Neutron-Diffraction Determination of the Structure of $CH_3CN \cdot 2HCl$

Sir:

Numerous reports[1-6] of experimental studies of the bichloride ion have appeared recently. Although the existence of this anionic species $(Cl-H-Cl)^-$ in both solution and the solid state appears to be well established, conclusive structure determinations on solid phases by diffraction methods have been lacking.

Among the many reported examples of compounds possibly containing the bichloride ion, $CH_3CN \cdot 2HCl$ is one of the simplest and most interesting. Both Hantzsch,[7] who made an early study of this material,

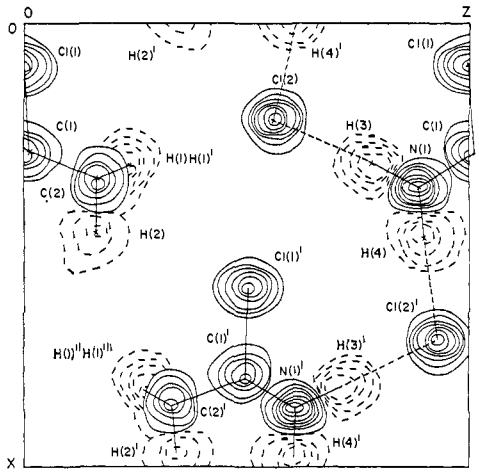

Figure 1. Fourier section at $y = 1/4$ in the unit cell: dashed circles (negative contours) in intervals of 300; positive contours in intervals of 500. The atoms in the asymmetric unit are Cl(1), C(1), C(2), H(1)', H(2), N(1), H(3), H(4), and Cl(2). The out-of-plane methyl hydrogen atoms [H(1), H(1)', H(1)'', and H(1)'''] have been projected onto the plane, and final positional parameters obtained from a full-matrix anisotropic least-squares refinement are indicated on the section with crosses (×). Bonded atoms in the acetimino group are connected by light solid lines. Dashed lines indicate hydrogen-bonding interactions.

and Janz and Danyluk,[8] who unexpectedly obtained the crystalline solid during conductivity studies of acetonitrile–hydrogen chloride, postulated that the structure was that of a nitrilium salt $[CH_3CNH^+(HCl_2)^-]$. The latter workers based their structure hypothesis largely on the similarity of the infrared spectrum of this compound in solution to that independently observed[2,9] for solid $(CN_3)_4NCl \cdot HCl$, which is assumed (with strong support) to contain the bichloride ion. However, it should be noted that Janz and Danyluk interpreted the spectrum of solid $CH_3CN \cdot 2HBr$ as indicative of an imino hydrohalide structure $[CH_3C(Br)=NH \cdot HBr]$, and they did not rule out the possibility of a similar structure for solid $CH_3CN \cdot 2HCl$.

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(2) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).
(3) D. W. A. Sharp, *ibid.*, 2558 (1958).
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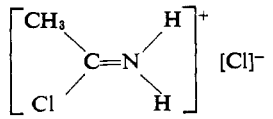
Another related compound, the hexachloroantimoniate(V) complex $[CH_3CN \cdot 2HCl, SbCl_5]$, has been recently the subject of a detailed infrared study.[10] The molecular structure resulting was found to be consistent with the imino hydrohalide model similar to the case of $CH_3CN \cdot 2HBr$. In view of the above uncertainties we have chosen to investigate the structure of $CH_3CN \cdot 2HCl$ by single-crystal neutron-diffraction methods.

Single crystals suitable for neutron diffraction were grown from anhydrous acetonitrile–hydrogen chloride solutions at −16° under dry nitrogen. Analysis of single-crystal material established the formula to be $CH_3CN \cdot 1.96HCl$. Crystals sealed in glass capillaries were examined by standard X-ray techniques. The orthorhombic cell with $a = 8.72 \pm 0.01$, $b = 6.93 \pm 0.01$, and $c = 8.63 \pm 0.01$ A contains four molecules. The diffraction symbol is mmmPn·a indicating Pnma and $Pn2_1a$ as possible space groups. A statistical test indicated the presence of a center of symmetry establishing the former space group.

Essentially complete three-dimensional neutron-diffraction data (511 independent reflections) were collected at −5° with λ 1.08 A. The structure was solved from the three-dimensional neutron Patterson function with some assistance from an X-ray projection. All atoms except two methyl hydrogens lie in mirror planes. The basic molecular structure is that of the imino hydrohalide model



as is evident from the Fourier section shown in Figure 1. The Cl^- ion is involved as an acceptor in two hydrogen bonds which lie in the molecular plane and which serve to tie together the planar acetimino groups. Bonding between planes is very weak in agreement with the physical properties of the crystal. Although this crystal is rather unstable toward loss of HCl, the bond lengths and angles appear normal. After two cycles of full matrix anisotropic least-squares refinement[11] the weighted $R = [\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma w F_o^2]^{1/2}$ was 0.085 for all reflections. A full report will appear later.

Acknowledgment. We wish to acknowledge the support of the U. S. Atomic Energy Commission.[12]

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(11) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(12) The present report is assigned Serial No. RLO-1778-3 for indexing purposes.

(13) Metallurgy Division, Argonne National Laboratory, Argonne, Ill.

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New Aspects of the Mechanism of Sulfenyl Chloride Additions to Olefins

Sir:

The addition of alkane- and arenesulfenyl chlorides to unsaturated systems has received considerable at-

Table I. Methane- and Benzenesulfenyl Chloride–Olefin Adducts[a]

Reactants		% adduct ratio[b]			
		Initial		Rearranged	
$CH_2{=}C<$	RSCl	$CH_2(Cl)-C(SR)<$	$CH_2(SR)-C(Cl)<$	$CH_2(Cl)-C(SR)<$	$CH_2(SR)-C(Cl)<$
$CH_2{=}CHCH_3$	CH_3SCl	85	15	12	88
$CH_2{=}C(CH_3)_2$	CH_3SCl	80	20	17	83
$CH_2{=}CHCH(CH_3)_2$	CH_3SCl	94	6	10	90
$CH_2{=}CHC(CH_3)_3$	CH_3SCl	95	5	11	89
$CH_2{=}CHC_6H_5$	CH_3SCl	2	98		
$CH_2{=}CHCH_3$	C_6H_5SCl	68	32	15	85
$CH_2{=}CHCH(CH_3)_2$	C_6H_5SCl	87	13	15	85

[a] All sulfenyl chloride–olefin additions with the exception of 1-propene (−75°) were carried out at −20 to −25° using methylene chloride as a solvent. Distillation *in vacuo* provided samples which gave satisfactory elemental analyses. Some cases were further characterized by comparison with authentic samples. [b] The adduct ratio was calculated from the relative intensity of their characteristic nmr signals. Protons α to the chlorine appear *ca.* 1 ppm downfield to those α to sulfur.

tention.[1,2] Ionic electrophilic additions to double bonds have been thoroughly studied with 2,4-dinitrobenzenesulfenyl chloride, which is a convenient model reagent because of its outstanding stability. The *trans*-stereospecific addition[3-7] and other mechanistic details[8,9] observed with this reagent have led to the general postulate of an episulfonium ion intermediate for such reactions. The predominant adduct orientation from this sulfenyl chloride[10,11] as well as from 2-haloalkanesulfenyl chlorides[12,13] have been reported to be Markovnikov.

In contrast to this generally accepted adduct orientation, we have found that methane- and benzenesulfenyl chlorides add to a variety of terminal olefins to give anti-Markovnikov products in high selectivity. These initial adducts then rearrange to the Markovnikov-oriented products on standing at ambient temperatures (Table I).

It was felt that the rearrangement of the initial adducts made it necessary to reexamine the stereochemistry of such additions. This was particularly warranted since the previous support for the *trans* configuration of the adducts was indirect and primarily based on the specific case of 2,4-dinitrobenzenesulfenyl chloride. We have now confirmed exclusive *trans* addition by nmr analysis of both the norbornene and acenaphthalene adducts. In the case of the acenaphthalene adduct (I) the reported difference in the coupling constants of vicinal protons ($J_{1,2\text{-}cis} \sim 8$ cps; $J_{1,2\text{-}trans} \sim 2$ cps)[14] provided a useful tool for its stereochemical structure assignment. The diagnostic nmr parameters for the 2-*endo*-chloro-3-*exo*-phenylthionorbornane (Figure 1) are in good agreement with those of analogous examples.[15-17]

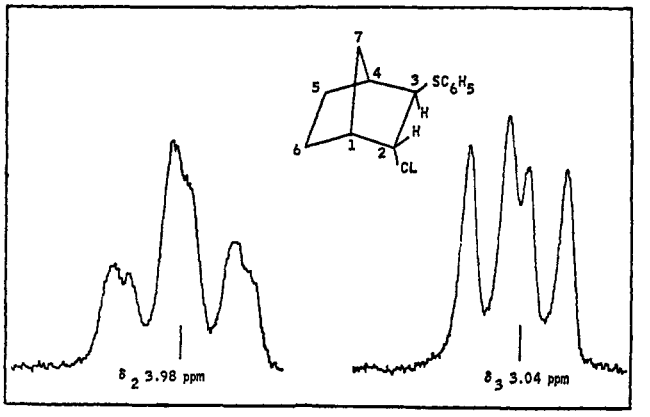
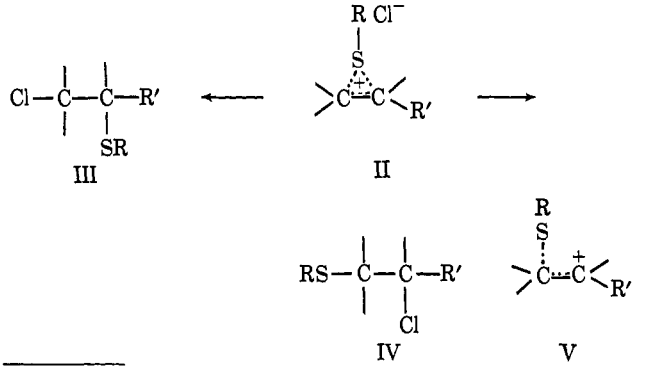
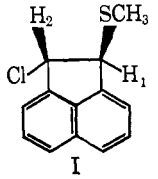


Figure 1. Partial nmr spectrum of 2-*endo*-chloro-3-*exo*-phenylthionorbornane. All spectra were determined in CCl_4 using TMS as an internal standard; chemical shifts are measured in ppm downfield from the standard. $J_{1,2} = 4.1$ cps, $J_{2,3} = 3.9$ cps, $J_{2,6\text{-}exo} = 1.0$ cps, $J_{3,4} = 0$, $J_{3,7\text{-}anti} = 2.6$ cps.

Thus, all the data are compatible with an episulfonium ion intermediate (II).[18] On the other hand, no evidence has been found for an attack at a single terminus and concommitant development of a carbonium ion as in structure V.





I

$\delta H_1 = 4.73$ ppm; $\delta H_2 = 5.60$ ppm; $J_{1,2} = 2.3$ cps

(1) N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp 375–396.
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(16) F. A. L. Anet, *Tetrahedron Letters*, 3399 (1964).
(17) J. I. Musher, *Mol. Phys.*, 6, 93 (1963).
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The subsequent ring opening of II by the chloride, however, cannot simply be predicted on the basis of the electronic effects underlying the Markovnikov rule. In the case of alkyl substituents apparently little or no partial charge is developed on the carbon atoms involved in intermediate II. Therefore, steric factors control the formation of products III. This is particularly surprising in view of the poor nucleophilicity of the chloride ion. With electronically more biased substrates, such as styrene, electronic effects become increasingly important in II, thus affording Markovnikov products IV.

Further data substantiating the above mechanistic conclusions, defining the scope of this reaction and the nature of the rearrangement, will be presented in a full paper.

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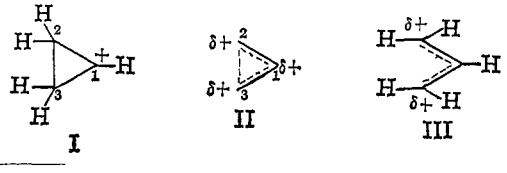
Steric and Electrocyclic Control of Cyclopropyl Tosylate Solvolysis Rates

Sir:

Carbonium ion reactions of cyclopropyl derivatives generally lead to allyl rather than to cyclopropyl products.[1,2] The cyclopropyl cation (I) must have a high propensity toward rearrangement to the more stable allyl cation (III). Despite the slow rate of acetolysis of cyclopropyl tosylate,[2] which masks the presence of anchimeric assistance,[3] it appears likely that the ionization and ring-opening processes are concerted.[3-5] The solvolysis transition state resembles II (or III) rather than I, with considerable charge delocalization to C-2 and C-3 and away from C-1.[4-6] Carbonium ion stabilizing substituents produce abnormally small rate enhancements when substituted for hydrogen at C-1 in cyclopropyl derivatives,[5,6] but substantial rate accelerations result from attachment at C-2 or C-3.[4,5]



I II III

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(2) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 73, 5034 (1951).

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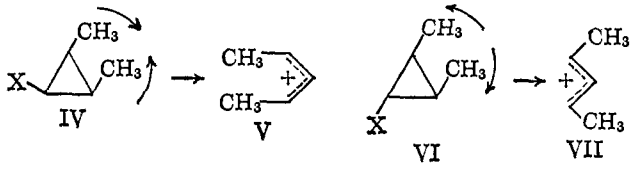
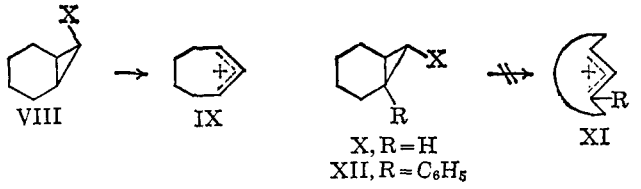
(6) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, 83, 2719 (1961).

Woodward and Hoffmann predicted that electrocyclic opening of cyclopropyl cation I to allyl cation III should be stereospecific and "disrotatory," *i.e.*, groups in I *cis* at C-2 and C-3 should rotate *toward* or *away from* one another in proceeding to III.[7] The direction of disrotatory opening should further depend on the stereochemical disposition of the leaving group, in the manner shown below,[7] as also has been suggested by DePuy.[5]



IV V VI VII

The implications of these predictions with regard to solvolysis rates of cyclopropyl derivatives are definite. *If ring opening and ionization are simultaneous*, VI should react faster than IV. In VI the *cis*-methyl groups would move apart, relieving strain, while in IV they would move closer together, increasing strain. *If ionization precedes ring opening and a cyclopropyl cation intermediate intervenes*, then there should be little difference in the solvolysis rates of IV and VI.



VIII IX X, R = H XII, R = C_6H_5 XI

Extension of these ideas to the bicyclic series leads to predictions the reverse of those in monocyclic systems. Compounds with *endo* configurations, as in the norcaryl derivative VIII, should react rapidly by a concerted mechanism because the *cis*-allylic configuration IX is favored in a ring structure. By contrast, *trans* opening (such as X to XI) is impossible, at least with rings with common size, and unassisted solvolysis through classical-type transition states might be anticipated for *exo* isomers X.

Experimental results partially verifying these predictions have been published recently.[5,8] DePuy and co-workers have found *trans*-2-phenylcyclopropyl tosylate to acetolyze 15 times faster than the *cis* isomer.[5] The norcaryl derivative XII was reported qualitatively to be very unreactive under the same conditions.[5] Cristol, Sequeira, and DePuy[8] showed that acetolysis of VIII (X = Cl) was at least 180 times faster than X (X = Cl). The rate of X (X = Cl) was too slow to be measured under these conditions, and no comparison could be made with cyclopropyl itself, for the acetolysis rate of cyclopropyl chloride was not determined.

Acetolysis of the corresponding cyclopropyl tosylates[9]

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(9) Cyclopropanols were prepared by the method of J. Paust and U. Schöllkopf (*Angew. Chem.*, 77, 262 (1965)) and were converted to tosylates by conventional procedure. Stereochemical assignments were made by analysis of the nmr spectra, taking particular advantage of the magnitude of the C*H*–C*H*OTs coupling constants: *cis*, *ca.* 6.5 cps; *trans*, *ca.* 2.5 cps.[5,8]