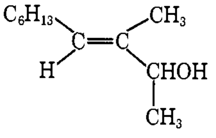

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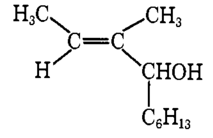

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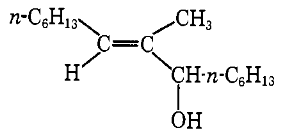

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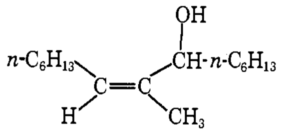

16

with the unsaturated secondary alcohol formed by the carbonyl addition of hexyllithium to the aldehyde **7** which was derived as outlined above.[17] In this instance it would seem that elimination from intermediate racemic β,β'-dioxido phosphonium ion can follow the two possible directional modes if higher temperatures (0–20°) are used in the last step of the reaction, since under these conditions **15** and **16** are produced in a ratio of 3 to 1.

We have also studied the alkylation of β-oxido phosphonium ylides as a possible stereospecific route to trisubstituted olefins. However, we find that this reaction fails completely with most alkyl halides and proceeds moderately well only with methyl iodide. In addition, the alkylation is *not stereospecific* (*cf.* ref 4) as is shown by the reaction of **4** with trideuteriomethyl iodide which produces a mixture of *cis* and *trans* isomers of 2-trideuteriomethyl-2-nonene (50% yield) in ratios of 1:1 to 3:1 depending on reaction conditions.[18]

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[17] The nmr spectrum of the major isomer (**15**) (in CCl_4) manifested peaks due to olefinic proton, the proton of the –CH–O unit, and the olefinic methyl group at 5.29, 4.87, and 1.55 ppm, respectively, whereas the corresponding protons in the minor isomer (**16**) (in CCl_4) exhibited peaks at 5.14, *ca.* 4.47, and 1.62 ppm, respectively.

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Kinetically Linear Vinyl Cations in the Solvolysis of Stereoisomeric 1-Iodo-1-cyclopropylpropenes

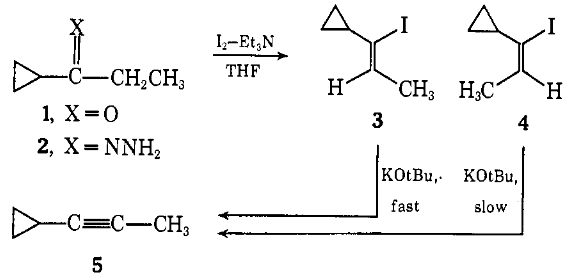
Sir:

Strong evidence now exists that vinyl cations intervene as discrete intermediates in the solvolysis of certain ethylenic derivatives.[1] Despite active recent interest in such reactions, however, a fundamental problem has remained unsolved—the stereochemistry of SN1 substitution at the vinyl center. This has been due in many cases to an inability to synthesize or separate stereoisomers of starting sulfonates, or to the fact that stereochemically distinct enol products are often rapidly converted to ketones in aqueous media.[1]

Ionization of appropriately substituted 1-cyclopropylvinyl halides[1a] provides a system ideally suited to investigation of this stereochemical question. We now report a study of such an ionization which shows that in at least this case, vinyl halides undergo silver-catalyzed substitution with complete randomization of stereochemistry. Our study provides further evidence that vinyl cations intervene in the ionization of both 1-cyclopropyl-1-haloethylenes and "homoallenic" derivatives, and that the vinyl cation intermediates attain an effectively linear structure before they are trapped by solvent acetic acid at room temperature.

Treatment of the hydrazone (**2**) of cyclopropyl ethyl ketone[2a,b] (**1**) with iodine and triethylamine (dried over NaOH and distilled from phenyl isocyanate) in tetrahydrofuran at room temperature[2c] produces compounds **3** and **4** (ratio 62:38) in 40% yield. These materials are separable by preparative vapor chromatography (vpc) and were shown to have the gross structure 1-iodo-1-cyclopropylpropene on the basis of spectral and analytical data. That the major product (**3**) is the *trans* isomer (and the minor product, **4**, its *cis* relative) was indicated by a downfield shift of the vinyl hydrogen signal of **4** in the nmr relative to **3** (**3**, δ 5.62 ppm; **4**, δ 6.25 ppm). The stereochemical assignments were confirmed by the observation that **3** reacts at least 10 times faster than **4** with KO-t-Bu in DMSO at room temperature[3] to produce cyclopropylmethylacetylene (**5**).

Scheme I



Ionization of *trans*-iodide **3** proceeded rapidly at room temperature when carried out in silver acetate–acetic acid. The mixture of products produced (>95% yield) contained the components illustrated in Scheme II and listed in Table I. Analytical vpc of this mixture was carried out using two 12 ft × $^{1}/_{8}$ in. columns, one packed with 20% Carbowax 20M on Chromosorb P and the other 15% tris-β-(cyanoethoxy)propane (TCEP) on Chromosorb W. Every one of the solvolysis products was obtained in pure form by preparative gas chromatography on a 10 ft × $^{1}/_{4}$ in. diethylene glycol succinate (DEGS) column (followed in some cases by single or double chromatography on 10 ft × $^{1}/_{4}$ in. 20% TCEP) and identified by spectral and analytical techniques.

Ionization of *cis*-iodide **4** under identical conditions gave a distribution of products (Table I) essentially iden-

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[1] (a) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969); (b) M. Hanack and T. Bässler, *ibid.*, **91**, 2117 (1969); (c) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (d) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969); (e) L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7282 (1968); (f) P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968); (g) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, **1439** (1969); (h) W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967); (i) G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968); (j) Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, **91**, 5246 (1969); (k) P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969).

[2] (a) M. Julia, S. Julia, and S.-Y. Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961); (b) V. A. Slabey and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 1473 (1952); (c) D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962); (d) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[3] *trans* elimination of vinyl halides under E2 conditions has been shown to occur more rapidly than *cis* elimination in a number of cases. See, for example, G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **4**, 49 (1965).

Scheme II

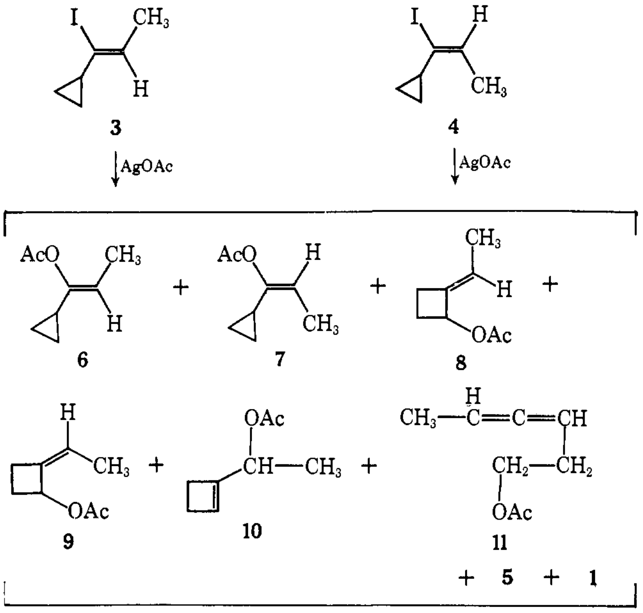


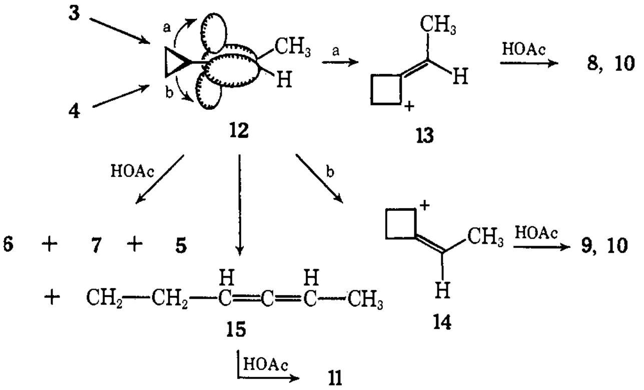
Table I. Products Formed in the Reaction of Stereoisomeric 1-Cyclopropyl-1-iodopropenes with Silver Acetate in Acetic Acid at 25°

Starting material and conditions	Products (%)[a,e]							
	1	**5**	**6**	**7**	**8**	**9**	**10**	**11**
3, AgOAc, HOAc[b]	1.2	16.2	31.4	36.2	3.1	8.0	3.4	0.5
4, AgOAc, HOAc[b]	1.0	17.3	32.1	33.5	2.8	8.9	3.9	0.5
3, AgOAc, HOAc[c]	1.3	20.1	30.3	33.5	3.0	9.0	2.3	0.5
4, AgOAc, HOAc[c]	0.4	16.6	33.5	31.2	3.2	10.3	4.3	0.5
3, AgOAc, HOAc[d]	2.6	19.2	29.7	34.3	2.9	7.4	3.5	0.5
4, AgOAc, HOAc[d]	0.5	18.7	33.7	31.3	2.9	8.7	3.7	0.5

[a] Error in the product percentages (based on repetitive runs and repetitive vpc injections in the same run) is *ca.* ±2 absolute per cent for the large peaks and ±1 absolute per cent for the minor peaks. [b] Excess silver acetate present (heterogeneous conditions). [c] Carried out under conditions of high dilution, with all AgOAc dissolved (homogeneous conditions). [d] 0.4 *M* NaOAc present in solution. [e] Product percentages were determined by digital-readout disk integration of vapor phase chromatographic peaks and are corrected for differential detector response in the case of the major products (**5**, **6**, and **7**).

tical within the limits of experimental error with that produced from its *trans* isomer **3**.[4] Furthermore, the product distributions did not change when the ionization was carried out under homogeneous or heterogeneous conditions, and also was not affected by the presence of sodium acetate in solution. Appropriate control experiments demonstrated that the major products were stable to the reaction conditions. That the minor products were also stable was indicated by the fact that the product distribution was determined to be the same at 31, 65, and 100% reaction and after long exposure of the reaction mixture to AgOAc–HOAc–AgI.

It is clear from these observations that the products formed from both **3** and **4** arise from the same set of intermediates. The most likely structure for the initial intermediate is the linear vinyl cation **12**, which rearranges in competition with solvent trapping to both the allylic ions **13** and **14** and to a small extent to the allenic ion **15**.[5]



As was observed in the case of the parent cyclopropyl vinyl cation,[1a] there is apparently only a weak driving force for rearrangement of **12** to **13** or **14**. This is probably due both to the cyclopropyl stabilization of **12**, as well as to poor overlap of the developing p orbital with the double bond orbitals in the rearrangement transition state.

It is significant that **4** reacts at least 9.5 times more rapidly with AgOAc than does **3**, a preference exactly opposite to that observed in the (presumably E2) reaction of these iodides with KOtBu. It is therefore very unlikely that the silver-catalyzed reaction proceeds by an E2-type mechanism with solvent acting as base.[4] Furthermore, the AgOAc rate difference provides additional evidence that **4** goes directly to a linear vinyl cation upon ionization; we feel that acceleration of **4** is due at least partially to relief of steric interaction between the cyclopropyl ring and methyl group as the ionizing center approaches sp hybridization. The difference in ground-state energies of **3** and **4** implied by this rationalization is supported by equilibration studies in AgI–HOAc, which give a **3**:**4** equilibrium constant of *ca.* 4.0.[6]

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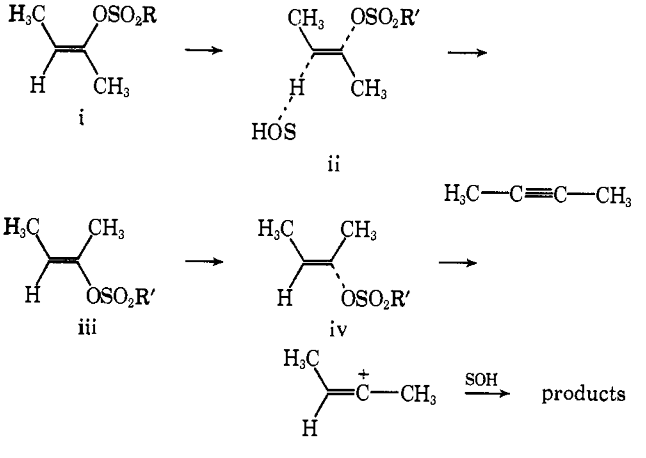
(4) These observations contrast with those of Peterson and Indelicato[1k] and Stang and Summerville,[1c] who have found that simple *trans*-vinyl sulfonates (*e.g.*, i) probably ionize *via* E2-like transition states (ii), whereas ionization of their *cis* isomers (iii) appears to involve much less C–H bond breaking (iv).



(5) Similarities in product distribution provide confirmatory evidence for the intervention of vinyl cations in the solvolysis of homoallenic sulfonates. *Cf.* (a) T. L. Jacobs and R. S. Macomber, *J. Amer. Chem. Soc.*, **91**, 4824 (1969); (b) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969); (c) M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2511, 2515 (1969).

(6) The rapid ionization rate of **4**, however, poses the possibility that **3** might produce products by prior isomerization to **4**, followed by rapid reaction of **4** with AgOAc. However, knowledge of the $3 \rightleftharpoons 4$ equilibrium constant and the product distribution from the direct ionization of **4** allows one to estimate the amount of products produced by prior isomerization of **3** to **4** and the amount produced directly by reaction of silver acetate with **3**. This calculation shows that at most 14% of the products from **3** could have arisen by the prior isomerization

Vinyl anions normally isomerize very slowly, even at room temperature or above,[7] whereas the corresponding radicals interconvert at a measurable rate at −78° [8,9] Extrapolating to the cationic case, vinyl cations might be expected to be linear or very rapidly equilibrating, a judgment in accord with theoretical calculations[10] and with the experimental observations reported here.[11,13]

Acknowledgments. We are grateful to the National Institutes of Health (Grant No. GM 16231-01) and the Arthur A. Noyes Fund for partial support of this work.

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route. Another possibility is that **3** and **4** produce the same products because they each undergo addition of HOAc followed by elimination of HI. This is rendered very unlikely by the observation that the vinyl acetate product formed from cyclopropyl vinyl iodide[1a] in AgOAc–DOAc contains *no* deuterium by nmr, ir, and mass spectral analysis (unpublished results of S. A. Sherrod and R. G. Bergman).

(7) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 130–135; (b) D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5765 (1966); (c) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967).

(8) (a) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); (b) R. M. Kopchik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90**, 6733 (1968); (c) L. A. Singer and N. P. Kong, *ibid.*, **89**, 6805 (1967); (d) R. C. Newman, Jr., and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).

(9) For a theoretical calculation of the barriers to inversion in vinyl radicals and anions, see M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, **91**, 3654 (1969).

(10) (a) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968); (b) H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969); (c) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968); (d) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (e) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).

(11) In our opinion, the less likely alternative is that the vinyl cation **12** is in fact a rapidly interconverting mixture of two bent ions. However, if the ions are bent, and they react with acetic acid at a diffusion-controlled rate[12] ($k \cong 10^9$ l./(mol sec)), a steady-state treatment indicates that identical product distributions can only arise from **3** and **4** if the rate constant for interconversion of "bent" stereoisomers of **12** is of the order of 10^{11} sec^{-1} or larger.

(12) S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965).

(13) Note Added in Proof. After this communication was submitted for publication, a study of the stereochemistry of SN1 substitution of 1,2-dianisyl-2-phenylvinyl halides was reported: Z. Rappoport, and Y. Apeloig, *ibid.*, **91**, 6734 (1969). The product stereochemistry is randomized, as is observed in our system.

(14) National Science Foundation Predoctoral Fellow, 1968–present.

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Free Radical Formation during Ozonation of a Hindered Olefin

Sir:

Although radicals are often produced from homolytic cleavages of ozone adducts[1] or insertion compounds[2] of certain saturated organic substances, no radical has heretofore been characterized or observed, to our knowledge, as a primary product of ozonation of an olefin. We wish now to report evidence for a free radical as an initial and major product of the ozonation of trimesitylvinyl alcohol (I).

Reaction of 10 mmol of I in 150 ml of 3:1 methylene chloride–methanol with 10 mmol of ozone in a nitrogen stream at −78° produced a black solution which, after being swept with nitrogen, exhibited a strong epr signal (broad singlet, 7–8 G in width, with a *g* value of 2.004 in methylene chloride–methanol, methylene chloride, or pentane). Upon reaching room temperature the reaction mixture lost its color and epr signal. The recovery of I was 58–60%. When the ozonation was carried out in pentane and the resulting solution was evaporated at −55° (0.5 mm), a purple solid was obtained, which appeared to be a mixture of the radical and I. When the solid was redissolved, an identical epr signal as before was observed. A carbon tetrachloride solution of the radical was stable for 1–2 days. The radical cannot be generated from solution of I by treatment with oxygen.

We assign structure III to the radical, based on the following evidence. When the ozonation in CH_2Cl_2–CH_3OH was repeated and hydroquinone (1 mol equiv) was added to the −78° reaction mixture, the color immediately disappeared and a 63% recovery of I was made. The ozonation was again repeated and 1.0 mol equiv of galvinoxyl, an efficient radical scavenger,[3] was added. At −35° the color and epr signals of both radicals disappeared, leaving a yellow solution. Less than a 10% recovery of I was obtained. Galvinoxyl was converted to hydrogalvinoxyl (mp 155–156°, ir)[4] and various other, probably coupling, products. Galvinoxyl was shown not to react with a solution of I in methylene chloride–methanol at −35°; at room temperature the galvinoxyl color slowly faded to yellow during a 1-day period.

These experiments show that the radical was III and was present in the −78° ozonation reaction mixture to the extent of at least 50%. At higher temperatures it readily abstracts hydrogen from its environment and reverts back to I; this occurs at −78° in the presence of hydroquinone. Addition of galvinoxyl, however, destroys III, as evidenced by the lower recovery of I. The radical III also reacts with ozone. Upon treating I with 3 mol equiv of ozone in methylene chloride–methanol at −78°, the color of the radical III disappeared; the products, however, have so far been intractable.

Further evidence for structure III for the radical is, first, that oxidation of I with sodium hypochlorite produced the same radical, as evidenced by an identical epr signal (see above). Sodium hypochlorite oxidation of 2,2-dimesitylvinyl alcohol gives a compound[5] which we have shown to have structure X [ir carbonyl band at 1720 cm^{-1}; nmr, peaks at τ 0.24 (s, aldehydic proton), 3.98 (s, olefinic proton), 3.3–3.45 (aromatic protons), 7.75–8.2 (methyl protons)], a dimer of radical IX. By analogy the radical from I should be III. Second, radical III absorbed in the same uv region (λ_{max} 280) as the original vinyl alcohol (I) but with a higher extinction coefficient, indicating a similar structure. Also, the ir spectrum of the solid mixture of the radical and I was nearly identical with that of I. Third, from the reaction mixture utilizing 1 mol equiv of ozone a 2–3% yield of a colorless compound assigned structure VIII was isolated [mp 158–159° (ethanol); *Anal.* C, H agrees with $C_{29}H_{32}O$; mol wt 396.2466 (high-resolution mass spectroscopy); ir, no hydroxyl or carbonyl absorption, ether band at 1100 cm^{-1}; nmr (all singlets), τ 3.28 (4 protons each), 3.36 (1 proton), 7.61, 7.68, 8.10 (3 protons each), 7.77, 7.97, 8.03 (6 protons each)]. The route to VIII is suggested as VI → VII → VIII (see Scheme I).

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(1) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

(2) H. M. White and P. S. Bailey, *ibid.*, **30**, 3037 (1965).

(3) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

(4) G. M. Coppinger, *ibid.*, **79**, 501 (1957).

(5) R. C. Fuson, P. L. Southwick, and S. P. Rowland, *ibid.*, **66**, 1109 (1944).