus of the π system are expected for *Z* and *E* isomers, in analogy to the expectations for methylbutadienes.³ Thus, the most likely possibility for differential polarization is a through-space interaction with C_2 in the *Z* isomers. This view is consistent with qualitative expectations based on the theory of nonbonded interactions.

Nonbonded electronic interactions occur when atoms not formally bonded to each other approach closely enough for orbital overlap. Epiotis has pointed out that a simple, qualitative evaluation of the nature of such interactions can be achieved by classifying them as aromatic, antiaromatic, or nonaromatic if the nonbonded orbital interaction can complete a continuous cycle of overlapping orbitals.^{2,14,15} This use of the aromaticity concept is similar to its application in evaluating transition states of pericyclic reactions.^{16,17} With Hückel topology for the cyclic array of orbitals, stabilizing nonbonded interactions will occur if the cycle is aromatic (containing $4n + 2$ electrons), and destabilizing interactions will occur if the cycle is antiaromatic ($4n$ electrons). For example, Epiotis has suggested that the greater stability of the syn conformer of methyl vinyl ether, **17**, relative to the anti conformer, is due to the attractive nonbonded interaction in which a methyl group orbital of π symmetry¹⁵ completes a furan-like

aromatic cycle involving the double bond and an oxygen lone pair.¹⁸



In α,β -unsaturated methoxycarbenium ions, nonbonded interactions occur within a similar cycle, as shown for the *Z* isomer **18**, where C_3 is considered to be exocyclic to the furan-like ring created by the methyl, oxygen, C_1 , and C_2 orbitals. To make another analogy, the orbital array in **18** is similar to the p orbital basis set of fulvene, **19**. The effect of this interaction on the charge distribution can be predicted by considering the resonance structures **20**–**22**. Resonance structure **22**, which places positive charge at C_3 , will have an aromatic cycle while structures **20** and **21** will have nonaromatic cycles due to the C_2 - C_3 π bond being cross-conjugated with the possible cycle. Thus, structure **22** should contribute more heavily to the resonance hybrid for the *Z* isomer than would the corresponding resonance structure for the *E* isomer, in which the nonbonded interaction is absent. The increased contribution of **22** will result in greater positive charge at C_3 and thus accounts for the observed NMR deshielding. Resonance structure **22** is analogous to the fulvene resonance structures which give aromatic character to the five-membered ring and leave the exocyclic carbon electron deficient.

Experimental Section

Preparation of Acetals and Ketals. The dimethyl acetals or ketals of propenal, 2-butenal, cyclopentanone, and cyclohexanone were prepared by the following general procedure.¹⁹ The aldehyde or ketone (0.20 mol) and trimethyl orthoformate (0.20 mol) were added to a warm solution of 0.010 mol of ammonium nitrate in 10 mL of anhydrous methanol in a flask fitted with a reflux condenser. After stirring for 8 h, the solution was filtered, 0.60 g of Na_2CO_3 was added, and the product was distilled under reduced pressure from this solution.

The dimethyl ketals of cyclohex-2-enone and cyclopent-2-enone were prepared from the saturated cycloalkenones by the general procedure for cyclohex-2-enone dimethyl ketal described by Garbisch.²⁰ The same procedure was followed for preparation of cyclohex-2-enone dimethyl-*d*₆ ketal, except that pentane was used as the solvent instead of methanol, and a sixfold excess of CD_3OD was used for ketal formation.

Acetone dimethyl acetal was a commercial product (Aldrich).

Preparation of Carbenium Ions. The methoxycarbenium ions were prepared by dropwise addition of a cooled solution of 1 mmol of the acetal or ketal precursor in 1 mL of SO_2ClF to a vortex-stirred solution of 1 mL of FSO_3H in 1 mL of SO_2ClF at -78 °C (Dry Ice-acetone bath). The cation solutions were transferred to a precooled 10-mm NMR tube and stored at -78 °C. The deuterated cation, 4-methyl-*d*₃, was prepared from a 60:40 mixture of deuterated to undeuterated cyclohex-2-enone dimethyl ketal with CD_2Cl_2 as the solvent. Hydroxycarbenium ions were prepared by the same procedure, with aldehydes or ketones as the precursors and FSO_3H or FSO_3H - SbF_5 (1:1) as the acid.

NMR Spectroscopy. ¹³C spectra of the carbocations were recorded at -80 °C on a JEOL FX-60Q spectrometer operating at 15.0 MHz, on external lock. The 10-mm sample tubes held concentric 2-mm capillary tubes of tetramethylsilane as reference. Data were accumulated in 500–2000 pulses of 60° flip angle, with 8192 or 16384 data points and a spectral width of 4000 Hz. The spectrum of deuterated **4** was obtained at -70 °C on a Varian XL-300 operating at 75.4 MHz, while locked on the CD_2Cl_2 solvent signal. The entire spectrum was measured with a spectral width of 17985 Hz and 32000 data points, but key segments of

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the spectrum were measured with narrow spectral widths to obtain good digital resolution (ca. 0.001 ppm/point).

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Registry No. 4, 94483-98-4; 5, 71717-56-6; 6, 94483-99-5; 7, 94484-00-1; 8, 76266-28-9; 9, 52066-98-5; 10, 94484-01-2; 11, 71298-10-7; 12,

94484-02-3; 13, 57344-16-8; 14, 41798-19-0; 15, 43022-03-3; 16, 18682-96-7; CH₂=CHCHO, 107-02-8; CH₃CH=CHCHO, 4170-30-3; CH₂=CHCH(OMe)₂, 6044-68-4; CH₃CH=CHCH(OMe)₂, 21962-24-3; HC(OEt)₃, 122-51-0; D₂, 7782-39-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 1,1-dimethoxycyclopentane, 931-94-2; 1,1-dimethoxycyclohexane, 933-40-4; 3,3-dimethoxycyclohexene, 1728-18-3; 3,3-dimethoxycyclopentene, 94484-03-4; 3,3-dimethoxy-d₆-cyclohexene, 94484-04-5.

Photochemical Rearrangements of *o*- and *m*-Dichlorobenzene Cations to *p*-Dichlorobenzene Cation in Solid Argon

Ronald S. Friedman and Lester Andrews*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received May 29, 1984

Abstract: Matrix photoionization experiments with *o*- and *m*-dichlorobenzene and 1,2,4-trichlorobenzene produced and isolated for spectroscopic study not only radical cations of the precursor compound but also rearranged cation products. It is postulated that a bridged chloronium ion is formed upon excitation to the lone pair hole state which serves as an intermediate in rearrangements among the excited-state di- and trichlorobenzene cation isomers. The chlorine lone pair hole excited state facilitates a "chloronium ion walk" around the aromatic ring.

Photochemical rearrangements of molecular cations in solid argon have been described, including the benzyl-tropylium cation transformation¹ and the rearrangement of alkylbenzene and cycloheptatriene cations to methylenecyclohexadiene cation species.²⁻⁴ These rearrangements proceed following activation by irradiation into a cation absorption band. Thus, the presence of *p*-dichlorobenzene cation absorptions in matrix photoionization experiments using the *o*- and *m*-dichlorobenzene precursors could be due to intramolecular photochemical rearrangements of the precursor cations in the matrix. A viable mechanism for this rearrangement involves the formation of an excited bridged chloronium ion species as an intermediate. There is strong evidence for the existence of bridged halonium ions in SbF₅ solutions,^{5,6} and ab initio molecular orbital studies have demonstrated the stability of the bridged intermediate in the addition of Cl⁺ to ethylene.⁷

Rearrangements among halobenzenes have been observed in solution, for example, the transformation of 1,2,4-tribromobenzene to the 1,3,5-isomer upon treatment of potassium anilide in liquid ammonia.⁸ However, it has been proposed that these occur via a series of nucleophilic displacements by aryl anions on an aryl halide.⁸ The mechanism for the dichlorobenzene cation rearrangements observed in the matrix more closely resembles that seen in sigmatropic reactions; for example, a plausible explanation for the interconversion between 1,4,4-, 1,3,3-, and 1,2,2-trimethylcycloheptatriene involves sigmatropic carbon skeletal rearrangements between norcaradiene intermediates.⁹ Specific experiments performed to characterize rearrangements between di- and trichlorobenzene cation isomers will be described in the following report.

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Experimental Section

The cryogenic apparatus and argon resonance photoionization sources have been described previously.¹⁰⁻¹² Room-temperature equilibrium vapors of the dichlorobenzenes and 1,2,4-trichlorobenzene were mixed with argon and CH₂Cl₂ in a 2-L can to yield Ar/CH₂Cl₂/reagent ratios of 900-500/1/3-1. Due to the slightly lower volatility of 1,3,5-trichlorobenzene, the equilibrium vapor pressure at 35 °C was mixed with argon, and experiments were done with and without CH₂Cl₂ added to serve as an electron trap. All the chlorobenzene mixtures were deposited onto a sapphire window (20 ± 2K) at a rate of 1 mmol/h for 3-5 h during exposure to argon-discharge 11.6-11.8 eV (vacuum ultraviolet) radiation from a 1- or 3-mm orifice discharge tube powered by a microwave discharge unit using maximum (80%) and minimum (20%) stable power. Mercury arc 220-1000-nm (UV-vis) lamp photolyses were subsequently performed for 15-30-min periods for all samples.

A Cary 17 spectrophotometer was used to record ultraviolet and visible spectra before and after vacuum ultraviolet irradiation and UV-vis photolyses. The uncertainty in the bands was ±0.2 nm unless otherwise indicated. All the chlorobenzenes were obtained from Aldrich Chemical Co., except for *o*-dichlorobenzene which was supplied by Matheson, Coleman, and Bell; no further purification was necessary.

Results

Experiments with different chlorine-substituted benzene precursors will now be described individually.

***m*-Dichlorobenzene.** Several experiments have been performed previously with *m*-dichlorobenzene (MDCB).¹³ Additional experiments were conducted with less intense argon resonance photoionization in order to minimize secondary photoprocesses. Spectra following vacuum ultraviolet irradiation through a 3-mm orifice with maximum (80%) discharge power exhibited vibronic systems with origins at 542.8 (accompanied by a vibronic band at 529.5 nm) and 520.6 nm with band absorbances of 0.15 and 0.17, respectively, which have been assigned to the MDCB and *p*-dichlorobenzene (PDCB) cations.¹³ Photolysis at 590-1000 nm had no effect on the absorptions; however, the 542.8-nm absorption

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