Stabilized Vinyl Cations

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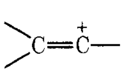
The chemistry of vinyl cations has grown to such an extent in the last few years that since 1970 not only have one *Accounts* article[1] and three comprehensive reviews[2] appeared on this topic, but it is now possible to write an Account about a specific branch of vinyl cation chemistry, the stabilized vinyl cations.

Owing to the rapid development that has taken place in this field during the last 5 years, we know that vinyl cations (1) as disubstituted carbenium ions show many similarities in their general properties and reactivity with the much better known saturated or trisubstituted carbenium ions (2).



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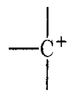

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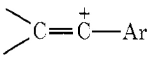
The reactions which have been observed with trisubstituted carbenium ions, such as rearrangements and substitution and elimination reactions, have also been observed during the generation of vinyl cations. Especially in the case of rearrangement reactions, a large variety of different reactons have been observed, including alkyl, aryl, and even hydride shifts toward and across the double bond, when a vinyl cation is involved.

Until 1969 vinyl cations in general were not considered to be very attractive intermediates because they were thought to be highly unstable and therefore difficult to generate, due to the ground-state stabilization of the vinyl precursor. The breakthrough in the chemistry of vinyl cations came when it became clear that vinyl cations (1) are not an elusive intermediate but, as in the case of the saturated carbenium ions (2), they can be most easily generated in simple solvolysis reactions if two requirements are met. (1) For the solvolysis, particularly favorable leaving groups should be employed, especially the so-called "super leaving" groups, the trifluoromethanesulfonate anion (triflate)[2] or the still faster reacting nonafluorobutanesulfonate anion (nonaflate).[3] (2) The intermediate vinyl cations should be stabilized by substituents with electron-donating ability. When other leaving groups less inclined to undergo SN1 reactions, e.g., tosylate or halide, are used in a solvolysis reaction, the vinyl compounds will undergo heterolysis of the carbon–halogen bond only when the resulting vinyl cations are stabilized by such groups.

The purpose of this Account is to summarize the attempts that have been made to stabilize vinyl cations using different groups with electron-donating ability. Such species are not only important for studying the properties of solvolytically generated vinyl cations but might allow the first spectroscopic evidence for the formation of vinyl cations to be obtained.

Because vinyl cations are disubstituted carbenium ions, the stabilizing substituents can be linked to the positive carbon atom in two ways: a singly bonded substituent produces a secondary vinyl cation (1, R $\neq$ H), whereas, when the β-carbon atom of the vinyl structure 1 is part of the substituent, we obtain structures which may be especially stabilized as in the case of the allenyl cation (5) or the cyclopropylidenemethyl cation 8 (vide infra).

For stabilizing the vinyl cations all those electron-donating substituents that have been effective in stabilizing saturated carbenium ions are suitable. Aryl and vinyl groups have been used to stabilize a vinyl cation in the classical way, and applying the above-mentioned two possibilities for binding the groups to the positively charged carbon atom the structures 3–5 are obtained.



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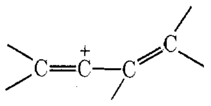

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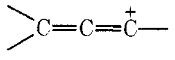

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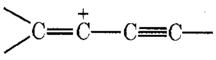

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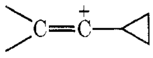
The vinyl cations 6 in which the positive charge is stabilized by a triple bond have not been generated.

Vinyl cations can be stabilized especially well in a nonclassical way by the overlap of the vacant p orbital of the vinyl cation with the bent bonds of a cyclopropyl group. Again there are two possibilities for utilizing the powerful stabilizing effect of the cyclopropane ring on a positive charge. A cyclopropane ring bonded singly leads to the secondary vinyl cation 7, whereas, if the β-carbon atom of the vinyl structure belongs to the cyclopropane ring, we obtain a cyclopropylidenemethyl cation 8. The particular stability of 8 arises from its special geometry allowing a particularly suitable overlap of the participating orbitals (vide infra).



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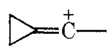

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Classical Stabilization

The α-Arylvinyl Cations (3). Among the first ex-

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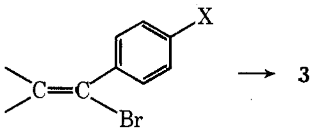
(1) M. Hanack, *Acc. Chem. Res.*, **3**, 209 (1970).

(2) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975).

(3) L. R. Subramanian and M. Hanack, *Chem. Ber.*, **105**, 1465 (1972).

amples of vinyl cation intermediates formed in solvolysis reactions were the α-arylvinyl cations (**3**) generated in the SN1-solvolysis reactions of a series of α-bromostyrenes of structure **9**, in which X represents an electron-releasing substituent (NH_2, OCH_3). Since the report about the intermediacy of such vinyl cations by Grob and Cseh[4] a large number of α-arylvinyl derivatives (halides and sulfonates) have been solvolyzed, and the special properties of the intermediate vinyl cations **3** have been studied.[5] Using α-arylvinyl bromides as precursors in the solvolysis reactions many basic mechanistic studies have been carried out, mainly by Rappoport, who has recently given an Account in this journal,[6] and his co-workers.



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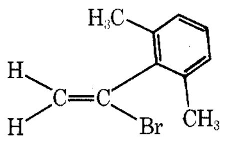

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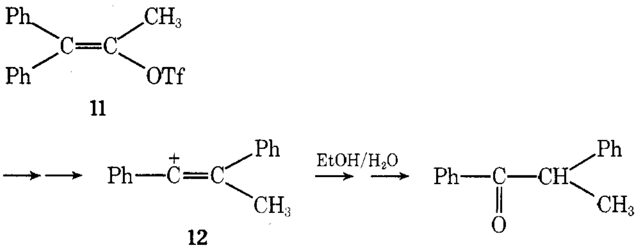
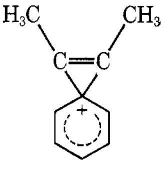
α-Arylvinyl systems (**9**) are stabilized by aryl–C=C conjugation in the ground state. The vacant p orbital, which develops to form the vinyl cation **3** as the leaving group departs, can only conjugate with the phenyl ring in the transition state, after rotation of the phenyl ring to achieve coplanarity of the vacant p orbital with the π orbitals of the phenyl ring and deconjugation of the aryl–C=C interaction. It was shown that steric hindrance to coplanarity by two ortho substituents as in **10** destabilized the ground state, making the phenyl ring and the vinyl π system nearly orthogonal. The developing p orbital can now be directly conjugated with the phenyl ring. In fact, in 80% EtOH k_{10}/k_9 (X = H) is 10^5, thus showing a lowering of the total activation energy in the solvolysis of **10**.[7]

An α-aryl-stabilized vinyl cation (**12**) was acclaimed as the first example of a rearrangement reaction across the double bond of a vinyl derivative.[8] During the solvolysis of 1-methyl-2,2-diphenylvinyl triflate (**11**) one of the phenyl groups migrates across the double bond to give the more stable vinyl cation **12** from which the ketone **13** is formed in practically quantitative yield.



11 **12** **13**

Many rearrangement reactions of this type have been observed since this first example was reported.[2] It was found that such rearrangements may occur with participation of the β-aryl group, including the formation of a vinylidenephenonium ion **14**. This was shown by the solvolysis reactions of the *E* and *Z* isomers of 3-phenyl-2-buten-2-yl triflates and their α- and β-CD_3 analogues.[9]



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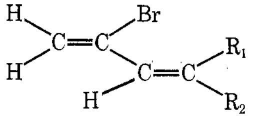
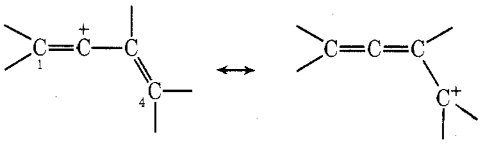
The Dienyl Cations (4). The stabilizing effect of a vinylic double bond has been observed in the solvolysis reaction of substituted bromodienes. It has been shown that unsubstituted 2-bromobutadiene (**15a**) solvolyzes very slowly in 80% aqueous ethanol; however, methyl-substituted 2-bromobutadiene (**15b**) shows a reaction rate which is about 10^4 times faster.[10] The rate-accelerating effect of the methyl substituents is due to the distribution of the positive charge in the mesomeric vinyl cation **16**. The electron deficiency at C-4 is partially compensated by the methyl groups. A necessary condition for the charge distribution shown in **16** is that the planes of the double bonds in **15b** be perpendicular to each other.



15a, $R_1 = R_2 = H$
b, $R_1 = R_2 = CH_3$



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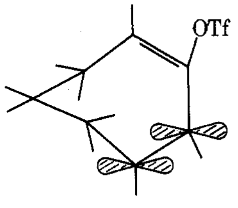
The requirement of noncoplanarity of the double bonds for the formation of dienyl vinyl cations has also been demonstrated by the solvolysis reactions of cyclic 1,3-dienyl triflates.[11] Cycloheptadienyl triflate (**17**) and cyclooctadienyl triflate (**18**) both solvolyze in 50% ethanol with the formation of the corresponding vinyl cations. **17** and **18** show characteristic reaction rate differences in comparison with the cyclic vinyl triflates of the same ring size but containing only one double bond. **17** solvolyzes with almost the same rate as 1-cycloheptenyl triflate; **18** solvolyzes about 10^3 times faster than 1-cyclooctenyl triflate. The introduction of



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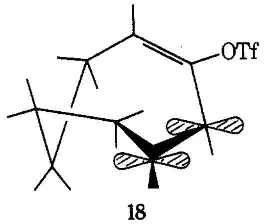

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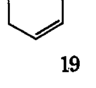

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[4] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

[5] C. A. Grob and H. R. Pfaendler, *Helv. Chim. Acta*, **54**, 2060 (1971); C. A. Grob and R. Nussbaumer, *ibid.*, **54**, 2528 (1971).

[6] Z. Rappoport, *Acc. Chem. Res.*, **9**, 265 (1976).

[7] K. Yates and J. J. Périé, *J. Org. Chem.*, **39**, 1902 (1974).

[8] M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Am. Chem. Soc.*, **92**, 3802 (1970).

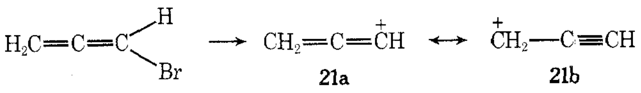
[9] P. J. Stang and T. E. Dueber, *J. Am. Chem. Soc.*, **95**, 2683 (1973).

[10] C. A. Grob and R. Spaar, *Helv. Chim. Acta*, **53**, 2119 (1970).

[11] E. Lamparter and M. Hanack, *Chem. Ber.*, **106**, 3216 (1973).

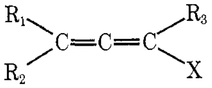
a second double bond as in **17** and **18** should lead to an increased strain in comparison with the corresponding compounds containing only one double bond if a linear vinyl cation is formed. Thus for **17** and **18** a lower reaction rate should have been expected. The comparatively high rates of **17** and **18** therefore indicate that the intermediate vinyl cation has been stabilized by the second double bond in the allylic position. The necessary condition for a stabilizing interaction of the participating orbitals in **18** can be achieved easily, owing to the flexibility of the eight-membered ring. In **17** the stabilizing effect between the interacting orbitals is less suitable. In the case of cyclohexadienyl triflate (**19**) with the double bonds almost in one plane, solvolysis no longer occurs via a vinyl cation mechanism, but in nucleophilic solvents such as ethanol–water it solvolyzes via a sulfur–oxygen cleavage.[12]

The Allenyl Cations (5). The unsaturated analogue of an allylic cation is the allenyl cation **5**. Unlike other simple alkyl vinyl halides allenyl bromide (**20**) reacts under solvolytic conditions, thus showing some stabilization of the formed vinyl cation **21a** (which is mesomeric with the propargyl cation **21b**) by the allenyl double bond.[13] The solvolyses of substituted haloallenes of structure **22** were studied in detail in aqueous acetone and aqueous ethanol.[14] The solvolyses showed first-order kinetics; a large excess of added nucleophile had no effect on the rates of solvolysis. Common ion rate depressions were observed, and the solvent dependence of the reaction rates was consistent with a heterolysis of the C–X bond leading to stabilized allenyl cations **5**. The formation of an allenyl cation (**5**) in the solvolysis of haloallenes was also confirmed by measuring the α- and β-secondary deuterium isotope effects.



$$H_2C{=}C{=}C(H)Br \longrightarrow CH_2{=}C{=}\overset{+}{C}H \longleftrightarrow \overset{+}{C}H_2{-}C{\equiv}CH$$

20 21a 21b



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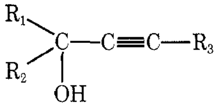
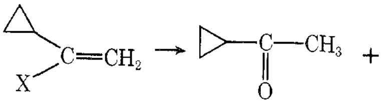


23

Alkynyl cations **21b**, models for vinyl cations, were the first ones from which spectral data were available. By treating alkynyl alcohols **23** with either concentrated sulfuric acid or SbF_5–FSO_3H in SO_2 the corresponding alkynyl cations were generated, and the ^1H NMR and uv data were recorded.[15] On the basis of these data it was concluded that the mesomeric form **21a** was an important contributor to the structure of such ions. More recently the charge distribution in akynyl cations was estimated more accurately by ^{13}C NMR spectroscopy.[16] Here also it could be shown that the positive charge is extensively delocalized, and **21a** contributes much to the ion structure.

Nonclassical Stabilization

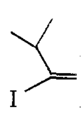
Cyclopropylvinyl Cations (7). In 1969 two short communications appeared in which the well-known stabilizing effect of a cyclopropane ring on a positive charge was used to stabilize a vinyl cation generated in a solvolysis reaction.[17] Both the chloride **24a** and the iodide **24b** react, even at room temperature, with silver salts in acetic acid, yielding **25** and **26**. The analogous iodide **27** does not react in acetic acid with silver salts at room temperature and undergoes silver-catalyzed conversion to isopropyl methyl ketone only at 150 °C. **24a** and **24b** solvolyze with first-order kinetics in aqueous methanol buffered with triethylamine at 140–160 °C to give **25** as the main product. All the data were consistent with the formation of a vinyl cation stabilized by the neighboring cyclopropane ring.



24a, X = Cl
b, X = I

25

26



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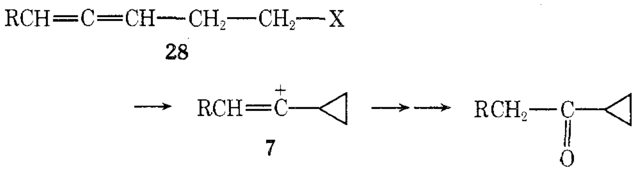
The intermediacy of a cyclopropylvinyl cation (**7**) was proposed by us in 1964 when we studied the solvolysis reaction of homoallenyl derivatives **28**.[18] As shown independently by Bertrand and his co-workers[19] homoallenyl compounds **28** (X = OTs, halogens) solvolyze in various aqueous solvents to form alkyl cyclopropyl ketones (**29**), indicating the intermediate formation of the cyclopropylvinyl cation **7**. In comparison with the homoallyl rearrangement, this reaction, which proceeds with participation of one of the allenyl double bonds, was called the "homoallenyl rearrangement".



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7

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That a stabilized cyclopropyl vinyl cation (**7**) is the first intermediate in the solvolysis of homoallenyl compounds has been shown convincingly by more careful product and kinetic studies of several vinylcyclopropyl derivatives (halogens and tosylates) and their isomeric homoallenyl counterparts. It was shown, for example, that the iodide **24b** and its homoallenic isomer **28** (R = H; X = I) yielded the same solvolysis products (>65% cyclopropyl derivatives) in comparable amounts.[20] Another example for the intermediate formation of **7** in the homoallenyl rearrangement is the product comparison study of the tosylates **30, 31**, and **32**, following solvolysis in acetic acid.[21] The solvolysis

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(12) M. Hanack and H. Bentz, unpublished results.

(13) C. V. Lee, R. J. Hargrove, T. E. Dueber, and P. J. Stang, *Tetrahedron Lett.*, 2519 (1971).

(14) M. D. Schiavelli, T. C. Germroth, and J. W. Stubbs, *J. Org. Chem.*, **41**, 681 (1976), and references cited therein.

(15) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965); H. G. Richey, L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Phillips, *ibid.*, **87**, 4017 (1965); H. G. Richey, Jr., J. C. Phillips, and L. E. Rennick, *ibid.*, **87**, 1381 (1965).

(16) G. A. Olah, R. J. Spear, P. W. Westermann, and J. M. Denis, *J. Am. Chem. Soc.*, **96**, 5855 (1974).

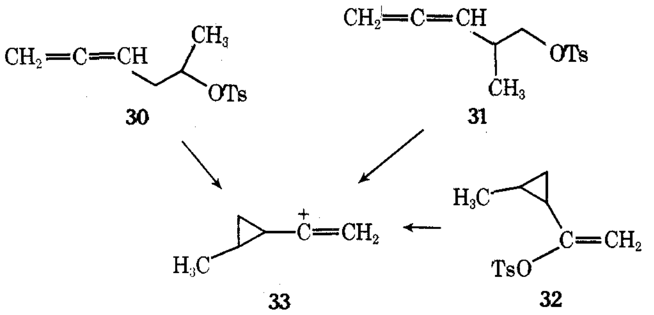
(17) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 2115 (1969); T. Bässler and M. Hanack, *ibid.*, **91**, 2117 (1969).

(18) M. Hanack and J. Häffner, *Tetrahedron Lett.*, 2191 (1964); M. Hanack and J. Häffner, *Chem. Ber.*, **99**, 1077 (1966).

(19) M. Bertrand and M. Santelli, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **259**, 2251 (1964); M. Bertrand and M. Santelli, *Tetrahedron Lett.*, 2511, 2515 (1969).

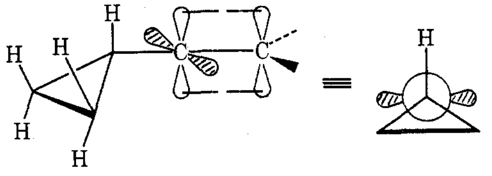
(20) D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, **93**, 1941 (1971).

(21) Th. V. Lehmann and R. S. Macomber, *J. Am. Chem. Soc.*, **97**, 1541 (1975).

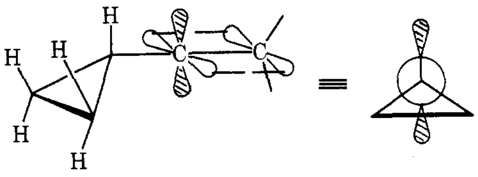


products of the three tosylates **30, 31,** and **32** are very similar in both composition and stereochemistry and are best described as arising from a single intermediate, the cyclopropylvinyl cation **33.**

For the cyclopropylvinyl cation **7** the so-called bisected **34** and the perpendicular structure **35** are possible with respect to the spatial direction of the vacant orbital. According to MO calculations the linear cyclopropylvinyl cation is more stable in the bisected conformation **34,** which provides maximum overlap of the vacant p orbital with the orbitals of the cyclopropane ring.[22] This is analogous to the saturated cyclopropyl carbinyl cation.



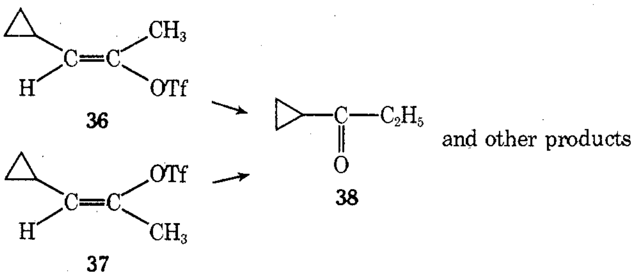
34 bisected

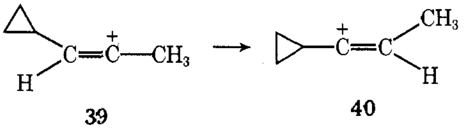


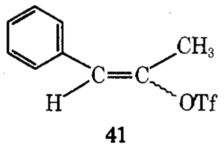
35 perpendicular

The powerful stabilizing effect of a cyclopropane ring on a vinyl cation is also demonstrated by its ability to supply a driving force for a hydride shift, a reaction which is very common during the generation of a saturated carbenium ion. During the solvolysis of (*E*)- and (*Z*)-3-cyclopropyl-2-propen-2-yl triflates, **36** and **37,** respectively, in solvents of different ionizing power and nucleophilicity, under the stabilizing influence of the β-cyclopropane ring, a 1,2-hydride shift across the double bond ensues. This was the first observation of such a reaction in the solvolysis of a vinyl derivative.[23] The (*E*)- (**36**) as well as the (*Z*)-vinyl triflate (**37**) on solvolysis in 60 and 80% trifluoroethanol at 80 °C yields between 11 and 17% cyclopropyl ethyl ketone (**38**). The formation of **38** can only be explained by the intermediate formation of the vinyl cation **39** generated in the solvolysis of either the triflate **36** or **37. 39** subsequently rearranges by a 1,2-hydride shift across the double bond to form the cyclopropyl vinyl cation **40** which reacts further with the solvent to form **38.**

In comparison with **36** and **37** the corresponding phenyl derivative **41** in its *E* or its *Z* form undergoes a 1,2-hydride shift across the double bond to the extent of 4–6%. This again shows the especially large stabilizing effect of a cyclopropyl group on a vinyl cation when compared with a phenyl group.[23b]





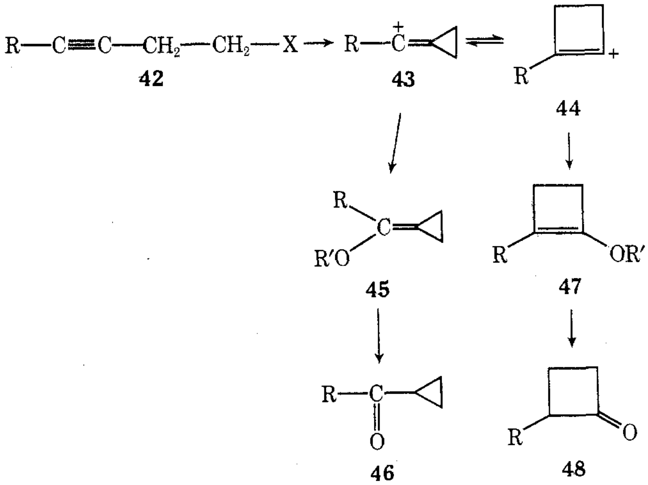


41

Cyclopropylidenemethyl (8) and Related Cations. As pointed out before, in the cyclopropylidenemethyl cation **8** one carbon of the cyclopropane ring is already a part of the vinyl system. It has been predicted that **8** in general should be particularly stable because of its special geometry.[24] The electron-donating cyclopropane ring, because of the short C–C distance of the double bond, is closer to the positive center, and the axis of the vacant orbital of the vinyl cation lies in the plane of the three-membered ring. In this way there is an especially favorable geometry for an overlap of the participating orbitals. The stability of **8** was confirmed by MO, ab initio, and MINDO/3 calculations (vide infra).

Cyclopropylidenemethyl cations **43** (Scheme I) were first proposed by us[25] as intermediates in the "homopropargyl rearrangement" in which, during solvolysis, reactive homopropagyl derivatives (**42**) can be rearranged, with the formation of the enol ethers **45** and **47** or cyclopropyl ketones **46** and cyclobutanones **48** depending upon the solvent. The mechanism of this re-

Scheme I



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(22) D. R. Kelsey and R. G. Bergman, *J. Am. Chem. Soc.*, **93,** 1953 (1971).

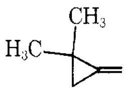
(23) (a) K. P. Jäckel and M. Hanack, *Tetrahedron Lett.*, 1637 (1974); (b) K. P. Jäckel and M. Hanack, *Justus Liebigs Ann. Chem.*, 2305 (1975).

(24) T. Bässler and M. Hanack, *Tetrahedron Lett.*, 2171 (1971).

(25) M. Hanack, J. Häffner, and J. Herterich, *Tetrahedron Lett.*, 875 (1965); M. Hanack, S. Bocher, J. Herterich, K. Hummel, and V. Vött, *Justus Liebigs Ann. Chem.*, **733,** 5 (1970).

action which includes the vinyl cation **43** and the cyclobutenylvinyl cation, **44** is given in Scheme I.

According to the solvolysis results, even primary cyclopropylidenemethyl cations can be generated, as was shown with compounds **49**,[26] **50**,[24] and the *Z* and *E* isomers of **51**.[27] **49** solvolyzes exclusively with the formation of rearranged acetylenic derivatives, **50** solvolyzes comparatively fast in methanol–water mixtures with rearrangement and formation of cyclobutanone **48** (R = H). From the kinetic data and the products, we proposed a vinyl cation mechanism for both solvolysis reactions.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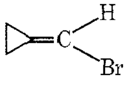
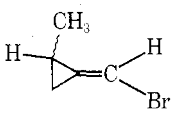
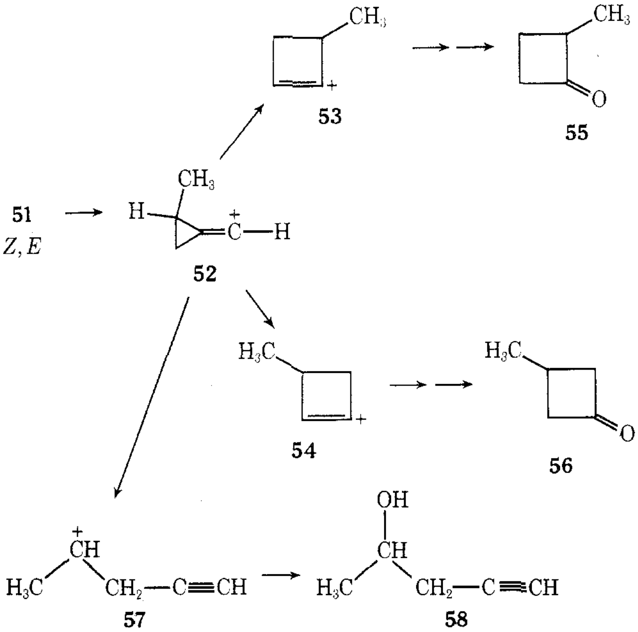

50

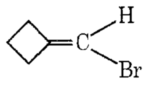

51

That a vinyl cation is involved in the solvolysis of such primary cyclopropylidenemethyl halogens was shown from the solvolysis of (*Z*)- and (*E*)-1-bromoethylidene-2-methylcyclopropane (**51**).[27] Comparison of the solvolysis rates of (*Z*)- and (*E*)-**51** with that of **50** (k_{rel} = 27 for (*Z*)-**51** and 10 for (*E*)-**51**) in methanol–water mixtures of different ionizing power and nucleophilicity shows both isomers solvolyze with rate enhancements typical for compounds which are methyl substituted in the cyclopropane ring of a cyclopropylcarbinyl system, compared with the nonsubstituted analogue. In addition (*E*)- and (*Z*)-**51** solvolyze with complete rearrangement and formation of the cyclobutanones **55** and **56** as well as the acetylenic alcohol **58** (see Scheme II). The intermediate formation of **52** is proved by the fact that both (*Z*)- and (*E*)-**51** form the rearranged products in exactly the same ratio. This excludes a synchronous ring opening without the intermediacy of **52**.

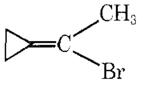
A comparison with the homologous cyclobutylidenemethyl bromide (**59**) is well suited to show how the reactivity of a vinyl bromide is increased through the stabilizing effect of the cyclopropane ring in **49**, **50**, and **51**. Even at temperatures up to 180 °C (solvent methanol–water) **59** was recovered unchanged after 21 days, showing that **59** exhibits the low reactivity of a "normal" vinyl bromide.[24]

Scheme II




59

A series of cyclopropylidenemethyl bromides **60–64**, leading to secondary cyclopropylidenemethyl cations, were synthesized and their solvolytic behavior was studied.[28–30] Additional stabilization of the positive charge in the cyclopropylidenemethyl cations **8** should be obtained by electron-releasing substituents in the *α* position. As expected, the kinetic data and the products formed have evidenced the formation of stabilized cationic intermediates **8**. The solvolysis products of the compounds **60** to **64** are dependent upon the substituents but follow the general pattern of rearrangement shown in Scheme III.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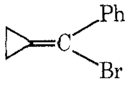
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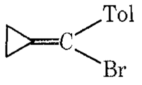
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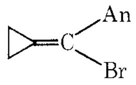
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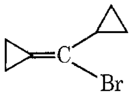
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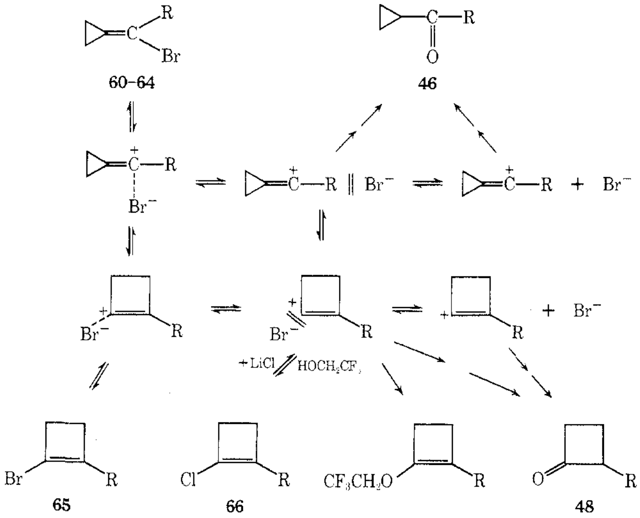
Scheme III



As an example, the methyl-substituted compound **60** is given: **60** was solvolyzed in various solvents in the presence of triethylamine as buffer, producing methyl cyclopropyl ketone (**46**, R = CH_3), 2-methylcyclobutanone (**48**, R = CH_3), and 1-bromo-2-methyl-1-cyclobutene (**65**, R = CH_3) (Scheme III).[28] A surprising result was the formation of the rearranged bromide **65** (R = CH_3), which in all solvolysis reactions of **60** using 60%

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[26] A. Ghenciulescu and M. Hanack, *Tetrahedron Lett.*, 2870 (1970).

[27] G. Hammen, T. Bässler, and M. Hanack, *Chem. Ber.*, **107**, 1676 (1974).

[28] M. Hanack, T. Bässler, W. Eymann, W. E. Heyd, and R. Kopp, *J. Am. Chem. Soc.*, **96**, 6686 (1974).

[29] J. Salaün and M. Hanack, *J. Org. Chem.*, **40**, 1994 (1975).

[30] J. L. Deroque, F. B. Sundermann, N. Youssif, and M. Hanack, *Justus Liebigs Ann. Chem.*, 419 (1973).

Table I
Comparison of the Solvolysis Rates of Cyclopropylidenemethyl Bromides 50, 60–64 in 80% Aqueous Ethanol at 100 °C

	k,[a] s^{-1}	k_{rel}	m
50	7.1×10^{-8}[a]	1	0.53[b]
60	6.6×10^{-5}	10^3	0.64[c]
61	1.54×10^{-4}	2.2×10^3	
62	7.65×10^{-4}[a]	1.08×10^4	0.85[d]
63	3.78×10^{-2}[a]	5.32×10^5	
64	6.4×10^{-3}[a]	0.9×10^5	0.89[e]

[a] Extrapolated. [b] At 130 °C. [c] At 90 °C. [d] At 74.5 °C. [e] At 48.8 °C.

and 80% trifluoroethanol and liquid SO_2 as a solvent was the main product. The formation of **65** (R = CH_3) can be ascribed to an internal return with simultaneous structural rearrangement and is direct evidence for a vinyl cation mechanism. The formation of the cyclobutenyl bromide **65** (R = CH_3) by other mechanisms, e.g., an addition–elimination mechanism, is clearly excluded. The addition of LiCl in the solvolysis of **60** leads to the formation of a considerable amount of 1-chloro-2-methyl-1-cyclobutene (**66**, R = CH_3). The predominance of the rearranged bromide **65** (R = CH_3) under all solvolysis conditions suggests an ion-pair mechanism. The formation of a rearranged chloride in the trapping experiments with LiCl shows the presence of solvent-separated ion pairs while the bromide **65** should result from tight ion pairs.

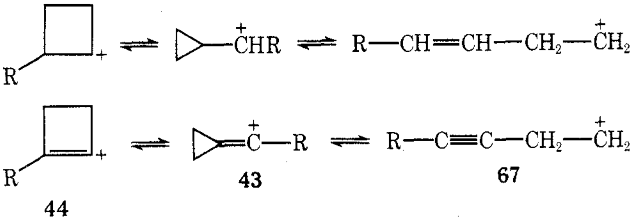
The kinetic data of the bromides **60–64** are given in Table I. An increase in the solvolytic rate (implying an increase in the stabilization of the intermediate vinyl cation) is clearly observed when the functional carbon of the vinyl bromide is successively substituted by a more powerful electron-releasing group. In going from methyl (**60**) through phenyl (**61**), *p*-tolyl (**62**), and cyclopropyl (**64**) to *p*-anisyl (**63**), a rate increase of two powers of ten is observed[28–30]

As can be seen from Table I the secondary methyl derivative **60** is distinguished by a noticeable increase in reaction rate (~10^3) from the parent compound **50**, showing the higher stability of a secondary vinyl cation vs. a primary vinyl cation in general. The rate ratio between the phenyl (**61**) and the tolyl (**62**) derivatives compared with the methyl derivative (**60**) is low, indicating considerable ground stabilization of **61** and **62** due to conjugation between the phenyl ring and the double bond. To stabilize the positive charge in **61** the phenyl ring must be rotated around 90° for a favorable overlap of the participating orbitals. Within the range of aryl-substituted cyclopropylidenemethyl compounds **61, 62,** and **63,** the rates increase as expected with the increasing electron-releasing ability of the substituent in the para position of the aromatic ring: the bromide **62** reacts 5 times faster than **61** owing to the inductive effect of the *p*-methyl group in the phenyl ring. The effect of a *p*-methoxy group was strongly marked, **63** reacting 245 times faster than the parent compound **61** under the same conditions. Such a substituent effect on the solvolysis rates suggests a unimolecular ionization process and the formation of an intermediate vinyl cation. The especially high stabilizing effect of a cyclopropyl group is shown in the solvolysis rate of **64** which is of the same order (10^5 times faster than the parent compound **50**) as that obtained with the vinyl bromide **63** (effect of a *p*-anisyl substituent). **64** shows a Winstein–Grunwald *m* value of 0.89, which is the highest reported to date for a reaction proceeding through a vinyl cation.

Concerning the solvolysis products of **61** to **64** a general picture can be drawn: the higher the stability of the intermediate vinyl cation, the less the amount of rearranged products. **61** already solvolyzes in 80% aqueous ethanol with formation of phenyl cyclopropyl ketone (**46**, R = phenyl) as the main product. **62** and **63** show the same pattern; increasing amounts of nonrearranged aryl cyclopropyl ketones (**46**, R = tolyl, *p*-anisyl) are formed with, as mentioned in the case of **60**, the cyclobutenyl bromides **65** (R = tolyl, anisyl). The same is true for cyclopropylcyclopropylidenemethyl bromide (**64**) which sololyzes in 80% aqueous ethanol with the formation of 66% dicyclopropyl ketone (**46,** R = cyclopropyl), 7.5% of the rearranged 2-cyclopropylcyclobutanone (**48**, R = cyclopropyl), and 8.5% of the cyclobutenyl bromide **65** (R = cyclopropyl) (see Scheme III). 18% of homopropargyl bromide **42** (R = cyclopropyl; X = Br) was also formed.[31]

The high reactivity of the cyclopropylidenemethyl bromides resembles the solvolytic reactivity of cyclopropylcarbinyl halides, and one has to discuss the rearrangement reaction of **60–64** in similar terms according to Scheme IV. Accordingly **43** would rearrange to a cyclobutenylvinyl cation (**44**) which in turn rearranges to the homopropargyl cation **67**. As this rearrangement must be reversible, by solvolyzing either cyclobutenyl derivatives leading to **44** or homopropargyl derivatives leading to **67**, the same product composition, or almost the same product composition, must be expected as when one solvolyzes cyclopropylidenemethyl compounds (Schemes I and IV).

Scheme IV



Homopropargyl compounds of structure **42** solvolyze in solvents of high ionizing power and low nucleophilicity with formation of cyclopropylidenemethyl and cyclobutenyl compounds (Scheme I).[25] From the many examples investigated a few will be mentioned. 3-Pentyn-1-yl derivatives **42** (R = CH_3, X = OTs, OTf) undergo solvolysis reaction in solvents of high ionizing power (CF_3COOH, trifluoroethanol) with participation of the triple bond to give either cyclopropyl methyl ketone (**46**, R = CH_3) or methylcyclobutanone (**48**, R = CH_3) (Scheme I). Using trifluoroethanol as solvent it was possible to trap the intermediate vinyl cation as the corresponding trifluoroethyl ether **47** (R′ = CH_2CF_3) (Scheme I).[32] In all solvolysis reactions studied with 3-pentyn-1-yl derivatives **42** (R = CH_3), mostly **47** and **48** (R = CH_3) as well as very small amounts of the cyclopropyl compounds **45** and **46** (R = CH_3), were formed. On the other hand, the phenylhomopropargyl derivatives (**42**, R = phenyl, X = OTs, OTf) solvolyze

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(31) R. Kopp and M. Hanack, unpublished work.

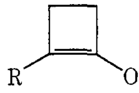
(32) H. Stutz and M. Hanack, *Tetrahedron Lett.*, 2457 (1974).

in 80% trifluoroethanol buffered with pyridine, forming mainly phenyl cyclopropyl ketone (**46**, R = phenyl). In this case very little of the cyclobutanone **48** (R = phenyl) is formed. The same is true for the cyclopropylhomopropargyl derivatives **42** (R = cyclopropyl, X = OTs, OTf) in which under the same solvolysis conditions the main product is dicyclopropyl ketone (**46**, R = cyclopropyl) (Scheme I).[33]

The solvolysis product compositions of the homopropargyl compounds **42** are in good agreement with the products obtained in the solvolysis reactions of the corresponding cyclopropylidenemethyl bromides **50** and **60–64.** The composition of the products resulting from the solvolysis of the homopropargyl derivatives is dependent upon the substituent. More highly electron-donating substituents favor the formation of the cyclopropyl compounds **45** or **46.**

A great deal of work was invested in the question of whether or not the third "homopropargyl isomer", a cyclobutenyl derivative (**68**), could also undergo a solvolysis reaction with formation of the same product composition as shown in the equilibrium of vinyl cations in Scheme IV. While no doubt exists about the stabilization of a cyclopropylidenemethyl cation **43** as indicated by MO and ab initio calculations, the question whether or not a cyclobutenylvinyl cation (**44**) can be formed is less clear. Although older MO calculations show stabilization in the parent cyclobutenyl cation **44** (R = H) through nonclassical interaction between the vacant orbital of the positively charged carbon atom and the C_2–C_3 bond,[34] ab initio and MINDO/3 calculations show no stabilization for this cation.[35]

44 should be highly strained since there is no possibility of achieving a linear structure which is energetically favorable for a vinyl cation. On the other hand, the experimental results which were obtained with cyclobutenyl derivatives **68** (R = H) point to the fact that they solvolyze via a vinyl cation mechanism. The most convincing example for this mechanism is shown with cyclobutenyl nonafluorobutanesulfonate (nonaflate) (**68**, R = H) itself.[36a] Comparing, for example, the relative rates of a series of cyclic vinyl nonaflates it was shown that with increasing ring size the reaction rate increased considerably.[3] Cyclooctenyl nonaflate (**71**) solvolyzes 12 800 times faster than the cyclohexenyl nonflate, while the next lower homologue, the cyclopentenyl nonaflate (**69**), reacts very slowly (0.05 of the rate of **70**) and most probably not via a vinyl cation mechanism.[36b] Going to cyclobutenyl nonaflate (**68**, R = H), one observes a dramatic increase of the solvolysis rate (3685) compared with cyclohexenyl nonaflate (**70**). Careful mechanistic studies have excluded an addition–elimination mechanism for **68**, and the conclusion was drawn that **68** solvolyzes via a vinyl cation which is stabilized by nonclassical interaction.[36a,b]



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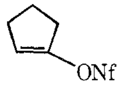

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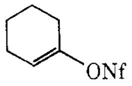

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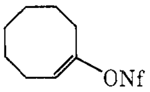

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Nf = $SO_2C_4F_9$

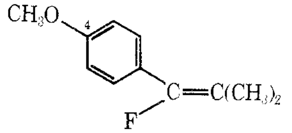
k_{rel} 3685 (R = H) 0.05 1 12 800

2-Substituted cyclobutenyl nonaflates (**68**) were also investigated with the following results: 2-methylcyclobutenyl nonaflate (**68**, R = CH_3) solvolyzes mostly with the formation of 2-methylcyclobutanone (**48**, R = CH_3)[37] and very little rearranged products. 2-Phenylcyclobutenyl nonaflate (**68**, R = phenyl) and 2-anisylcyclobutenyl nonaflate (**68**, R = anisyl), on the other hand, solvolyze in 80% ethanol mostly with rearrangement, forming, as in the case of the other "homopropargyl derivatives", cyclopropyl ketones (**46**, R = phenyl, anisyl).[38]

The solvolysis reactions of the cyclobutenyl nonaflates **68,** leading to the same product compositions as in the case of the cyclopropylidenemethyl (**50, 60–64**) and homopropargyl derivatives (**42**), must therefore proceed through an ionic mechanism which is best represented by Scheme IV. The question whether or not we are dealing with separate ions **43** and **44** or a common nonclassical intermediate has not been solved. As pointed out above the cyclobutenyl cation in its classical structure, as shown in **44**, is highly strained.

Spectroscopic Evidence for Vinyl Cations. The high stabilizing effect of a *p*-anisyl group was used for the first time by us to attempt to generate a "free" vinyl cation and to observe its spectroscopic properties by ^1H and ^{13}C NMR. For this purpose the *p*-anisylvinyl fluoride **72** was treated at −73 °C with SbF_5 in SO_2ClF and the ^1H and ^{13}C NMR spectra of the stable solutions of **72** + SbF_5 were recorded.[39] In comparison with **72** the ^1H NMR spectrum of the reaction product **72** + SbF_5 showed peaks that were downfield shifted between 0.50 and 1.6 ppm. The aromatic region of the spectrum was similar to that of the *p*-methoxybenzyl cation, investigated under the same conditions by Olah,[40] as regards both the chemical shift of the protons and the nonequivalence of the two ortho and meta protons.

In the ^{13}C NMR spectrum of **72** + SbF_5 the β-methyl groups were shifted only slightly downfield and appeared as a single signal; the C–F couplings were no longer visible. An especially large downfield shift (30 ppm) was observed for the C-4; again this signal is shifted downfield by about the same amount as the corresponding signal in the spectrum of the *p*-methoxybenzyl cation. The signals of the ortho and meta carbon atoms were shifted downfield by about 20 and 13 ppm, respectively; again the two meta and ortho positions are not equivalent, presumably due to the frozen rotation of the *p*-methoxy group at low temperatures. Although not all the lines had yet been assigned accurately, the ^{13}C NMR spectrum of **72** + SbF_5 was in accord with a linear vinyl cation. Besides the anisyl vinyl derivative **72,** other aryl-substituted vinyl halides (**73,**



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[33] M. Hanack, H. Stutz, and W. Schoberth, unpublished results.

[34] H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969).

[35] P. v. R. Schleyer and Y. Apeloig, unpublished results.

[36] (a) L. R. Subramanian and M. Hanack, *Angew. Chem.*, 84, 714 (1972); (b) unpublished work.

[37] K. Subramanian and M. Hanack, *Tetrahedron Lett.*, 3365 (1973).

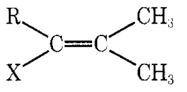
[38] M. Hanack, E. Carnahan, and A. Krowczynski, unpublished results.

[39] H. U. Siehl, J. C. Carnahan, Jr., L. Eckes, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 13, 675 (1974).

[40] G. A. Olah, R. D. Porter, C. L. Jenell, and A. M. White, *J. Am. Chem. Soc.*, 94, 2044 (1972).

R = tolyl, phenyl) (fluorides and chlorides) labeled in various positions with a high concentration of ^{13}C were reacted with SbF_5 at low temperatures in nonnucleophilic solvents (SO_2ClF, CH_2Cl_2, SO_2). If the aryl substituent in **73** is not an anisyl but a tolyl or a phenyl group, the results are less clear,[41] though it has been reported that the phenyl vinyl chloride **73** (R = phenyl) can be converted into the corresponding vinyl cation.[42] Our own results indicate moreover that there are serious differences between fluorides and chlorides and that, besides a vinyl cation, other still not identified species may be formed when arylvinyl chlorides of structure **73** (R = tolyl and phenyl, X = Cl) are reacted with SbF_5.[41]

In addition to the above-mentioned experiments ferrocenylvinyl cations **74** were generated from ethynylferrocenes by protonation.[43] A direct NMR spectroscopic observation of such ferrocenylvinyl cations was possible in CF_3COOH solution if the reactive center was sterically shielded by a proximate *tert*-butyl group (**74**). Another example of the generation of a quite similar species to the vinyl cation is that of the thiirenium ion (**75**), a long-lived bridged vinyl cation.[44]



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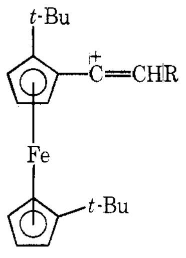

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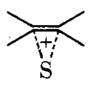

75

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(41) H. U. Siehl, C. Liddiard, and M. Hanack, unpublished results.

(42) S. Masamune, M. Sakai, and K. Morio, *Can. J. Chem.*, **53**, 784 (1975).

(43) T. S. Abram and W. E. Watts, *J. Chem. Soc., Chem. Commun.*, 857 (1974); *J. Organomet. Chem.* **87**, C39 (1975).

(44) G. Capozzi, O. Lucchi, V. Lucchini, and G. Modena, *J. Chem. Soc., Chem. Commun.*, 248 (1975).

Azirine Photochemistry

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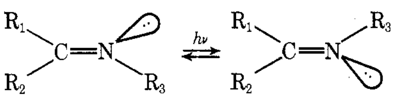
Although kinetic and spectroscopic studies of the electronically excited carbonyl group are legion,[1] the photochemistry of the structurally related imine system has received little mechanistic attention. This is surprising in view of the many studies that have been made of the descriptive photochemistry of imines[2-4] and of their spectroscopic behavior.[5]

The possibilities of both n–π* and π–π* excitation of this chromophore promise a variety of interesting physical and chemical conversion processes. While chemical reaction of the excited state of an imine has often been observed, a more frequently encountered phenomenon for simple imines is fast, efficient, radiationless deactivation. The low photoreactivity of the imine system can be attributed to rotation about the π bond in the excited state, which allows dissipation of electronic energy.[6] In rigid systems, this mode of energy dissipation is not available, and these cyclic imines have maximum opportunity to undergo reaction from an electronically excited state.



In 1970 we initiated an investigation of the photochemistry of small-ring cyclic imines, in which syn–anti photoisomerization about the C–N double bond should be a high-energy, structurally prohibited process.[7] We were particularly interested in the three-membered azirine ring since this cyclic imine had been little studied except for a few instances in which either photodimerization[8,9] or photorearrangement[10] occurred. 2*H*-Azirines are versatile substrates which can serve as useful precursors for the synthesis of other heterocyclic rings.[11]

Albert Padwa was born in New York City in 1937. He received his B.A. and Ph.D. from Columbia University where he worked with Cheves Walling. After a year of postdoctoral work with Howard Zimmerman at the University of Wisconsin, he joined the Ohio State University faculty in 1963. In 1966 he moved to SUNY Buffalo, where he is now Professor of Chemistry. His research interests lie principally in the fields of organic photochemistry, molecular rearrangements, and the reactions of small-ring heterocyclic compounds.

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