that of a methane molecule. This geometry may be readily confirmed with scale models. The most probable configuration appears to be one where the cyclohexane ring is in the chair form, stands at an angle with the plane of the surface, and discharges the β hydrogen from the backside of the molecule. Thus, the *deep* crack or crevice envisioned by Pines is evidently not required. Something similar must be envisaged for hydroxyapatite.

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σ–π Conjugation Effects in the Acid Cleavage of Allylmercuric Halides

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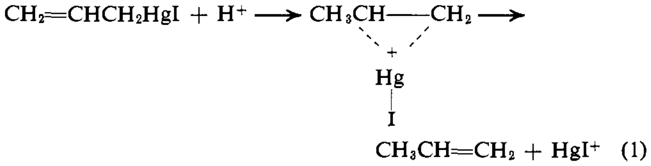
Abstract: Extended Hückel molecular orbital calculations suggest that the minimal energy conformation of allylmercuric bromide has the carbon–mercury bond perpendicular to the nodal plane of the olefinic π system resulting in delocalization of the double bond. A unique reaction pathway for the acid cleavage of allylmercuric halides is described. The extent of σ–π stabilization in the transition state for this cleavage reaction is shown to depend upon the conformation of the allylmercuric halide, the hybridization at the allylic carbon atom, and the polarizability of the carbon–mercury bond.

Organometallic compounds containing an allyl group bonded to a metal often exhibit enhanced reactivity toward electrophilic reagents. For example, allylmercuric iodide is rapidly cleaved by aqueous perchloric acid affording propene.[1] This reaction is some six orders of magnitude faster than the hydration of propene,[2] although both reactions involve attack of proton on the carbon–carbon double bond. This unusual reactivity has been attributed[3] to the extensive involvement of the mercury in the transition state of the reaction. The rate-determining step in allylmercuric iodide cleavage by aqueous acid has been shown by kinetic studies to be proton transfer to carbon. Kinetic isotope effects suggest that the reaction coordinate does not involve large components of heavy atom motions.[1b] Solvent effects on the ultraviolet spectra of allylmercuric iodide have led to the suggestion[3] that the ground state of this molecule exists in a conformation that can readily form an olefin–mercuric iodide π complex which closely resembles the transition state for this protolysis reaction (eq 1). To accommodate this mechanism the mercury atom must be rotated approximately 90° out of the nodal plane of the double bond in the ground state. Allyltin and other allylmetallic compounds are also cleaved by acid at rates that are markedly in excess of the rate of protonation of propene.[4a] It has been established for some time that the R_3MCH_2 group ($M = Si, Ge, Sn$) has a greater electron-releasing capacity than the R_3M group.[4b] This effect is often cited as evidence for $p\pi$–$d\pi$ bonding and more recently has been attributed in part to hyperconjugation of the carbon–metal bond (σ–π conjugation).[4c–e] Stabilizaton of neighboring cationic centers by carbon–metal bonds has also been involved with benzylmercury halides,[5a,b] α-ferrocenyl carbonium ions,[5c–e] and in the formation of cyclopropanes from 3-tosyloxyalkyltrimethyltin.[5f] A variety of spectroscopic evidence also has been reported that supports a ground-state interaction between the σ C–M bond and an allylic double bond.[6a–d] The concept of σ–π conjugation, and the requirement that the C–M bond and the axis of the electron-deficient π orbital must be coplanar, has recently been demonstrated by Traylor[5e,7] and Pitt.[8]



$$CH_2{=}CHCH_2HgI + H^+ \longrightarrow \underset{\overset{\cdot\,\cdot\,+\,\cdot\,\cdot}{\underset{|}{Hg}}\atop I}{CH_3CH{-}{-}CH_2} \longrightarrow CH_3CH{=}CH_2 + HgI^+ \quad (1)$$

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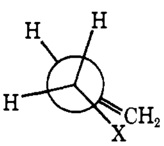
These studies, based upon charge-transfer spectra, permit a separation of the inductive effects and the hyperconjugative interaction of the -MR_n group. Our interest in theoretical calculations on mercurinium ion intermediates and the careful kinetic and spectral studies on allylmercury iodide[1,3] prompted us to use allylmercuric bromide for a theoretical investigation of carbon–metal hyperconjugation. We wish to report our data, based upon extended Hückel molecular orbital calculations, which support the mechanism proposed by Kreevoy and coworkers[1,3] for the acid cleavage of allylmercuric iodide and provide theoretical evidence for carbon–mercury σ–π stabilization in the transition state of this reaction.

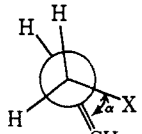
We first directed our attention toward calculating the minimum energy conformation of allylmercuric bromide. However, the paucity of experimental data concerning the conformation of organomercurials prompted us to first utilize EH calculations to examine the conformation of allyl halides where an abundance of experimental evidence is available. The barrier to internal rotation and the conformation of allyl halides have been a subject of interest for many years. These compounds, which represent simple allylic systems, are of particular interest since they also exhibit enhanced reactivity relative to their corresponding saturated analogs. Thus, the relationship of the rotamer populations to their chemical reactivity, and the propensity of these compounds to form stabilized allylic ions, are problems of considerable interest to the theoretical organic chemist.

Microwave spectroscopy[9a] has shown 3-fluoropropene to exist in two rotational isomers, cis and gauche, with the cis rotomer being lower in energy by 0.166 kcal/mol.[9b] The cis–gauche and gauche–trans–gauche rotational barriers were shown to be 3.12 and 1.49 kcal/mol, respectively.[9c] The microwave spectrum of 3-chloropropene has also established this molecule to exist in two rotameric forms. However, it was suggested that the gauche conformation was probably more stable than the cis form.[9d]



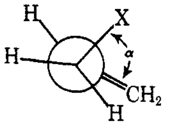
1

cis form, $\alpha = 0°$



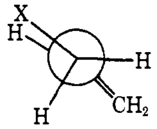
2

gauche form, $\alpha = 60°$



3

gauche form, $\alpha = 120°$



4

trans form, $\alpha = 180°$

X = F, Cl, Br, Hg^+, HgBr

Electron-diffraction studies[9e] on allyl halides (X = Cl, Br, I) excluded the two coplanar forms, **1** and **4**, and suggested that these three halides existed predominantly in the gauche forms **2** and **3**. However, nmr studies[9f] indicate that these compounds exist as two rotamers, cis and gauche, with the population of the cis form decreasing as the size of the halogen atom increases from chlorine to iodine. The fraction of these compounds that exists in the lower energy gauche forms was calculated from these data to be 0.78, 0.95, and 1.0 for X = Cl, Br, and I, respectively. The energy difference between the two rotamers of 3-chloropropene was calculated from the nmr spectra to be 100 ± 30 cal/mol, with the gauche form being of lower energy.[9g] In a subsequent nmr study, the relative abundance of the gauche conformers of the allyl halides was determined to be 0.65, 0.84, 0.97, and 1.0, X = F, Cl, Br, and I, respectively.[9h] Infrared spectroscopy[10,11] has also suggested the existence of two rotational isomers for 3-halopropenes at 25° with the proportion of the cis rotamer following the same trend as suggested by the nmr data.

Experimental Section

Extended Hückel (EH) calculations, as developed by Hoffmann,[12] were carried out as previously described.[13] All matrices were diagonalized by the Givens[14] method and molecular coordinates were calculated[15] internally from bond angles and bond lengths. The three-carbon allylic moiety was located in the xy plane with the y axis extending through the length of the carbon–carbon double bond. Bond angles for sp^2 and sp^3 carbon atoms were taken as 120 and 109.5°, respectively. Carbon–carbon bond distances were taken as 1.35 and 1.51 Å. Carbon–hydrogen bond distances were taken as 1.09 Å except for a carbon–proton bond distance of 1.2 Å in the transition state **9**. A C–X bond distance of 1.40, 1.82, 2.00, and 2.074 was used where X = F, Cl, Br, and Hg, respectively. The mixing coefficients or hybridization parameters for varying the geometry of the allylic carbon from sp^3 to sp^2 were taken from Mislow.[16]

Results and Discussion

The calculated energy minima for the most stable configuration of the allyl derivatives (Figure 1) were at α = 108, 105, 104, 94, and 90° for X = F, Cl, Br, HgBr, and Hg^+, respectively. The trend noted with the increase in the size of the substituent X would be anticipated on the basis of spectral data for the allyl halides where an increase in the size of the substituent destabilized the planar cis and trans conformers. The calculations were carried out with normal bond angles and distances. The geometry at C-3 was constrained to the tetrahedral configuration as the substituent X was rotated about the C_2–C_3 bond axis. This represented the minimum energy configuration in all cases except where X = HgBr (*vide infra*). The EH calculations show the cis confomers, **1**, of the allyl halides to

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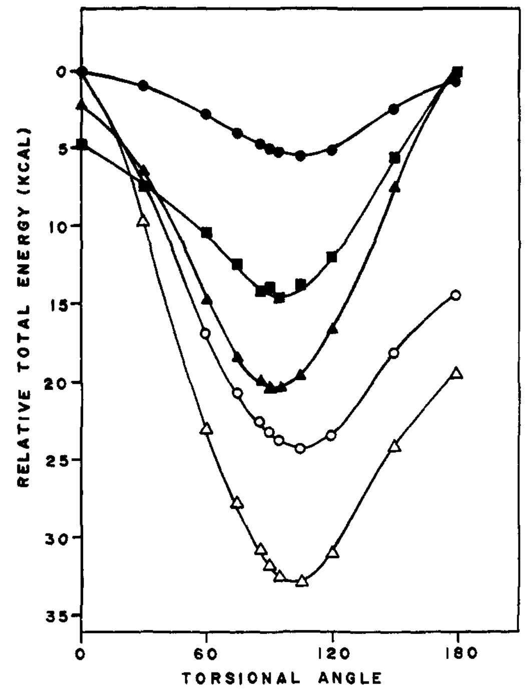
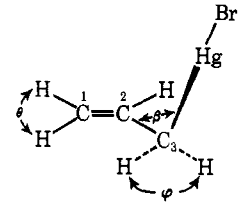


Figure 1. Relative rotational barriers for: allyl fluoride (●); allyl mercury cation (■); allylmercuric bromide (▲); allyl chloride (○); and allyl bromide (△).

be more stable than their corresponding trans conformers, **4**. Conversely, the trans form of the allyl mercury compounds was shown to be preferred. The magnitude of the rotational barriers is in general exaggerated and in the case of allyl fluoride, the calculations do not adequately reflect the experimental energy differences between the cis and gauche forms.[9b,c] However, allyl chloride and bromide do exhibit an energy minimum relatively close to the 120° gauche form in good agreement with experimental data. The relative rotational barriers (Figure 1) calculated do appear to be sensitive to the van der Waals radius of the substituent and the polarizability andl ength of the C–X bond. A measure of the steric influence of the substituents is reflected in the differences in the free-energy content of axial and equatorial cyclohexane derivatives. An nmr study has established the *A* value for the mercuri acetate group to be very small or zero.[17a] Similar conclusions had previously been reached for the conformational preference of cyclohexylmercuric bromide.[17b] The *A* values for fluoro, chloro, bromo, iodo, and mercuri substituents are 0.250, 0.513, 0.480, 0.431,[18] and ~0.0, respectively. The corresponding covalent radii for these substituents are 0.64, 0.99, 1.14, 1.33,[19a] and 1.30 Å,[19b] respectively. Thus, the greater rotational barrier for allyl bromide and chloride than for allylmercuric bromide and allyl mercury cation is in accord with a longer, more diffuse carbon–mercury bond.

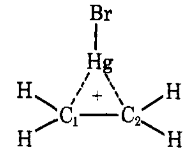
Additional information about the conformation and molecular structure of allylmercuric halides comes from infrared and nuclear magnetic resonance spectral data. The carbon–carbon double bond stretching frequency of allyl halides is typically between 1640 and 1650 cm^{-1}, while the ultraviolet maximum usually found in unconjugated double bonds occurs below 200 nm. Allyl compounds with ionic character, and hence delocalized double bonds, exhibit lower carbon–carbon stretching frequencies. Allyllithium, which on the basis of nmr studies exists predominantly as a delocalized symmetrical allyl anion, exhibits a carbon–carbon stretching frequency in the region of 1525–1540 cm^{-1} and an ultraviolet absorption at 310–320 nm.[20] Allylmercuric chloride and bromide have been assigned the intermediate or gauche conformation on the basis of infrared spectral data.[21a] Allylmercuric iodide has a carbon–carbon stretching frequency of 1623 cm^{-1} [21b] and a solvent-dependent uv absorption in the general region of 230–250 nm.[3] These data suggest that the double bond in **5** is partially delocalized.

On the basis of uv[3] and kinetic[1] data, Kreevoy advanced the argument that allylmercuric iodide exists in a conformation such as **5** (α = ~90°) where a substantial overlap exists between the excited state wave function and the ground state. We had previously reported[13] EH calculations that suggest $HgBr^+$ and ethylene to form a symmetrical mercurinium ion **6** with a substantial interaction existing between mercury and carbon, ρC_1–Hg = 0.180, that closely parallels the observed behavior of mercuric salts in oxymercuration reactions. If a bonding interaction between the mercury and the double bond in allylmercuric iodide was responsible for the occurrence of a strong band in the ultraviolet at 248 nm, in water, it should be discernible by this method of calculation. Our EH calculations on allymercuric bromide, in the gas phase, *do not* reveal a bonding interaction between the π system of the double bond and mercury. In fact, on the basis of overlap populations, the net interaction between these two chromophores is antibonding (Table I). For all of the allyl derivatives studied, the antibonding between the substituent X and C_1 of the double bond, ρC_1–X, diminishes on rotation about the C_2–C_3 bond from 0 to 180°. The C_2–X interaction is smallest at α = 90° but increases again in magnitude as it approaches either 0 or 180°. The covalent bonding of the substituent X to carbon, ρC_3–X, is also seen to diminish at the 90° conformation. The slight reduction in $\rho\pi$ and the increase in the C_2–C_3 bonding with **5** are due almost entirely to an increase in the overlap populations of the carbon $2p_z$ orbitals of the π system with the readily deformable carbon–mercury σ bond.



5

$\alpha = 90°$



6

The calculated energy difference between the highest occupied (HOMO) and the lowest unoccupied molecular

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Table I. EH Calculations on Allyl Derivatives

Configuration, α, deg	X	Q_{C_1}[b]	Q_{C_2}	Q_{C_3}	Q_X	$\rho_{C_1=C_2}$	$\rho_{\pi C_1-C_2}$	$\rho_{C_2-C_3}$	ρ_{C_1-X}	ρ_{C_2-X}	ρ_{C_3-X}	HOMO, eV	LUMO, eV
0[a]	F	−0.084	+0.069	+0.508	−0.610	1.337	0.507	0.798	−0.0310	−0.0973	0.381	−12.29	−6.16
90	F	−0.049	+0.063	+0.499	−0.610	1.343	0.508	0.771	−0.0106	−0.0967	0.365	−12.48	−6.50
180	F	−0.081	+0.070	+0.508	−0.610	1.340	0.513	0.785	+0.0041	−0.1068	0.365	−12.20	−6.30
0	Cl	−0.098	+0.049	+0.210	−0.240	1.355	0.507	0.784	−0.0985	−0.1295	0.574	−11.75	−6.14
90	Cl	−0.092	+0.058	+0.210	−0.217	1.356	0.507	0.772	−0.0256	−0.1035	0.540	−11.65	−6.28
180	Cl	−0.089	+0.059	+0.212	−0.251	1.347	0.513	0.768	+0.0084	−0.1345	0.546	−11.66	−6.29
0	Br	−0.102	+0.044	+0.127	−0.145	1.358	0.506	0.783	−0.1216	−0.1263	0.563	−10.97	−6.13
90	Br	−0.105	+0.055	+0.133	−0.117	1.342	0.502	0.781	−0.0302	−0.0917	0.522	−11.18	−6.27
180	Br	−0.088	+0.057	+0.133	−0.161	1.349	0.513	0.765	+0.0097	−0.1282	0.532	−11.13	−6.29
0	Hg^+	−0.077	+0.059	+0.027	+0.909	1.351	0.508	0.793	−0.0497	−0.0727	0.549	−12.28	−8.98
90	Hg^+	−0.072	+0.063	+0.050	+0.904	1.333	0.491	0.798	−0.0214	−0.0485	0.520	−12.23	−8.95
180	Hg^+	−0.078	+0.069	+0.056	+0.876	1.344	0.513	0.768	+0.0045	−0.0684	0.536	−12.22	−8.95
0	HgBr[c]	−0.094	+0.030	−0.189	+0.644 −0.385	1.355	0.508	0.770	−0.0544	−0.0827	0.628	−11.41	−6.24
90	HgBr	−0.133	+0.029	−0.165	+0.662 −0.367	1.333	0.490	0.799	−0.0212	−0.0529	0.587	−11.13	−6.36
180	HgBr	−0.094	+0.036	−0.180	+0.626 −0.384	1.356	0.512	0.746	+0.0063	−0.0821	0.627	−11.14	−6.29
90[d]	HgBr	−0.208	+0.042	−0.195	+0.788 −0.409	1.288	0.448	0.842	−0.0415	+0.0170	0.481	−10.50	−6.99
90[e]	HgBr	−0.223	+0.072	−0.223	+0.795 −0.389	1.013	0.210	1.013	+0.1600	+0.2294	+0.160	−9.89	−7.22

[a] All structures have sp^3 geometry at C_3 unless otherwise noted. [b] Charges were iterated to self-consistency (0.01 e) using a charge sensitivity factor of 2.00 eV/electron.[13] [c] The charge on bromide is listed directly under the charge on mercury, Q_X. [d] Structure **7**. [e] Structure **8a**.

Table II. Bonding Mode for Allyl Derivatives

Configuration	Orbitals on X[a] bonding to C_3				Orbitals on C_3[a]			Orbitals on Hg bonding to Br			Total
α, deg	X	% s	% p	% d	% s	% p	% p_z on C_3[b]	% s	% p	% d	energy, kcal/mol
90[c]	F	40.73	59.27		35.23	64.77					−10,634
90	Cl	24.60	75.40		28.56	71.44					−9,431
90	Br	15.40	84.60		25.67	74.33	94.48				−9,230
0	HgBr	60.40	37.92	1.68	14.78	85.22					−13,592
90	HgBr	59.32	38.43	2.25	13.56	86.44	74.78	44.57	55.43		−13,610
180	HgBr	59.65	38.28	2.07	12.27	87.73					−13,590
90	Hg^+	92.23	4.18	3.59	12.15	87.85					−11,099
90[d]	Hg^+	94.01		5.99		100.00	100.00				−11,087
90[d]	HgBr	62.07	33.46	4.47		100.00	100.00	54.13	44.07	1.80	−13,632
90[e]	HgBr	63.64	23.95	12.41		100.00	100.00	61.32	37.05	1.63	−13,617
90[f]	HgBr	63.51[g]	24.07	12.42		100.00	100.00	61.25	37.12	1.63	−13,618
		28.25[h]	71.05			100.00	99.3				
	HgBr[i]	58.37	39.58	2.04	13.66	86.34		46.42	56.48		

[a] Relative bonding is based upon Mulliken overlap populations. [b] Based upon total 2p overlap population. [c] Structure **5**; all compounds have sp^3 geometry at C_3 unless otherwise noted. [d] The allyl system is planar with Hg bonded to C_3 and sp^2 hybridization at all three carbon atoms, **7**. [e] Structure **8** with the Hg over C_2. [f] The C–C bond distances are averaged at 1.43 Å, **8a**. [g] Bonding to C_2. [h] Bonding to C_1. [i] Bonding in methyl mercurybromide.

orbital (LUMO) is smaller for **5**, α = 94°, than for the cis or trans conformer, indicating that this conformation would yield the greatest shift to longer wavelengths in the ultraviolet, if these are in fact the orbitals actually involved in the observed transition. The observed[3] maximum in the uv spectrum of allylmercuric iodide is consistent with the extended conjugation indicated by structure **7**, where this calculated energy difference is only 3.511 eV. A greater separation in the charge distribution about the double bond and the bromomercuri group in **5** and **7** than in **1** and **4** could also contribute to the observed red shift in polar solvents (Table I).

Further support for some delocalized bonding in allylmercury compounds comes from nmr studies. Diallylmercury,[22] allylmercuric acetate,[23] and allylmercuric chloride[24] exhibit nmr spectra consistent with a σ-allyl structure. However, concomitant allylic rearrangement and intermolecular exchange reactions were invoked to explain temperature and solvent effects on the nmr spectra of diallylmercury.[22] An acetone-d_6 solution of allylmercuric chloride, in the presence of small quantities of $HgCl_2$, exhibited an AX_4 nmr spectrum with loss of ^{199}Hg satellites suggesting an intermolecular exchange mechanism. An extremely rapid (statistical exchange <25 sec at *ca.* 20°) exchange of mercury with $^{203}HgCl_2$ has also been observed with allylmercuric chloride.[24] This exchange with $HgCl_2$ is particularly relevant to the nature of the bonding in

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(22) H. E. Zieger and J. D. Roberts, *J. Org. Chem.*, **34**, 2826 (1969).

(23) P. D. Sleezer, S. Winstein, and W. E. Young, *J. Amer. Chem. Soc.*, **85**, 1890 (1963); P. D. Sleezer, Dissertation, University of California at Los Angeles, 1963, University Microfilms, Inc., 64-4437.

(24) W. Kitching and B. F. Hegarty, *J. Organometal Chem.*, **16**, 29 (1969).

allylmercuric halide since it is generally considered that $HgCl_2$ is not electrophilic enough to react with an unstrained carbon–carbon double bond. However, a symmetrical intermediate, which would be consistent with the nmr results, can readily be envisioned by attack of $HgCl_2$ on C_1 of the planar allylic structure **7**.

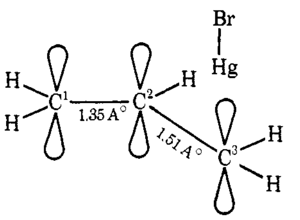
The above experimental observations prompted us to examine the effect of the interaction of the carbon–mercury σ bond with the olefinic π system as the hybridization at C_3 is varied from sp^3 to sp^2. Indeed, the sp^2 configuration of allylmercuric bromide with the HgBr group directly over C_3 at a 90° angle to the planar allyl moiety, **7**, is 20 kcal/mol lower in energy than **5** (Table II). Conversion of **5** to **7** resulted in a significant increase in the σ–π interaction between the carbon $2p_z$ orbital on C_3 and the π orbital on C_2 (Table III). However, the allylmercury cation ($CH_2{=}CHCH_2Hg^+$), which utilizes the relatively diffuse 6s orbital to a far greater extent than with allylmercuric bromide, prefers tetrahedral geometry at C_3 (Table II). Since the spectral data indicated that the carbon–mercury bond in **5** is still principally σ in nature, it was not surprising that movement of HgBr along the C_3–C_2 bond axis of **7** resulted in an increase in energy. The π-allyl complex **8**, with the bromomercuri group directly above C_2, was 15 kcal/mol higher in energy than **7** while a symmetrical π-allyl complex, **8a**, where the carbon–carbon bond distances are an average (1.43 Å) of the bond distances in **7** (1.35 and 1.51 Å), was 16 kcal/mol less stable than **7**.[25a] Since the calculations probably accentuate the energy differences between conformers, the calculated activation energy for the transformation of **7** to **8a** did not appear to be so great that one could totally exclude an intramolecular allylic rearrangement[22] in diallylmercury.[25b]

Table III. C_2–C_3, $2p_z$–$2p_z$ π Overlap Populations for Allyl Derivatives[a]

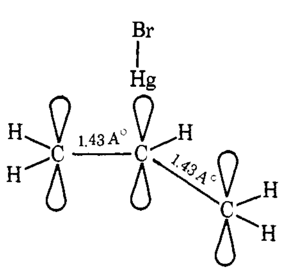
X	β		$\rho_{2p_z\text{-}2p_z}$
F	109.5		0.0103
Cl	109.5		0.0096
Br	109.5		0.0178
Br	90.0		−0.0029
Hg^+	109.5		0.0456
Hg^+	90.0		0.0562
HgBr	109.5		0.0465
HgBr	90.0		0.0784
Br	109.5	H^{+b}	0.0704
Br	90.0	H^+	0.0606
Hg^+	109.5	H^+	0.0952
Hg^+	90.0	H^+	0.1022
HgBr	109.5	H^+	0.1598
HgBr	90.0	H^+	0.2290

[a] All molecules are in the α = 90° configuration as in **5**. [b] The proton is added from the side opposite X (ν = 90°) in all compounds as in **9**.

The general trend observed with the C_3–X bonding in allyl derivatives is an increase in the 2p orbital participation on carbon as the atomic number of the substituent increases. The orbitals on mercury involved in bonding to carbon in allylmercuric bromide show the percentage of 6s, 6p, and 5d character to be quite similar to that calculated for CH_3HgBr (Table II).[25c] These values are in good agreement with the concept of sp hybrid orbitals being largely responsible for the bonding in linear covalent compounds of Hg(II). The relatively stable inner 5d orbitals on mercury, with a VO IP of −15.66 eV, differ too much in energy to interact appreciably with the orbitals on carbon and bromine.



7



8a

The planar allylmercuric bromide **7**, and the π-allyl derivatives **8** and **8a**, are essentially bonded to mercury by $2p_z$ orbitals on carbon with a small antibonding interaction with the carbon 2s orbitals. The symmetrical complex **8a** is also of particular interest since the bonding to the terminal carbons, ρC_1–Hg = 0.160, is almost as strong as the bonding to the central carbon atom, ρC_2–Hg = 0.229. Stabilization of the π system on carbon by delocalization increases the contribution of the Hg 5d orbitals to the mercury–carbon bonding since the energy difference between these orbitals diminishes. However, the 6p orbital on mercury is largely responsible for the bonding to C_1 in **8a** with an antibonding contribution of the 5d orbitals. Furthermore, the total bonding of all three carbon atoms to mercury (ρC–Hg = 0.549) is almost as great as the covalent carbon–mercury bond in **5** (ρC_3–Hg = 0.587). The mercury–bromine bond is typically sp in nature with a notable increase in participation of the 6s orbital on mercury with the π-allyl structure. It should be emphasized, in view of the approximations inherent in the calculations, (a) that more significance be placed on the trends involved in the relative change in orbitals involved in bonding than the calculated hybridization for an individual molecule; (b) that **7** need not be completely planar as indicated by our calculations but that the hybridization and bonding mode of allylmercuric halides are certainly "atypical" relative to the allyl halides. However, there is qualitative agreement with experimental data since the bromomercuri group in **5** is neither a purely σ-bonded allyl compound nor a symmetric π-allyl structure **8a**, but exhibits an energy minimum that is intermediate between these two extremes, **7**. Also of significance is the fact that allyl halides exhibit normal sp^3 bonding at C_3 by this method of calculation.

We next examined the effect of conformation and hybridization at C_3 on the rate-determining transfer of proton to C_1 of allylmercuric bromide (Table IV). Our calculations indicate a slight preference for attack by proton on C_1 of **5** from the side opposite the HgBr group (ν = 90°) and no preference for orientation of addition (ν = 90 or 270°) to the planar allylic structure **7**. Addition of the proton to **5** is accompanied by a continuous decrease in energy with concomitant changes

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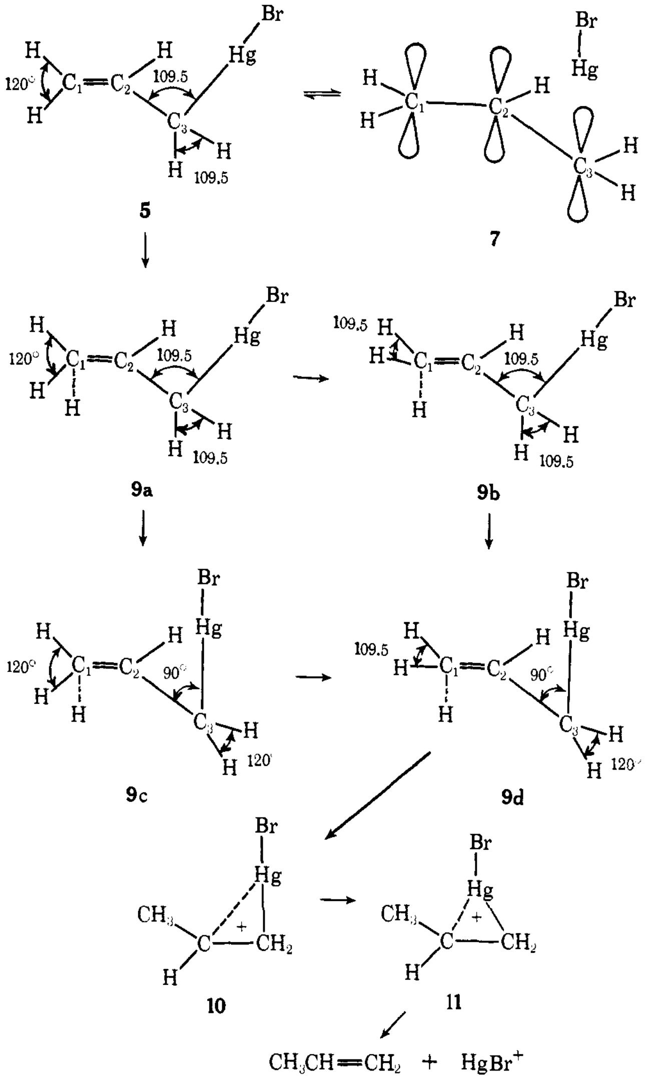
(25) (a) The mercury atom was held at a fixed distance, z = 2.074 Å, above the plane of the allylic system in all calculations. (b) EH calculations also indicated that diallylmercury has a delocalized double bond with the same conformation as **5**. (c) The mode of bonding shown in Table II is based on the relative percentage of the orbitals involved in the bonding calculated from the Mulliken overlap populations for the total number of valence electrons in the molecule.

in hybridization from sp^3 to sp^2 at C_3 and from sp^2 to sp^3 at C_1 (Scheme I). These changes in geometry, as the transition state is approached, result in a stronger C–H$^+$ bond and a reduction in ρC_3–Hg. The C_1–C_2 bond order is also seen to diminish while ρC_2–C_3 increases as the newly developing double bond is formed. In the transition state[1,3] **9**, for this acid cleavage, the incipient carbonium ion at C_2 may be stabilized by the neighboring bromomercuri group and by σ–π conjugation[26] (Table III). However, the mercury is only effective as a neighboring group when the allylmercuric halide is in the planar configuration **7** where delocalization of the 6s and 6p electrons on mercury exhibits a ρC_2–Hg = 0.085. Tetrahedral geometry at the allylic carbon atom results in a slightly negative ρC_2–Hg. By comparison, the σ–π interaction between the polarizable C_3–Hg σ bond and the 2p$_z$ π orbital on C_2 is considerably stronger; ρ = 0.229 in the protonated structure **9d**. This suggests that considerable double bond character between C_2 and C_3 is developing in the transition state since the C_1–C_2 π overlap of the double bond in allylmercuric bromide is ρ = 0.49. The transition state for protolysis of allylmercuric bromide therefore probably closely resembles **9d** or **10** where the methyl group, C_1, is fully developed (C–C–H, 109.5°). The mercurinium ion **11**, where the HgBr group is symmetrically bonded to the olefinic double bond, is 0.7 kcal/mol more stable than **10** and is, therefore, a very likely intermediate that exists between the transition state and products. The carbon–carbon π bonding in **10** and **11** (ρ = 0.354 and 0.352) is essentially identical although the total overlap population between mercury and the olefinic carbon atoms, C_2–C_3, is slightly greater for the olefin π complex **11** (ρ = 0.379) than for the unsymmetrical ion **10** (ρ = 0.348). The position of equilibrium of mercurinium ions formed *via* electrophilic attack of Hg$^+$Br on an olefin lies far to the side of the starting materials. Propene is therefore evolved from the reaction mixture upon protolysis of allylmercuric halide.

Scheme I. Reaction Mechanism for Protolysis of Allylmercuric Bromide



We have previously suggested that the intermediates involved in electrophilic addition reactions with olefins are a continuum of acceptor–donor π complexes where the relatively stable olefin–silver π complex represents one end of the spectrum and the highly unstable fluoronium ion the other.[13] The stability of these onium ion intermediates depends to a large extent upon the degree of perturbation of the olefinic π system. Thus both **10** and **11** may be considered to be mercurinium cations which differ principally in the formal description of the bonding where **10** is stabilized principally by σ–π conjugation.

The calculations support the concept that hyperconjugation is not as important in the ground state of allyl derivatives, where a charge separation would be involved, as it is in a transition state for protolysis where there is no additional charge separation due to σ–π stabilization. However, the trend is noted that allyl compounds with polarizable substituents that can tolerate a positive charge exhibit increased delocalization (Table III). Significantly, rehybridization of C_3 to sp^2 in allyl bromide results in a decrease in σ–π overlap, while the opposite results were obtained with the allyl mercurials. These results would predict that a bromonium ion, an isolable intermediate[27] relative to the elusive mercurinium ion, would not result upon protonation of allyl bromide. Previous[13] EH calculations suggest that very little stabilization will be afforded a carbonium ion adjacent to bromine bonded to an sp^3 carbon atom. However, neighboring bromo and iodo participation does ensue upon the acid-catalyzed addition of hypochlorous acid to allyl bromide and iodide. The corresponding reaction of allyl chloride with hypobromous acid yields very little rearranged product since chlorine has a smaller tendency to participate.[28]

The significance of carbon–metal σ–π conjugation has been convincingly demonstrated by Traylor and coworkers[7a] based upon charge-transfer frequencies of organometallic compounds with tetracyanoethylene. In fact, this group has advocated for some time that σ–π conjugation is the major driving force involved in the protonation of benzylmercury halides.[7b] In a series of allyltin compounds the high reactivity toward electrophilic attack and the red shifts observed in the ultraviolet have been attributed to a ground-state interaction between the σ allyl–tin bond and the allyl group.[6d] These experimental data strongly support

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(26) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **59**, 707 (1948).

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(28) P. B. D. delaMare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 443 (1962); 3429 (1963).

Table IV. EH Calculations on Protonated Allylmercuric Bromide

Structure	β	φ	θ	ν	Q_{C_1}	Q_{C_2}	Q_{C_3}	Q_{Hg}	Q_{Br}	Q_{H^+}	$\rho_{C_1-H^+}$	$\rho_{C_1-C_2}$	ρ_π	$\rho_{C_2-C_3}$	ρ_{C_3-Hg}	ρ_{C_2-Hg}	ρ_{Hg-Br}	Total energy kcal/mol
9a	109.5[a]	109.5	120	90	0.123	0.427	−0.140	0.636	−0.380	0.169	0.574[e]	1.040	0.221	0.826	0.618	−0.079	0.573	−13,869
9a	109.5[b]	109.5	120	90	0.125	0.414	−0.145	0.652	−0.382	0.171	0.573[e]	1.042	0.221	0.846	0.622	−0.081	0.574	−13,870
9a	109.5[c]	109.5	120	270	0.093	0.354	−0.098	0.729	−0.329	0.137	0.606[d]	0.993	0.173	0.920	0.515	−0.013	0.519	−13,929
9a	109.5[c]	109.5	120	90	0.097	0.348	−0.093	0.734	−0.329	0.133	0.607[e]	0.993	0.174	0.926	0.507	−0.002	0.592	−13,935
9b	109.5[c]	109.5	109.5	90	0.069	0.373	−0.080	0.749	−0.320	0.107	0.636[e]	0.919	0.111	0.952	0.492	0.005	0.594	−13,945
9c	90[c]	120	120	90	0.067	0.297	−0.066	0.880	−0.382	0.090	0.644[e]	0.945	0.123	1.000	0.387	0.085	0.527	−13,985
9d	90[c]	120	109.5	90	0.046	0.306	−0.045	0.893	−0.376	0.076	0.682[e]	0.880	0.069	1.026	0.372	0.096	0.529	−13,993
9d	90[c]	120	109.5	270	0.039	0.306	−0.058	0.902	−0.367	0.079	0.694[d]	0.869	0.050	1.030	0.366	0.091	0.531	−13,993
10	90[f]	120	109.5	109.5	0.012	0.219	0.042	0.923	−0.310	0.024	0.810	0.782	0.354	1.205	0.247	0.101	0.532	−14,058

[a] Trans configuration **4**, $\alpha = 180°$. [b] Cis configuration **2**, $\alpha = 0°$. [c] $\alpha = 90°$ with all other angles in the table defined by structure **9**. [d] Proton added on the same side as the HgBr group at a distance 1.20 Å above the plane of the double bond. [e] Proton added from the side opposite the HgBr group; $C-H^+ = 1.20$ Å, as in **9**. [f] Unsymmetrical mercurinium ion of propene, $C-H^+ = 1.09$ Å, **10**.

the mechanism proposed in the present work that also invokes $\sigma-\pi$ conjugation in the protolysis of allylmercuric halides. Furthermore, EH calculations[29] corroborate the suggestion that $\sigma-\pi$ stabilization plays a major role in the protonation of benzylmercury compounds. It is also worthy of note that in the calculated minimum energy configuration for allylmercuric bromide (**7**), the stabilizing substituent HgBr does *not* require significant changes in geometry or in its distance from the developing carbonium ion as the transition state is approached. This is in excellent agreement with the kinetic data of Kreevoy[1,3] and the spectral data of Traylor[7a] which requires a truely delocalized transition state with little atom motion. Traylor[7a] has described this as a "vertical" stabilization process consistent with the Franck–Condon principle.

Finally, we wish to emphasize the relevance of these calculations to other substitution and rearrangement reactions with the allyl system. The reaction of crotylmercuric bromide with HCl is 10^7 times faster than with *n*-butylmercuric bromide, affording more than 99% 1-butene. Winstein and coworkers[23] proposed an SEi′ mechanism to account for the high rate and complete allylic rearrangement in this reaction and an SE2′ mechanism when the same reaction was carried out in acetic acid–perchloric acid. The above SEi′ mechanism and those exchange reactions with allyl mercurials referred to previously must involve a 90° conformation such as **5** (or the delocalized structure **7**) where the bonding π orbitals of the double bond and the mercury are both accessible to the attacking electrophile. For example, the molecular addition of HCl and the exchange of $HgCl_2$[24] with the higher energy planar cis configuration of the allyl mercurial, rather than the gauche conformer, would require bond rotation of the π orbital on C_1. This mechanism forfeits the stabilization due to delocalization of the allyl system and disrupts the stability of the carbon–carbon double bond. In view of the pronounced participation by mercury, it is quite likely that the transition state for these reactions has many of the characteristics described above for the cleavage of allylmercuric iodide. In the case of crotylmercuric acetate, the position of equilibrium does not favor the elimination of $HgOAc^+$ affording olefin, but under these same reaction conditions affords solvolysis products. One explanation for this dichotomy of reaction pathways is that the olefin is much more strongly perturbed[13] by $HgOAc^+$ than by $HgCl^+$ and the activation energy for protonation affording a mercurinium ion is greater than that for solvolysis where a resonance-stabilized crotyl cation is formed. The sp^3 hybridization of C_3 for allylmercury cation could also influence the course of the reaction since this would increase the activation energy of protonation relative to a planar structure such as **7** where the ligand on mercury is highly covalent. Furthermore, the basicity at C_1 is reduced due to the positive charge on mercury, and the extent of $\sigma-\pi$ conjugation with protonated allylmercury cation is considerably less than that observed with allylmercuric bromide.

As indicated above, trimethylallylsilane and the analogous germanium compounds also exhibit ultraviolet absorption maxima at longer wavelengths than isolated double bonds. This bathochromic shift has been at-

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(29) R. D. Bach and P. A. Scherr, manuscript in preparation.

tributed, on the basis of molecular orbital calculations, to dπ–pπ bonding between the double bond and silicon.[30] However, this requires the planar trans conformation **4** (X = $Si(CH_3)_3$) which on the basis of arguments presented in this paper would not be highly populated if at all. Thus, the effects of conformation and $\sigma-\pi$ delocalization of the double bond must be considered to fully explain the reasons for extended conjugation in these allyl organometallic compounds.

In summary, EH calculations suggest that allylmercuric derivatives should exist principally in a conformation intermediate between the two gauche forms **2** and **3** due in part to delocalization of the double bond. The activation energy for electrophilic addition to allyl mercurials is markedly reduced by $\sigma-\pi$ stabilization of the neighboring cationic center as depicted in the planar configuration **7**. These results further support the existence of mercurinium cations which may be formed either by the electrophilic addition of Hg^{2+} to an olefin or by protolysis of σ-bonded allylic mercurials. Although mercurinium ions have been postulated on the basis of experimental and theoretical data, they have only recently been observed by nmr spectroscopy.[31] In view of the current interest in the concept of a three-atom triangle which includes a metal atom that has also been proposed in metal–metal exchange processes,[32] we hope that molecular orbital calculations of this type will help to provide a unifying theory describing the nature of these cyclic intermediates.

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Oxidative Cleavage of Hydroquinone Ethers with Argentic Oxide

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Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received May 1, 1971*

Abstract: The scope and mechanism of argentic oxide (AgO)-oxidative ether cleavage of both naphtho- and benzohydroquinone dimethyl ethers have been investigated. The reaction is accomplished most efficiently in dilute, aqueous, acidified dioxane solution, the *p*-quinones being formed immediately at room temperature in high yield. Reaction in an $H_2{}^{18}O$ enriched milieu provides proof that aryl–oxygen bond cleavage is involved during the oxidation. Oxidation-sensitive functions such as alcohols, aldehydes, ketones, and olefins survive the reaction intact, illustrating the selectivity obtainable. *o*-Quinones also can be formed in moderate yield from 4,5-disubstituted 1,2-dimethoxy (or methylenedioxy)benzenes. In addition, where possible, polymethoxylated nuclei are demethylated to yield both *o*- and *p*-quinones. The application of these results to protection–deprotection of quinones as well as to demethylation of natural products is discussed.

The problem of demethylation of aryloxy methyl ethers ($ArOCH_3$) is a general one in synthetic organic chemistry. Classically these ethers have been cleaved only with strong, sometimes aprotic, acids and more recently under equally drastic nucleophilic conditions.[1] As a result the use of methyl ether protecting groups is limited by the stability of the nucleus and its substituents to the vigorous conditions required for their removal and some natural products containing methoxyl groups are demethylated nondestructively only with difficulty. However, if the molecule contains ortho or para methoxyl groups, then alternative oxidative demethylation pertains. The resulting quinone can be reduced quantitatively to the hydroquinone or catechol if simple demethylation were the desired overall reaction. Protection of a quinone as the dimethyl ether of the hydroquinone has considerable advantage for synthetic quinone chemistry in that it allows manipulation of the molecule under strongly anionic conditions which are precluded by the use of simple hydroquinone esters.[2] The small steric bulk and general unreactivity of the methoxyl group makes it an ideal blocking group and facilitates nucleophilic condensation reactions of the type already reported.[3] Since many quinones of biological interest bear acid-sensitive isoprenoid side chains, demethylation requires mildly acidic conditions, thus eliminating the most effective acidic reagents. In addition we have observed that hydroquinone dimethyl ethers are resistant to alkaline cleavage of the type which has been effective with simple anisoles.[4] Thus, a successful method of oxidative demethylation would be particularly attractive.

As reviewed in 1969,[5] oxidative demethylation of

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(2) Hydroquinones esterified with a bulky group such as pivaloyl have proved inert during Wittig reaction; see W. E. Bondinell, S. J. DiMari, B. Frydman, K. Matsumoto, and H. Rapoport, *ibid.*, **33**, 4351 (1968).

(3) W. E. Bondinell, C. D. Snyder, and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 6889 (1969); *J. Org. Chem.*, **36**, 3951 (1971).

(4) *E.g.*, we have found that 2,3-dimethyl-1,4-dimethoxynaphthalene is not demethylated by aqueous methylamine at 185° (ref 1c).

(5) O. C. Musgrave, *Chem. Rev.*, **69**, 499 (1969).