Effect of 2-Substitution on the Rearrangement of 1-Cyclopropylvinyl Cations

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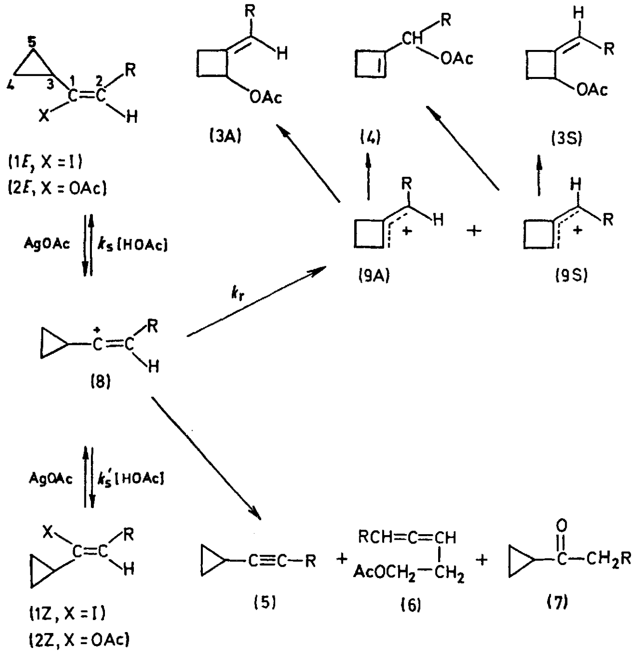
Summary 2-Substitution in 1-cyclopropylvinyl cations produces a steric effect on cation generation and solvent trapping, but an electronic charge-stabilizing effect on cyclopropyl-to-cyclobutyl rearrangement.

We have found that, in contrast to their effect on the ionization step,[1,2] 2-substituents in 1-cyclopropylvinyl cations [(**8**) Scheme] have a profound influence on the reactions which these cations undergo following generation. Our observations are of interest in view of the apparent reluctance of remote conjugating substituents to interact with developing charged centres in a number of other ionization reactions which have been discussed recently.[3]



Scheme

We report here rate (Table 1) and product distribution (Scheme; Table 2) data on the silver-catalysed ionizations of 1-cyclopropylvinyl iodides (**1*E*** and (**1*Z***) (R = cyclopropyl and 1-ethylpropyl†) and compare these systems with those discussed previously[2,4,5] (R = Me and R = H). Although there is some scatter in the data, ionization of all the substrates listed in Table 1 using silver acetate in acetic acid gave (somewhat surprisingly[6]) reasonable pseudo-first-order rate dependencies. The differences in ionization rates are only moderate; the fastest rates are observed in the isomers having the alkyl groups in a *cis* relationship.

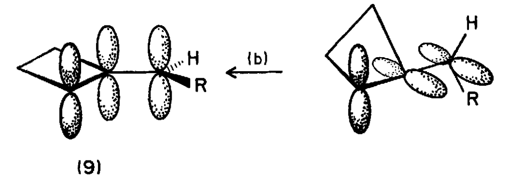


Figure. *Molecular motions involved in the rearrangement of the 1-cyclopropylvinyl cation* (**8**) *into the 2-methylenecyclobutyl cation* (**9**).

Comparison of the rate data and the (**2*E***)/(**2*Z***) product ratios indicates that the ionization velocities are influenced by both ground- and transition-state effects. If we may consider reaction of acetate with cation (**8**) to be the approximate microscopic reverse of ionization, the near equivalence of products (**2*Z***) and (**2*E***) (R = Me) suggests that the accelerated ionization of (**1*E***) (R = Me) is due to relief of nonbonded interactions between the methyl and

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† Satisfactory analytical data were obtained on all new compounds. Stereochemistries of starting materials were determined as described in ref. 5; stereochemistries of products were determined by n.m.r. with the aid of lanthanide shift reagents. Details will be reported in a full paper.

TABLE 1. *Rates on silver-catalysed ionization of 2-substituted 1-cyclopropylvinyl iodides at 25° in acetic acid*

R	Stereochem	Rate constant[a] (10^5 k, s^{-1})	k_{rel}	k_E/k_Z
Me	*E*	210 ± 2	27	
Me	*Z*	20·3 ± 2	2·6	10·3
Cyclopropyl ..	*E*	99 ± 10	12·5	
Cyclopropyl ..	*Z*	7·9 ± 0·2	1·0	12·5
1-ethylpropyl ..	*E*	867 ± 20	110	
1-ethylpropyl ..	*Z*	25 ± 3	3·2	34·7

[a] Pseudo-first-order rate constants under heterogeneous conditions with excess of silver acetate. Rate constants were measured by g.l.c. using digital integration; yields of all products were >95% in all cases.

TABLE 2. *Products formed on silver-catalysed ionization of 2-substituted 1-cyclopropylvinyl halides in acetic acid at 25°.*

		Products[c,d] %								
R	Stereochem	**(2*Z*)**	**(2*E*)**	**(3*S*)**	**(3*A*)**	**(4)**	**(5)**	**(6)**	P_4/P_3[e]	Ref.
H		97·0[a]		1·58		0·18	b	1·33	0·018	2
Me	*E*	32·6	33·1	2·71	8·76	3·91	17·7	1·17	0·18	5 this work
Me	*Z*	30·2	36·6	2·94	8·00	3·52	17·5	1·29	0·17	”
C_3H_5	*E*	17·6	24·9	2·70	13·5	30·5	9·78	0·98	0·89	this work
C_3H_5	*Z*	18·8	27·5	3·32	12·6	27·1	10·2	0·53	0·76	”
C_5H_{11}	*E*	11·8	54·5	2·80	3·37	<0·02	26·0	1·52	0·067	”
C_5H_{11}	*Z*	12·2	52·6	3·75	3·07	<0·02	26·6	1·82	0·075	”

[a] Includes 17·3% cyclopropyl methylketone. [b] The amount of cyclopropylacetylene formed was difficult to determine accurately due probably to volatility and silver salt formation. The P_4/P_3 ratio given is therefore a maximum value; the true ratio is undoubtedly even smaller. [c] Product stabilities were established in the case of major components by resubjection to the reaction conditions and in the case of minor components by following the product distribution during the course of reaction. [d] Product distributions determined under homogeneous and heterogeneous conditions were essentially identical (±1% in most cases). [e] [(**3*A***) + (**3*S***) + (**4**)]/[(**2*Z***) + (**2*E***) + (**5**)].

cyclopropyl groups as C-1 'linearizes'[7] during ionization. However, as R gets bulkier, the (**2*E***)/(**2*Z***) ratio increases, indicating that the '*Z*' transition state can also be destabilized by nucleophile-R interactions when R is large enough. Thus for (**1**) (R = 1-ethylpropyl), some of the difference in rate between the *E* and *Z* isomers may reflect steric hindrance to attack by the silver species in the *Z* isomer.

The product variations caused by changing the vinyl substituents seem to be unrelated to the ionization rate effects, providing further evidence that ionization and product formation occur in discrete steps.[8] Most striking, however, is the dependence of the amount of cyclopropyl-to-cyclobutyl rearrangement on substitution. The P_4/P_3 ratio increases from 0·018 to *ca.* 0·2 on going from R = H to R = Me and in the cyclopropyl case, the percentage of rearranged cyclobutyl product again jumps dramatically to *ca.* 45% of the mixture (P_3/P_4 ratio = *ca.* 0·85). In (**1**) (R = 1-ethylpropyl), the ratio drops back to *ca.* 0·07. We believe that a decrease in the rate of solvent-trapping of cation (**8**) due to steric hindrance by the R group does not explain these observations, since (**1**) (R = 1-ethylpropyl) rearranges less readily than does (**1**) (R = cyclopropyl). We are therefore left with an electronic effect as the most reasonable explanation; the ability of the remote cyclopropyl group to stabilize positive charge is apparently being felt in the rearrangement transition state. This is especially remarkable when one considers that in the most 'naive' molecular motion for rearranging cation (**8**) (Figure), a new orbital develops at C-3 which is orthogonal to the double bond π-orbitals,[2] and therefore cannot benefit from overlap with the R group. In order to explain our observations, therefore, motions (a) and (b) in the Figure must be occurring simultaneously (at least in the substituted systems), and a fully developed allylic cation has probably been generated by the time rearrangement is complete.

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[1] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, **90**, 7282; C. A. Grob and R. Spaar, *Helv. Chim. Acta*, 1970, **53**, 2119; Z. Rappoport and J. Kaspi, *J. Amer. Chem. Soc.*, 1970, **92**, 3220.

[2] R. G. Bergman and S. A. Sherrod, *J. Amer. Chem. Soc.*, 1971, **93**, 1925.

[3] W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **94**, 133; C. F. Wilcox jun., and H. D. Banks, *ibid*, 8231, 8232.

[4] R. G. Bergman and D. R. Kelsey, *J. Amer. Chem. Soc.*, 1971, **93**, 1941.

[5] R. G. Bergman,and D. R. Kelsey, *J. Amer. Chem. Soc.*, 1971, **93**, 1953.

[6] D. N. Kevill and V. M. Horvath, *Tetrahedron Letters*, 1971, 711; D. J. Pasto and J. P. Sevenair, *J. Amer. Chem. Soc.*, 1971, **93**, 711; G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, 1960, **82**, 704; E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1937, 1236.

[7] W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, 1971, **91**, 1513; Z. Rappoport and M. Atida, *J.C.S. Perkin II*, 1972, 2316.

[8] M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209.