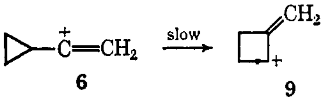
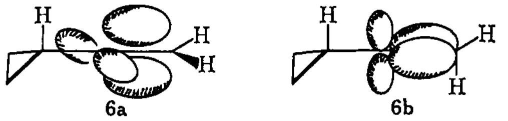
state to facilitate the reaction. Our observations fit nicely with those of Hanack and Häffner,[1b] Bly and Koock,[11] Bertrand and Santelli,[1a] and Jacobs and Macomber,[12] who have found that ionization of β-allenic sulfonates proceeds with anchimeric assistance



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]

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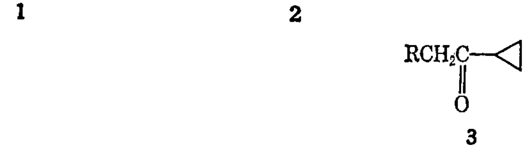
A Vinyl Cation. Solvolysis of 1-Cyclopropyl-1-chloroethylene

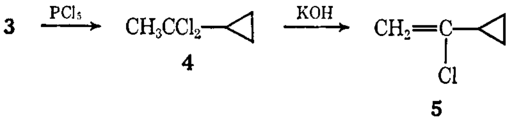
Sir:

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] These conclusions are supported by the strongly accelerated solvolysis rates.



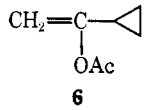
It thus became important to attempt the *direct* generation of vinyl cations (**2**) through solvolysis of suitable cyclopropylethylene derivatives and to determine whether they—in contrast to other vinyl derivatives[4]—possess particularly fast reaction rates. The rate constants, and also the product 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 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 comparison, under the same conditions and also at elevated temperatures 2-chloro-3,3-dimethyl-1-butene was completely unreactive to silver salts.



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[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).

[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.

In aqueous methanol buffered with triethylamine and in the absence of silver salts, the chloride **5** was also converted predominately to ketone **3** (R = H). The first-order rate constant for the reaction (k_{150}) was 2×10^{-5} sec^{-1}. This constant was invariant with increasing concentration of trimethylamine (up to a threefold excess).

It is, of course, possible that the accelerated rate of solvolysis of **5** is the result of complex formation between **5** and silver ion, and we are now studying this possibility. The complete absence of any observable reaction between Ag^+ and 2-chloro-3,3-dimethyl-1-butene, however, is evidence against a specific silver ion catalysis. We therefore interpret the foregoing observations, at present, in terms of the formation of an intermediate vinyl cation, **2**, which is stabilized through charge delocalization by the neighboring cyclopropane ring.[3] This interpretation is supported by the nonrearranging tendency of the intermediate, which leads to products which still possess the cyclopropane ring (*e.g.*, **3**, R = H, 1-cyclopropylethenyl acetate (**6**), and cyclopropylacetylene).

Further studies on cyclopropylethenyl derivatives with particular reference to the effect of ring substituents are now under way.

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Received February 12, 1969

The Optical Stability of Asymmetric Silyl Radicals

Sir:

Recent studies in these laboratories suggest that the photolyses of certain acylsilanes in nonpolar solvents involve Norrish type I cleavage of the acyl–silicon bond and the formation of radicals. Particularly compelling evidence for the intermediacy of silyl radicals[1] and a radical mechanism are the results of photolyses[2] under nitrogen in Pyrex glassware of solutions of acetyltriphenylsilane in carbon tetrachloride, in which triphenylchlorosilane (88%), acetyl chloride (45%), 1,1,1-trichloropropanone (15%), and hexachloroethane (45% based on the formation of 2 mol of $\cdot CCl_3$ radical/mol of acetylsilane) were isolated. Photolysis of acetyltriphenylgermane gave similar products. A reasonable mechanism for the formation of these products is as follows.

$$Ph_3SiCOCH_3 \longrightarrow Ph_3Si\cdot + CH_3CO\cdot$$

$$Ph_3Si\cdot + ClCCl_3 \longrightarrow Ph_3SiCl + \cdot CCl_3$$

$$CH_3CO\cdot + ClCCl_3 \longrightarrow CH_3COCl + \cdot CCl_3$$

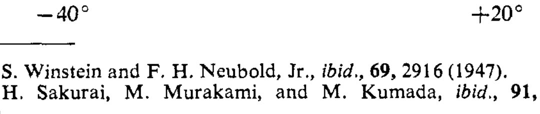
$$CH_3CO\cdot + \cdot CCl_3 \longrightarrow CH_3COCCl_3$$

$$2\cdot CCl_3 \longrightarrow Cl_3CCCl_3$$

The abstraction of chlorine from carbon tetrachloride by acyl radicals has been observed previously[4] as has the abstraction of halogen by silyl radicals.[1,5] Since the above reaction occurred quite rapidly (1 g of acetyltriphenylsilane was completely photolyzed in less than 40 min) it is probable that the radical intermediates are formed in high concentration, so it is not surprising that the coupling processes represented by the last two equations occur to a significant extent.

Because of the possible intermediacy of silyl radicals it seemed of interest to photolyze optically active acylsilanes in carbon tetrachloride since this could result in the generation of chiral silyl radicals. Photolysis of (−)-acetyl-1-naphthylphenylmethylsilane[6] in carbon tetrachloride led to the rapid disappearance of ketone and the isolation of 69% of 1-naphthylphenylmethylchlorosilane, bp 160° (0.5 mm) (Kugelrohr), which had low positive rotations corresponding to optical purities of about 10–20%,[7] together with acetyl chloride, 1,1,1-trichloropropanone, and hexachloroethane. This result suggested that if silyl radicals were being formed they were retaining at least some asymmetry prior to the abstraction of chlorine from the solvent, as proposed recently for a process which may also involve chiral silyl radicals.[5] It also suggests that the abstraction process occurs, as expected, with retention of configuration since (−)-acetylsilane and (+)-chlorosilane have the same relative configurations.[6,7]

Since it seemed highly probable that the low rotation of the chlorosilane was the result of racemization during the reaction or work-up, other runs were carried out in which the crude photolysate was immediately treated with lithium aluminum hydride in diethyl ether in order to convert the chlorosilane to silane, a reaction known to occur with high stereospecificity and to involve inversion of configuration. From two separate runs the 1-naphthylphenylmethylsilane, purified by chromatography of the crude reaction mixture on silica gel but not crystallized (to avoid possible enhancement of the optical purity), was found to have $[\alpha]^{22}D$ +18.1 and +21.3°, corresponding to 54 and 64% optical purities, respectively.



$$\underset{\substack{1\text{-Np}\\-40^\circ}}{\overset{Me}{PhSiCOCH_3}} \xrightarrow{h\nu} \underset{1\text{-Np}}{\overset{Me}{PhSi\cdot}} \xrightarrow{CCl_4} \underset{1\text{-Np}}{\overset{Me}{PhSiCl}} \xrightarrow{LiAlH_4} \underset{\substack{1\text{-Np}\\+20^\circ}}{\overset{Me}{HSiPh}}$$

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[1] S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometal. Chem.*, **15**, P17 (1968); A. Sitzki and K. Rühlmann, *Z. Chem.*, **8**, 427 (1968); G. A. Razuvaev, Yu. A. Alexandrov, V. N. Glushakova, and G. N. Figurova, *J. Organometal. Chem.*, **14**, 339 (1968); J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc.*, *A*, 510 (1968); R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.*, *C*, 2559 (1967); D. Cooper, *J. Organometal. Chem.*, **7**, 26 (1967); L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **85**, 2662 (1963); J. Curtice, H. Gilman, and G. S. Hammond, *ibid.*, **79**, 4654 (1957).

[2] The photolyses employed a Westinghouse PAR 38 100-W mercury spotlight which emits virtually no wavelengths below 350 mμ. Acylsilanes and -germanes have an $n-\pi^*$ absorption in the region 370–380 mμ.[3]

[3] A. G. Brook, D. G. Anderson, J. M. Duff, P. F. Jones, and D. M. MacRae, *J. Am. Chem. Soc.*, **90**, 1076 (1968).

[4] S. Winstein and F. H. Neubold, Jr., *ibid.*, **69**, 2916 (1947).

[5] H. Sakurai, M. Murakami, and M. Kumada, *ibid.*, **91**, 519 (1969).

[6] A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *ibid.*, **89**, 431 (1967).

[7] For information on the absolute configurations and optical rotations of a great number of optically active organosilicon compounds see L. H. Sommer "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.