Table I. Pmr Data of Dialkylhalonium Ions[a]

Ion		CH_3X^+	$-CH_2X-^+-CHX-^+$	CH_3CX-^+	$-CH_2CX-^+$	CH_3CCX-^+
$CH_3ICH_3^+$	1	3.42				
$CH_3BrCH_3^+$	2	3.84				
$CH_3ClCH_3^+$	3	4.13				
$(CH_3CH_2)_2Br^+$	4		4.66	1.44		
$(CH_3CH_2)_2Cl^+$	5		4.72	1.54		
$(CH_3CH_2)_2I^+$	6		4.20	1.83		
$CH_3ICH_2CH_3^+$	7	3.28 (3)	4.23 (2)	1.76 (3)		
$CH_3BrCH_2CH_3^+$	8	3.60 (3)	4.64 (2)	1.44 (3)		
$CH_3ClCH_2CH_3^+$	9	3.90 (3)	4.64 (2)	1.51 (3)		
$[(CH_3)_2CH]_2Br^+$	10		5.39 (1)	1.50 (6)		
$[(CH_3)_2CH]_2Cl^+$	11		5.76 (1)	1.56 (6)		
$[(CH_3)_2CH]_2I^+$	12		5.29	1.72		
$CH_3ClCH(CH_3)_2^+$	13	4.03	5.44	1.56		
$[CH_3(CH_2)_2]_2I^+$	14		4.12 (2)		1.50 (2)	0.66 (3)
$[CH_3(CH_2)_2]_2Br^+$	15		4.48 (2)		1.70 (2)	0.73 (3)

[a] From TMS in an external capillary tube. Spectra were recorded at −60° in SO_2 solution at 60 MHz. Relative peak areas are shown in parentheses. Usual multiplicities and couplings for alkyl groups were observed. The central position of the complex multiplet or of the overlapping peaks is given.

of the monoethylhalonium ions originally formed and of increasing tendency for exchange. This is also the expected order of stability since the larger halogen atoms are more capable of localizing positive charge leading to a greater stability of the CH_3XEt^+ species and hence less exchange with excess EtX to yield diethylhalonium ions.

Temperature-dependent pmr spectra of excess *i*-PrBr with SbF_5 in SO_2 solution displays two sets of septets (δ 3.76, 4.66) and doublets (δ 1.08, 1.44) at −95°. As the temperature is raised these peaks begin to merge, and they coalesce to a single well-resolved septet (δ 4.55) and doublet (δ 1.28) at −40°. Changes in concentration of *i*-PrBr apparently do not alter the equilibrium indicating that *i*-PrBr is taking part in both forward and reverse equilibrium processes. The only change observed was the increase in intensity of the septet at δ 3.76 and doublet at δ 1.08, demonstrating that these signals are those of nonassociated *i*-PrBr. These data are consistent with an equilibrium between diisopropylbromonium ion (**10**) and *i*-PrBr. Similar results were

$$2(CH_3)_2CHBr + SbF_5\text{-}SO_2 \xrightarrow{SO_2} \underset{\mathbf{10}}{(CH_3)_2CH\overset{+}{B}rCH(CH_3)_2\ SbF_5Br^-}$$

$$(CH_3)_2CH\overset{+}{B}rCH(CH_3)_2 + (CH_3)_2CHBr \rightleftharpoons (CH_3)_2CH\overset{+}{B}rCH(CH_3)_2 + (CH_3)_2CHBr$$

obtained with *i*-PrCl; however, the equilibrium is apparently fast even at −90° and cannot be frozen out.

Isopropylhalonium ions **10**, **11**, and **12** are also formed from *n*-propyl chloride, bromide, and iodide in SbF_5–SO_2 and CH_3F–SbF_5–SO_2, with methylisopropylchloronium ion **13** being the only cross-product detected. The *n*-propyl → isopropyl rearrangement occurs to varying degree in the order Cl (~100%) > Br (~40%) > I (~2%). Characteristic spectra were obtained from di-*n*-propyliodonium ion **14** and bromonium ion **15** present in the *n*-PrI and *n*-PrBr solutions.

The observation of dialkylhalonium ion formation in alkyl halide–antimony pentafluoride systems raises the question of their involvement in Friedel–Crafts alkylations and isomerizations. Alkyl halide–Lewis acid halide complexes (or for that matter any carbonium ion) can obviously alkylate excess alkyl halides (other than fluorides) to form dialkylhalonium ions; 1:1 or 1:2 alkyl halide–Lewis acid complexes can give 2:1 or 2:2 dialkylhalonium ion complexes. The dialkylhalonium

$$R\text{—}Cl\text{---}R\}Cl\text{→}AlCl_3 \qquad R\text{—}Cl\text{---}R\}Cl\text{→}Al_2Cl_6$$

ions must be assumed to exchange rapidly under ordinary Friedel–Crafts conditions with excess alkyl halides and also to dissociate according to the equilibrium

$$\overset{\delta+}{R}\text{—}Cl\}\overset{\delta+}{R}\text{---}Cl\text{—}R \qquad R\text{—}X\text{—}\overset{+}{R}\}M_zX_y^- \rightleftharpoons RX + RX\text{→}M_zX_{y-1}$$

That dialkylhalonium ions can be alkylating agents was shown in experiments using solutions of dialkylhalonium fluoroantimonates in sulfur dioxide solution at −70° in the presence of excess alkyl halides with no "free" antimony pentafluoride being present in the systems.

Further work with a variety of weaker Lewis acids is in progress. $GaCl_3$ in excess methyl bromide, for example, in SO_2 solution at −80° shows the presence of dimethylbromonium ion **2**.

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(9) Postdoctoral Research Investigator.

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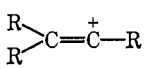
The Synthesis and Solvolysis of 1-Cyclopropyl-1-iodoethylene. Generation of an Unusually Stable Vinyl Cation

Sir:

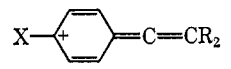
The increasing number of instances in which vinyl cations (general structure **1a**) are being suggested as intermediates in organic solution reactions[1] indicates

(1) For some recent examples, see (a) M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968); *Compt. Rend.*, **259**, 2251 (1964); **266**, 231 (1968); (b) M. Hanack and J. Häffner, *Tetrahedron Letters*, 2191 (1964); *Chem. Ber.*, **99**, 1077 (1966); M. Hanack and I. Herterich, *Tetrahedron Letters*, 3847 (1966); M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967); (c) R. Garry and R. Vessiere, *Bull. Soc. Chim. France*, 1542 (1968); (d) W. D. Closson and S. A. Roman, *J. Am. Chem. Soc.*, **88**, 6015 (1966); (e) H. R. Ward and P. Dwight Sherman, Jr., *ibid.*, **89**,

that the long-held belief in the relative instability of such species[2] is waning. However, these ions are normally generated *via* cyclization, deamination, and acetylene–protonation routes. In only a very few cases have vinyl cations been generated by solvolytic ionization of substituted ethylenes,[3] and in each of these cases an aromatic ring has been located at the ionization center so that structures such as **1b** can contribute to the stabilization of the cation generated.



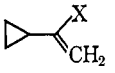
1a



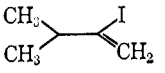
1b

We have now prepared 1-cyclopropyl-1-iodoethylene (**4**) and report its facile ionization to the "cyclopropylcarbinyl"-type[4] vinyl cation **6**. We believe this to be the first observation of SN1-type ionization of a vinyl halide which lacks aromatic substitution at the ionizing center, and our study provides some interesting information concerning cyclopropane ring delocalization, "homoallenyl" solvolytic reactions, and the properties of vinyl cations as rearrangement termini.

Treatment of the hydrazone **3** of cyclopropyl methyl ketone (**2**) with triethylamine and iodine in tetrahydrofuran[5] at 0° produces[6] a 20% yield of **4** in addition to unidentified, higher boiling materials. The pure iodide reacts immediately on contact with aqueous ethanolic silver nitrate at room temperature, precipitating silver iodide and producing cyclopropyl methyl ketone (**2**) as the predominant (>90%) organic product. In striking contrast, the analogous iodide **5**



4, X = I
7, X = $OCOCH_3$
8, X = $OSO_2C_7H_7$



5

(prepared in a similar fashion from isopropyl methyl ketone) is completely unreactive toward silver nitrate at room temperature and undergoes silver-catalyzed conversion to isopropyl methyl ketone only very slowly (~20% reaction in 36 hr) in a sealed tube at 150°.

Treatment of **4** with silver acetate in acetic acid rapidly gives the vinyl acetate **7** as the major product of the reaction (*vide infra*). Further, reaction of **4** with an excess of silver *p*-toluenesulfonate[7] in acetonitrile at room temperature produces the unusual vinyl *p*-toluenesulfonate **8** (17% yield of pure, white crystals isolated after two recrystallizations), indicating that the intermediate can be trapped even with the poorly nucleophilic *p*-toluenesulfonate anion.[8]

Careful product studies have been carried out on the silver acetate–acetic acid reaction; the product distribution is reported in Table I.

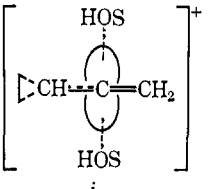
Table I. Products of the Reaction of 1-Cyclopropylvinyl Iodide (**4**) with Silver Acetate in Glacial Acetic Acid at 25°

Product	**7**	Cyclopropyl methyl ketone	2-Methylenecyclobutyl acetate	3,4-Pentadienyl acetate	Unidentified	Cyclopropylacetylene
% Formed	61.4	25.5[a]	1.5	2.3	0.5	8.7[b]

[a] Probably formed from **7** during work-up. [b] Y. M. Slobodin and I. N. Shokhor, *J. Gen. Chem. USSR*, **22**, 243 (1952).

Though silver(I) apparently accelerates the rate of ionization of **4**, it is not a necessary catalyst for the reaction. The iodide **4** is also converted to **2** in aqueous methanol buffered with triethylamine from 140 to 160°; the uncatalyzed ionization exhibits excellent first-order kinetics ($k = (1.93 \pm 0.02) \times 10^{-4}$ sec^{-1} at 150°) and is characterized by the following activation parameters: $\Delta H^{\pm} = 23.3$ kcal/mol, $\Delta S^{\pm} = -21.2$ eu. The rate is changed only slightly in going from 1 to 3 molar equiv of buffer, ruling out the intervention of a triethylamine addition–elimination pathway in the mechanism.

We feel that these results are most consistent with the intermediacy of cation **6**.[9] The fact that **6** feels no dramatic need to rearrange to the presumably stable allylic cyclobutyl ion **9** indicates that a fairly large degree of charge must be concentrated at the vinyl carbon, even though enough electron release from the cyclopropane ring occurs[10] in the ionization transition



i

1962 (1967); (f) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Am. Chem. Soc.*, **89**, 6993 (1967); (g) T. L. Jacobs and R. Macomber, *Tetrahedron Letters*, 4877 (1967); T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960); (h) R. C. Fahey and D.-J. Lee, *ibid.*, **90**, 2124 (1968), and earlier papers; (i) A. Nishimura, H. Kato, and M. Ohta, *ibid.*, **89**, 5083 (1967); (j) W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967); (k) J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *Tetrahedron Letters*, 5063 (1968); (l) M. Hanack, S. Bocher, K. Hummel, and V. Vött, *ibid.*, 4613 (1963) M. Hanack, V. Vött, and H. Ehrhardt, *ibid.*, 4617 (1968); (m) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *ibid.*, 4039 (1968); (n) G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968); (o) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966), and references cited there.

(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin "Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1956, p 141.

(3) (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) C. A. Grob, J. Csapilla, and G Cseh, *ibid.*, **47**, 1590 (1964); (c) S. J. Huang and M. V. Lessard, *J. Am. Chem. Soc.*, **90**, 2432 (1968); (d) L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7282 (1968).

(4) That cyclopropane rings stabilize adjacent cationic centers in the aliphatic series is well documented. For reviews, see (a) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967, Chapter 7; (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964); (c) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, 1963, Chapter 4.

(5) D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

(6) Satisfactory analytical and spectral data have been obtained on all new compounds reported.

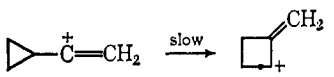
(7) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

(8) For a recent report of the synthesis and solvolysis of a number of other vinyl tosylates, see P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968).

(9) The structure of **6** as written is oversimplified. Our results clearly indicate that the electron deficiency at the vinyl carbon is relieved by electron release from the cyclopropane ring, and it is undoubtedly true that solvent molecules are closely associated with the cation and the transition state leading to its formation. A more complete representation of the structure of **6** may well be something like i.

(10) An estimate of the solvolysis rate enhancement attributable to conjugation of the cationic center with the cyclopropane ring is made very difficult by the apparent impossibility of causing model compounds such as **5** to undergo uncatalyzed, first-order ionization. Experiments are in progress to determine the relative rates and activation parameters of the silver-catalyzed ionizations of **4** and **5**, however, in order to obtain an estimate of the lower limit of rate enhancement present in the solvolysis of **4**.

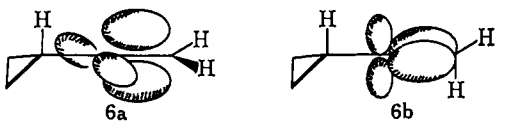
state to facilitate the reaction. Our observations fit nicely with those of Hanack and Häffner,[1b] Bly and Koock,[11] Bertrand and Santelli,[1a] and Jacobs and Macomber,[12] who have found that ionization of β-allenic sulfonates proceeds with anchimeric assistance



6 9

to give large amounts of products assumed to be derived from cyclopropylvinyl cations such as **6**.

It is most likely[13] that **6** has the "bisected" structure **6a** rather than its 90° rotamer **6b**, in order to allow for most favorable overlap between the empty p orbital and



6a 6b

the cyclopropane ring. Experiments directed toward establishing this structure and examining the linearity of the ion and its substituted derivatives are presently under way in our laboratory.[14]

(11) R. S. Bly and S. U. Koock, *J. Am. Chem. Soc.*, in press.
(12) (a) T. L. Jacobs and R. S. Macomber, paper in preparation; (b) R. S. Macomber, Ph.D. Dissertation, University of California at Los Angeles, 1968. We are indebted to Professors Bly and Jacobs for providing us with preprints of their papers in advance of publication.
(13) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).
(14) We are pleased to acknowledge the benefit of stimulating discussions with Professor Michael Hanack, who has kept us informed of parallel and independent work[15] being carried out in his laboratories, with Professor R. E. Ireland, who drew our attention to the vinyl iodide synthesis of Barton and coworkers,[5] and also with Professor J. D. Roberts. Thanks are also due to the Arthur A. Noyes fund for financial support.
(15) M. Hanack and T. Bässler, *J. Am. Chem. Soc.*, **91**, 2117 (1969).
(16) National Science Foundation Predoctoral Fellow, 1967–1969.

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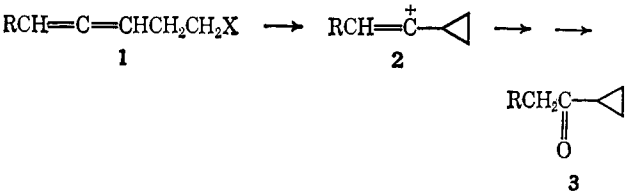
A Vinyl Cation. Solvolysis of 1-Cyclopropyl-1-chloroethylene

Sir:

Cyclizations with participation of allenic or acetylenic bonds to produce small rings have been studied intensively in recent years.[1] The facile solvolytic isomerization of some homoallenyl derivatives (**1**) to produce alkyl cyclopropyl ketones (**3**) offers a hint not only that the ground state is destabilized[2] but also that the intermediate vinyl cation (**2**) must be considerably stabilized by the neighboring cyclopropane ring.[3]

(1) M. Hanack and J. Häffner, *Tetrahedron Letters*, 2131 (1964); M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964); M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Letters*, 875 (1965); M. Hanack and I. Herterich, *ibid.*, 3847 (1966); M. Hanack and J. Häffner, *Chem. Ber.*, **99**, 1077 (1966); M. Hanack, I. Herterich, and V. Vött, *Tetrahedron Letters*, 3871 (1967); M. Bertrand and M. Santelli, *Compt. Rend.*, **266**, 231 (1968); *Chem. Commun.*, 718 (1968); M. Hanack, V. Vött, and H. Ehrhardt, *Tetrahedron Letters*, 4617 (1968); M. Hanack, S. Bocher, K. Hummel, and V. Vött, *ibid.*, 4613 (1968).
(2) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Am. Chem. Soc.*, **89**, 6993 (1967).
(3) *Cf.* M. Hanack and H.-J. Schneider, *Angew. Chem.*, **79**, 709 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

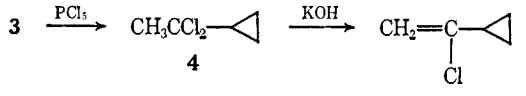
These conclusions are supported by the strongly accelerated solvolysis rates.



1 2 3

It thus became important to attempt the *direct* generation of vinyl cations (**2**) through solvolysis of suitable cyclopropylethylene derivatives and to determine whether they—in contrast to other vinyl derivatives[4]—possess particularly fast reaction rates. The rate constants, and also the product composition of these reactions, should provide qualitative data about the stability of the vinyl cation **2**.

We now report on the synthesis and solvolysis of 1-cyclopropyl-1-chloroethylene (**5**). Methyl cyclopropyl ketone (**3**, R = H) was converted to the dichloride **4** with phosphorus pentachloride.[5] When **4** was added dropwise to a solution of KOH in triethylene glycol (90°), a mixture of 1-cyclopropyl-1-chloroethylene (**5**), cyclopropylacetylene, and methylvinylacetylene together with unreacted **4** was obtained, after distillation from the reaction vessel under reduced pressure. The yield of **5** was 60%, as shown by gas

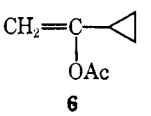


4 5

chromatographic analysis; nmr: τ 4.85, narrow multiplet (1 H), 4.95, narrow multiplet (1 H), 8.1–8.6, broad five-line pattern (1 H), 9.2–9.4, multiplet (4 H); mass spectrum: parent peak at *m/e* 104/102 (1:3), base peak at 67, other major peaks at 41, 39.

1-Cyclopropyl-1-chloroethylene (**5**) reacts immediately at room temperature with $AgClO_4$ in unbuffered acetic acid. Gas chromatographic analysis of the products showed them to be 80% cyclopropyl methyl ketone (**3**, R = H), 15% cyclopropylacetylene, 4% of one product, and less than 1% each of three further products, none of which has yet been identified.

When **5** was treated with silver perchlorate buffered with sodium acetate at 25° in dry acetic acid, 1-cyclopropylethenyl acetate (**6**) was the main product and was formed within a very few minutes. By compari-



6

son, under the same conditions and also at elevated temperatures 2-chloro-3,3-dimethyl-1-butene was completely unreactive to silver salts.

(4) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter 8. *Cf.* also C. A. Grob and C. Cseh, *Helv. Chim. Acta*, 47, 196 (1964); C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, 47, 1590 (1964).
(5) Y. M. Slobodin and I. N. Shokhor, *J. Gen. Chem. USSR*, **22**, 243 (1952). We were unable to reproduce these results unless the temperature was kept below 0° and highly purified PCl_5 was employed. Without these precautions quantitative opening of the cyclopropane ring occurs.