DISUBSTITUTED CARBENIUM IONS AS REACTIVE INTERMEDIATES IN ORGANIC CHEMISTRY

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Abstract – Recent results in the chemistry of disubstituted carbenium ions (vinyl cations and phenyl cations) are described separately under three different sections: From kinetic and solvolytic data of several 1-cyclobutenyl nonaflates, the inter-mediacy of a non-classical vinyl cation, namely the 1-cyclobutenyl cation **2** is established. Cycloaddition reactions of solvolytically generated vinyl cations with olefins to form cyclobutenyl- and cyclopropyl compounds are described and the mechanisms of the cycloaddition reactions are discussed. Phenyl cations have been generated by a novel route involving triple bond participation with vinyl cations.

INTRODUCTION

Disubstituted carbenium ions are an important class of reactive intermediates. Vinyl cations are the most illustrative examples of disubstituted carbenium ions and have been investigated very intensively during the last fifteen years (Ref. 1). In connection with our work on vinyl cations, some new results on the generation of phenyl cations, which also belong to disubstituted carbenium ions, will also be reported.

Vinyl cations **1** can be generated by a variety of methods, e.g. by the addition of electrophilic reagents to allenic or acetylenic bonds, by triple bond participation in a carbenium ion reaction, or by heterolysis of vinyl sulfonate esters. We shall be concentrating mostly on the latter mode of generation of vinyl cations (Scheme 1).
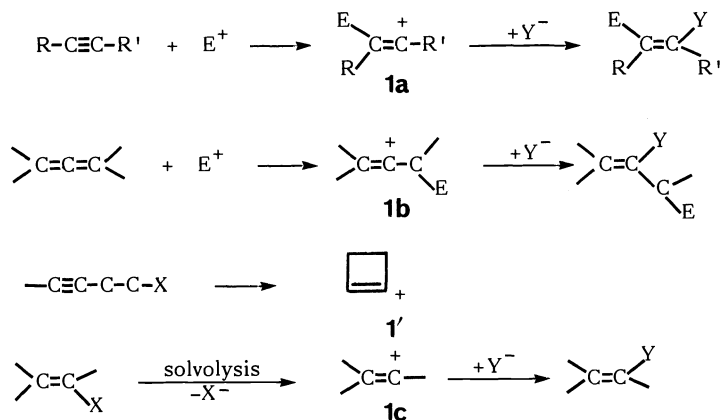
SCHEME 1. X = halogen or OSO_2R_F;
$R_F = CF_3$ (triflate), $R_F = C_4F_9$ (nonaflate)

A necessary requirement for the solvolytic generation of vinyl cations is either an appropriate sulfonate ester leaving group or stabilizing neighboring groups in the molecule. The super leaving groups trifluoromethanesulfonate (triflate) and nonafluorobutanesulfonate (nonaflate) are found (Ref. 2) to be the most suitable ones. A solvolytic generation of vinyl cations is also possible using other leaving groups, such as bromide ions, if the electron-deficient center is stabilized by neighboring electron donating groups like vinyl, phenyl, or cyclopropyl (Ref. 3). As in the case of sp^2-hybridized trisubstituted carbenium ions, vinyl cations undergo most of the reactions which are well established   for trisubstituted carbenium ions, e.g. substitution and elimination reactions, rearrangement reactions with and without participation of neighboring groups; they also

exhibit internal return effects etc. (Ref. 1). There is now good evidence that non-classical vinyl cations can exist, and a typical example is described below.

In the following, three different topics of the chemistry of disubstituted carbenium ions are discussed in more detail:

1. The chemistry of a non-classical vinyl cation, namely the 1-cyclobutenyl cation,

2. cycloaddition reactions of solvolytically generated vinyl cations with olefins, and

3. a novel route to phenyl cations via triple bond participation with vinyl cations.

THE CHEMISTRY OF THE 1-CYCLOBUTENYL CATION

Cyclic vinyl triflates, e.g. 1-cycloalkenyl triflates and nonaflates solvolyze with formation of the corresponding cyclic vinyl cations. In the solvolysis reactions of 1-cycloalkenyl triflates and nonaflates, the rates (e.g. in aqueous ethanol) decrease rapidly from cyclononenyl- to cyclohexenyl triflate; 1-cyclopentenyl triflate, and nonaflate solvolyse even more slowly. The rate-decrease from C_9 to C_6 is easily understood since the intermediate sp-hybridized vinyl cation prefers a linear structure, and this can be more easily accommodated by larger rings. 1-Cyclopentenyl triflate and nonaflate with a comparatively small ring therefore can not form a linear vinyl cation anymore but solvolyse with sulfur-oxygen cleavage (Ref. 4). 1-Cyclobutenyl nonaflate and triflate, on the other hand, react nearly as rapidly as those of C_8- and C_9. The surprisingly fast rates of the 1-cyclobutenyl derivatives have been attributed to the formation of the non-classical cation 2. The solvolysis mechanism of 1-cyclobutenyl nonaflate 3 in trifluoroethanol (TFE) is clearly S_N1; the only products formed are the trifluoroenol ether 4 and the acetal 5 (Ref. 5).
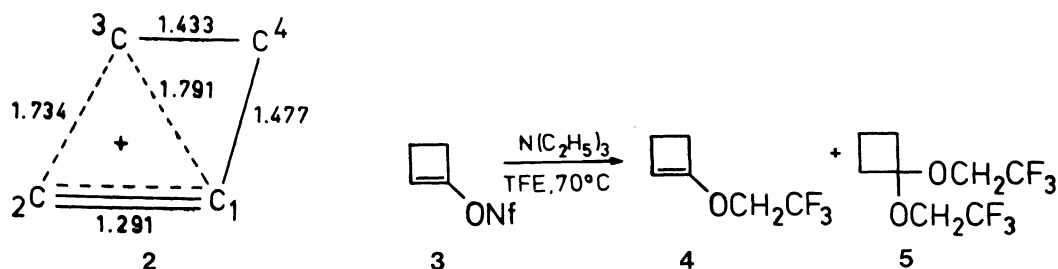
According to ab initio and MINDO/3-calculations, the intermediate 1-cyclobutenyl cation 2 is a bridged non-classical ion, in which C-3 is equi-distant from C-1 and C-2. The non-classical structure is due to the interaction of the vacant p-orbital on C-1 with the bent C-2-C-3 σ-bond (Ref. 6).

1-Cyclobutenyl cations 2' are also formed in the solvolysis reactions of 3-butenyl(homopropargyl) derivatives 6 and cyclopropylidenemethyl bromides 8. The solvolysis of 3', 6 and 8 leads, in spite of the different starting materials, to products of comparable compositions. Mainly the products 4', 5' and 9-12 are formed. This can be explained with an intermediate equilibrium of the vinyl cations 2' and 7 (Scheme 2) (Ref. 7).
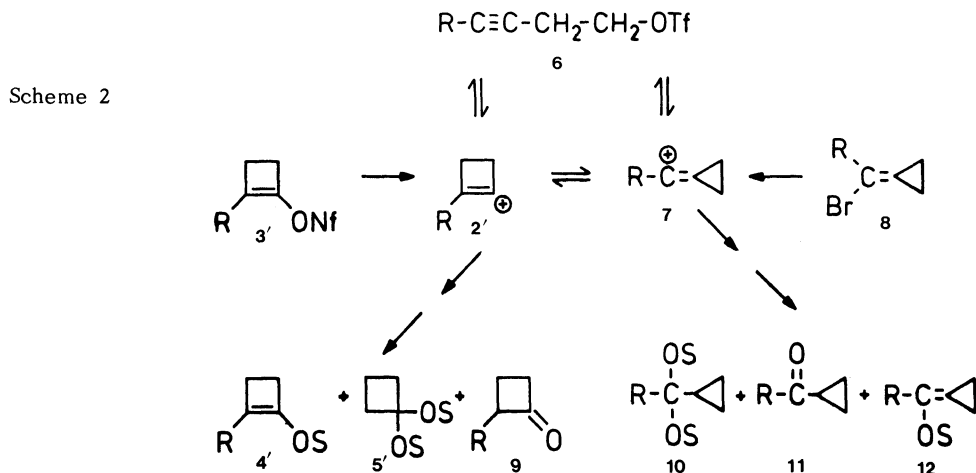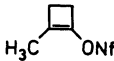
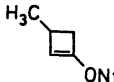$$R-C{\equiv}C-CH_2-CH_2-OTf$$

6

Scheme 2
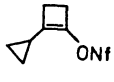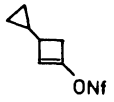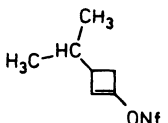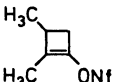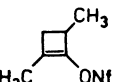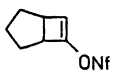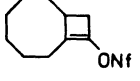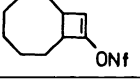
TABLE 1.   Absolute and relative rates of solvolysis of substituted 1-cyclobutenyl-nonaflate in 80% TFE

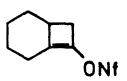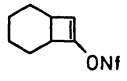| Nonaflate	Temp. [°C]	$k \cdot 10^4$ (s^{-1})	k_{rel} (70°C)	$\Delta H^{\ddagger}$
(cyclobutenyl)ONf **3**	70	0.152 ± 0.02 [a]	1	23.6
H$_3$C—(cyclobutenyl)ONf **13**	50	12.28 ± 0.14 [a]	600	20.2
H$_3$C—(cyclobutenyl)ONf **14**	50	0.301 ± 0.02	17	22.8
	70	2.52 ± 0.04		
CH$_3$—(cyclobutenyl)ONf **15**	70	1.4 ± 0.4	10	
(cyclopropyl)(cyclobutenyl)ONf **16**	50	8.74 ± 0.02	450	
(cyclopropyl)(cyclobutenyl)ONf **17**	50	0.281 ± 0.1	14	21.8
	70	2.09 ± 0.04		
(CH$_3$)$_2$CH—(cyclobutenyl)ONf **18**	50	0.252 ± 0.04	14	22.8
	70	2.10 ± 0.04		
(H$_3$C)$_2$(cyclobutenyl)ONf **19**	30	28.5 ± 0.4	1×10^4	
CH$_3$, H$_3$C (cyclobutenyl)ONf **20**	30	17.6 ± 0.5	5.5×10^3	
(bicyclo)ONf **21**	30	2.3 ± 0.4	900	20.6
	50	20.26 ± 0.4		
(bicyclo)ONf **22a**	15	70	4×10^4	
(bicyclo)ONf **22b**	30	3.05 ± 0.4	1.1×10^3	
(bicyclo)ONf **23a**	30	45	1.3×10^4	
(bicyclo)ONf **23b**	30	0.95 ± 0.4	400	

[a] Measured in ethanol–water.

The homopropargyl derivatives **6** react with participation of the triple bond via a S_N2-like transition state (Ref. 8) to form **2'** and **7**. The cyclopropylidenemethyl cations **7** are highly stabilized through interaction of the three-membered ring orbitals with the vacant p-orbital of the vinyl cation. Calculations (Ref. 6) have shown that the primary vinyl cation **7** (R = H) is about 5 – 7 kcal/mol lower in energy than **2'** (R = H). The existence of two stable $C_4H_5^+$-ions, which were assigned structures **2'** (R = H) and **7** (R = H) have been detected by mass spectroscopy in the gas phase (Ref. 9).

For the investigation of the stability, the rearrangement reactions, and the non-classical structure of the cyclobutenyl cation **2**, substituent effects in the 2-, 3-, and 4-position are important. We have synthesized and solvolyzed a series of substituted cylcobutenyl nonaflates of which the 3-substituted nonaflates are of special interest. In addition to the monocyclic cylcobutenyl nonaflates bicyclic systems also have been investigated. The results of the kinetic data in 80% TFE are summarized in Table 1 (Ref. 10).

The solvolysis rates of the differently substituted 1-cyclobutenyl nonaflates are very dependent upon the substituents. Higher rates are observed, if the reactive intermediate formed in the rate determining step, can be stabilized more by the substituent.

A methyl- or cyclopropyl group in the 2-position of the cyclobutenyl nonaflate causes an increase in their solvolysis rate by a factor of 600 and 450 respectively. The same substituents in the 3-position raise the solvolysis rates by a factor of 17 and 14 respectively, in comparison with the unsubstituted cyclobutenyl nonaflate **3**. The rate effects caused by the substituents in the 2- and 3-position of 1-cyclobutenyl nonaflates clearly show that the cyclobutenyl cations **2** formed indeed carry positive partial charges on carbon atoms 2 and 3. This is in accordance with the non-classical structure shown in **2**.

Substitution in the 2-position results in an additional steric effect contributing to an increase of the solvolysis rate. This is partly the reason for the higher solvolysis rate of the 2-substituted cyclobutenyl nonaflates in comparison with the 3-substituted isomers.

For comparison, the solvolysis rate of 4-methylcyclobutenyl nonaflate was measured: The rate is 10 times higher than the rate of the unsubstituted nonaflate **3**. This value is typical for the steric effect of a methyl group in a neighboring position to the nonaflate leaving group. It emphasizes the substituent effects in the 3-position of the cyclobutenyl cations, where a steric effect is not possible.

The cyclopropyl substituted nonaflates **16** and **17** do not solvolyze faster than the methyl substituted cyclobutenylnonaflates **13** and **14**. Hence the stabilizing effect of the methyl and the cyclopropyl group is only inductive. The isopropyl group in the 3-position in **18** has the same rate accelerating effect as the cyclopropyl group.

A methyl group in the 2-, 3- or 4-position of the 1-cyclobutenyl nonaflates leads to a rate increase of 600, 17, or 10. The dimethyl substituted nonaflates **19** and **20** show a rate increase of 10^4 and 5.5×10^3 times respectively over that of parent nonaflate **3**, in agreement with the additive effect of both the methyl groups in respective positions (Table 1).

The relative solvolysis rates of the bicyclic nonaflates **23a** and **22a** (1.3×10^4 and 4×10^4 respectively) are much higher than the rate of 2,3-dimethyl substituted cyclobutenyl nonaflate **19**, though both **22a** and **23a** can be considered as similarly disubstituted cyclobutenyl nonaflates. This can be explained on the basis of a higher ring strain of the bicyclic nonaflates, leading to an increased p-character of the σ-bonds in the four-membered ring, which in turn leads to a more favourable interaction of the C-2–C-3 σ-bond with the vacant p-orbital on C-1 in the non-classical cyclobutenyl cation formed. Moreover, the bicyclic nonaflates have higher ground state energies, which also cause a higher solvolysis rate. The ring strain increases from **23a** to **22a**; accordingly a higher solvolysis rate was measured for **22a** (Table 1).

The relative solvolysis rates of **21**, **22b** and **23b** are 900, 1100, and 400 respectively, which are higher than the additive rate effects that would have been found for alkyl substituents in the 3- and 4-position. This is also a result of the higher ring strain.

The products of the solvolysis of some of the nonaflates are listed in Table 2. The detailed results are described elsewhere (Ref. 10).

The products are formed by reaction of the equilibrating isomeric cations **2a, 6'** or **7'** with the solvent, as shown in Scheme 3. The product composition is very much dependent upon the substituents in the cyclobutenyl nonaflates.
Whereas with the non-substituted 1-cyclobutenyl nonaflate (**3**) no rearrangement reaction was observed, the product composition of the substituted cyclobutenyl nonaflates shows the following trend: Substituents in the 2-position favour the rearrangement of **2a** to form the cyclopropylidene methyl cation **7**. 3-Substituents on the other hand form the homopropargyl cation **6'** (cf. Scheme 3). In addition, the relative tendency for a rearrangement reaction is controlled by the substituent itself, e.g. the effect of a cyclopropyl group is much larger than the effect of a methyl or an isopropyl group. 3-Substituted cyclobutenyl cations (from the nonaflates **14**, **17** and **18**) rearrange more easily than the corresponding 2-substituted nonaflates. This points to a comparatively high stability of the secondary homopropargyl cation **6'** ($R^2 \neq H$)(Ref. 10).
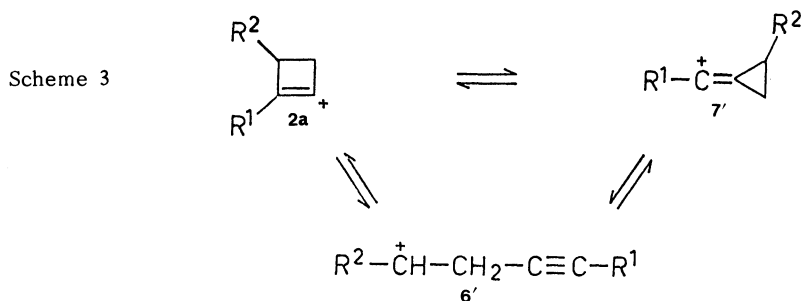
Scheme 3

TABLE 2. Major solvolysis products of selected 1-cyclobutenyl nonaflates in 100% TFE.

Nonaflate	Temp. °C	Products

CYCLOADDITION REACTIONS OF SOLVOLYTICALLY GENERATED VINYL CATIONS WITH OLEFINS

Cycloadditions of vinyl cations were reported (Ref. 11) during the investigations on electrophilic additions of hydrogen halides to alkynes and allenes. Also, allenyl cations can be reacted with dienes in cycloaddition reactions (Ref. 12).

Recently we described the first example of a cycloaddition reaction of solvolytically generated vinyl cations with olefins in which cyclobutenyl derivatives are formed in high yields (Ref. 13).

The solvolytic generation of vinyl cations for cycloaddition reactions can be carried out by two methods:

1. Reactive vinyl halogenides are treated with olefins in the presence of appropriate Lewis acids e.g. silver(I)- or copper(I)salts, or

2. vinyl triflates are solvolyzed directly in an olefin as the solvent.

For the silver salt method, silver tetrafluoroborate or hexafluoroantimonate are the most suitable salts, because they are soluble in inert solvents like dichloromethane or 1,2-dichloroethane. In addition, the corresponding anions are of low nucleophilicity. The highly reactive 1-bromo-1-(p-methoxyphenyl)-2-methyl-1-propene (24) was chosen as the precursor vinylbromide, which very easily forms the vinyl cation 25 in solvolysis reactions (Ref. 14). The products of the reaction of 24 with $AgBF_4$ and $AgSbF_6$ respectively and cyclic and acyclic olefins are listed in Table 3 (Ref. 15).

Cyclobutenes 26 are formed in the cycloaddition of the vinyl cation 25 with cyclic olefins, except in the case of cyclopentene and (E)-cyclooctene: With the isomeric 2-butenes, the main product is the cyclobutene 27. The structures of the cyclobutenes have been proven by ^{1}H-NMR spectroscopy as well as through their thermal valence isomerisation to form the corresponding dienes (Ref. 15b).

The reaction of 24 with $AgBF_4$, in all cases, also yields the vinyl fluoride 28, which is formed by the reaction of vinyl cation 25 with the tetrafluoroborate anion.

The formation of the cyclobutenes 26 (Table 3) could be related to the presence of silver ions in the reaction media. Silver, which very easily undergoes complex formation with unsaturated organic compounds could serve as a template catalyst, thereby supporting the formation of four-membered ring products. In this case, other complexing metal ions, e.g. the copper(I) ion, which easily forms complexes with olefins, should also catalyze the formation of four-membered ring products. The reaction of vinyl bromide 24 with copper(I)triflate olefin-complexes (Ref. 15b) indeed yields a product composition which is practically the same as in the reactions of 24 with $AgSbF_6$.

The stereochemistry of the silver catalyzed cycloaddition of vinyl cations has also been investigated with 1-bromo-1-(p-methoxy-phenyl)-1-propene (29). 29 was reacted with $AgBF_4$ to form the corresponding vinyl cation 30 in the presence of (Z)- and (E)-2-butenes.

The reaction of 30 with (Z)-2-butene leads to the cyclobutene 32 as the main product. (E)-2-Butene reacts to form the cyclobutenes 32 and 34 in a ratio of 4:1 (Scheme 4) (Ref. 15c).
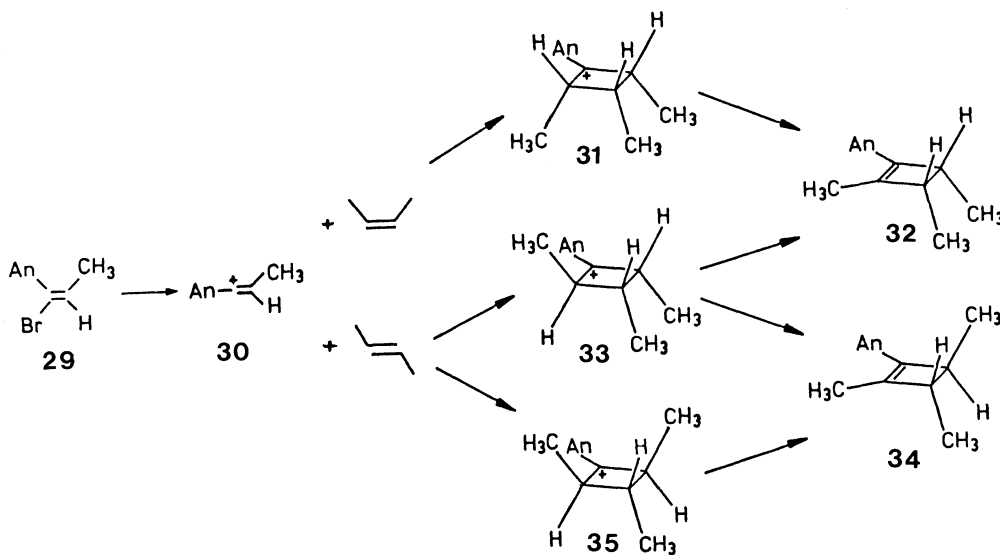
Scheme 4

The configuration of 32 and 34 was determined by ^{1}H-NMR spectroscopy. Additional evidence for the configuration was shown by their thermal stability. Thus, the product (Z)-cyclobutene 32 is thermally stable even at 170°C, while the (E)-isomer 34 rearranges quantitatively at the same temperature within one hour to form the butadiene 36.
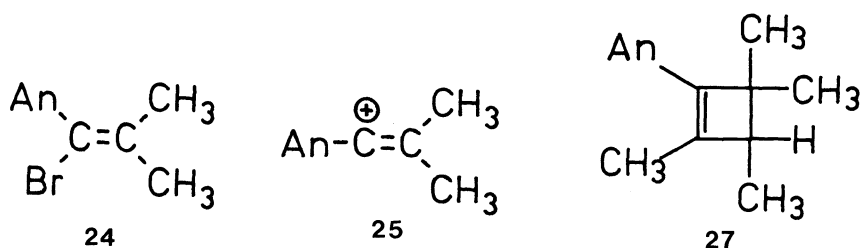
TABLE 3. Reaction of 1-(p-methoxyphenyl)-1-bromo-2-methyl-1-propene (**24**) with olefins in the presence of $AgBF_4$ or $AgSbF_6$.

Olefin	Silver-salt	Reaction products [%][a,b]	
		26	28
Cyclopentene	$AgBF_4$	–	5
n=3	$AgSbF_6$ [c]	–	–
Cyclohexene	$AgBF_4$	25	25
n=4	$AgSbF_6$	100	–
Cycloheptene	$AgBF_4$	73	12
n=5	$AgSbF_6$	85	–
(Z)-Cyclooctene	$AgBF_4$	49	22
n=6	$AgSbF_6$	71	–
(E)-Cyclooctene	$AgBF_4$	8	85
n=6	$AgSbF_6$	–	–
		27	
(Z)-2-Butene	$AgBF_4$	56	1
	$AgSbF_6$	80	–
(E)-2-Butene	$AgBF_4$	59	24
	$AgSbF_6$	85	–

[a]For a detailed presentation of all the products formed see Ref. 15b.

[b]Yield determined by gas chromatography.

[c]Mostly polymeric products were obtained.

34   **36**
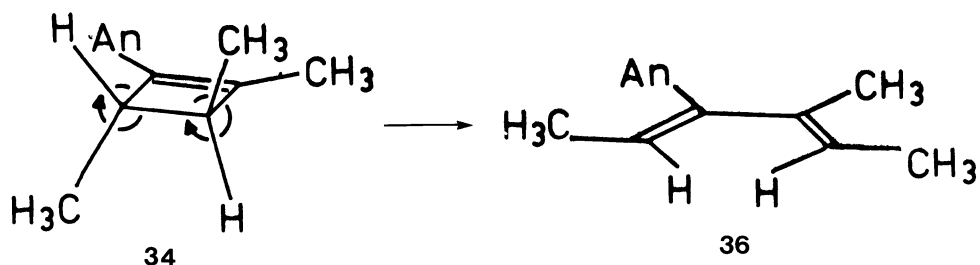
Because the ring opening of the cyclobutenes in a thermal reaction must be conrotatory, the (Z)-isomer **32**, due to the higher steric hindrance of the rotating methyl groups, is thermally more stable than the (E)-isomer **34**.

The cyclobutenes **32** and **34** are formed by elimination of a proton from the intermediate cyclobutyl cations **31**, **33** and **35**, which have been generated by the cycloaddition reaction of the vinyl cation **30** with the (Z)- and (E)-olefins. The stereospecific formation of **32** with (Z)-2-butene is only possible, if as an intermediate the all cis-cyclobutyl cation **31** is first formed (Scheme 4) (Ref. 15c).

The cycloaddition reaction is thus a syn-addition with respect to the olefin; with respect to the vinyl cation **30** endo-specificity occurs. Both observations are typical for a synchronous cycloaddition reaction. According to Scheme 4 vinyl cation **30** therefore reacts with (Z)- and (E)-2-butene in a $\pi^2 s + \pi^2 a$-cycloaddition to form the cyclobutenyl cations **31**, **33** and **35**. The nonstereospecific reaction with (E)-2-butene is in accordance with a one-step reaction. In the case of a stereospecific cycloaddition reaction to form the cyclobutyl cation **33**, the subsequent elimination reaction yields both cyclobutenes **32** and **34**.

If the silver ion not only plays an important role for the generation of the vinyl cations from vinyl halides, but also for the cycloaddition itself (template effect?), then a possible route to generate vinyl cations without the involvement of silver ions and its cycloaddition reactions would be especially interesting.

For this purpose, 1-(p-methoxyphenyl)-2-methyl-1-propen-1-yltriflate (**37**) was prepared and reacted with cyclic and acyclic olefins in the presence of a buffer. In addition, the triflate 37 was treated with some olefins with addition of $AgBF_4$ to test the influence of silver ions.

As can be seen from Table 4, all olefins in the silver free cycloaddition reactions, do not form cyclobutenes anymore, but the cyclopropane derivatives **38** and **39** respectively, are now the main products. By addition of $AgBF_4$ the product composition again is shifted towards the formation of the cyclobutenes **26** (Table 4) (Ref. 15b).
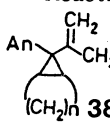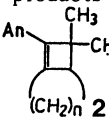
The reaction of triflate 37 with (Z)- and (E)-2-butene is stereospecific. The cyclopropane derivative 39a is formed from (Z)-2-butene and 39b is formed from (E)-2-butene.

37   **38**   **39**

a: $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$

b: $R^1 = R^4 = CH_3$, $R^2 = R^3 = H$
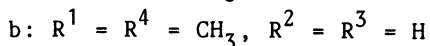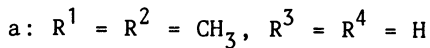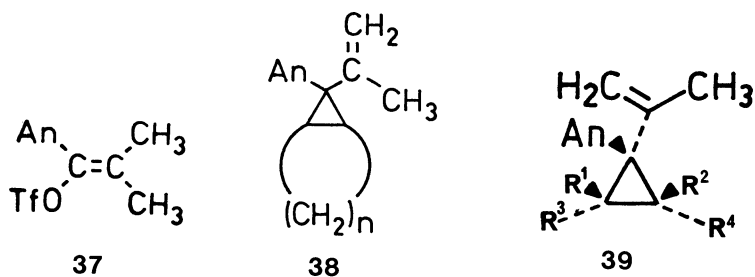
For the reaction of vinyl cation **25** with olefins, the routes given in Scheme 5 are feasible. All the pathways given in Scheme 5, similar to the ketene-addition to double bonds, start with a crossed arrangement of the vinyl cation **25** with the olefin. Only this arrangement allows an optimum overlap of the orbitals and a low steric hindrance of the substituents (Ref. 16). A detailed discussion of the reaction mechanism will be given elsewhere (Ref. 15b). The preferred formation of cyclopropane derivatives is a good indication that the reaction goes through a [2+1]-mechanism (route C in Scheme 5), which has been proposed theoretically (Ref. 17).

TABLE 4.   Reaction of 1-(p-methoxyphenyl)-2-methyl-1-propen-1-yl triflate (37) with olefins.

Olefin	Added salt	Reaction products [%][a,b]	
		An-⟨CH₂=C(CH₃)⟩(CH₂)n **38**	An-⟨C=C(CH₃)(CH₃)⟩(CH₂)n **26**
Cyclopentene n=3	–	70	–
Cyclohexene n=4	–	60	–
Cycloheptene n=5	–	80	–
	1 eq. AgBF₄	–	79
(Z)-Cyclooctene n=6	–	83	5
	1 eq. AgBF₄	6	67
(E)-Cyclooctene n=6	–	–	90
		39	27
(Z)-2-Butene	–	68	17
(E)-2-Butene	–	63	11

[a]For a detailed presentation of all the products formed see Ref. 15b.

[b]Yield determined by gas chromatography.

Scheme 5
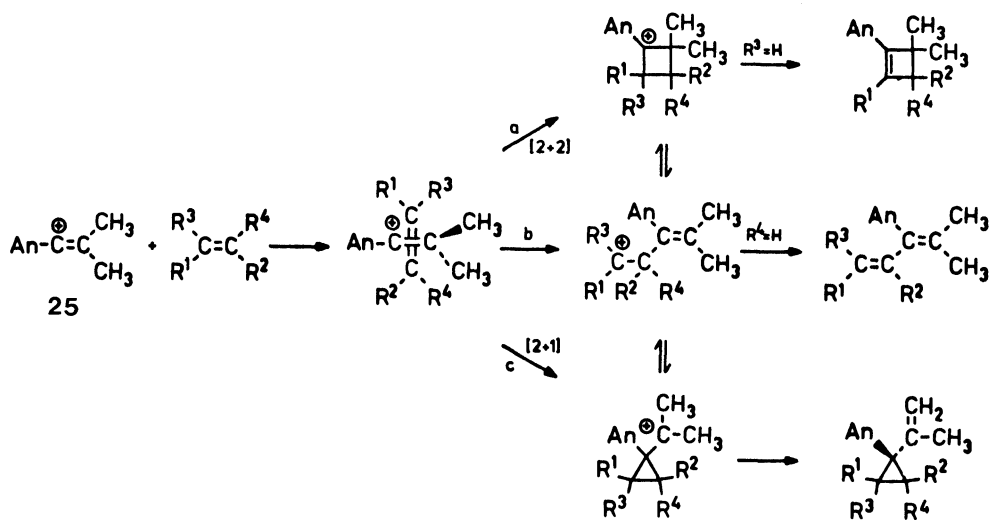
The role of the silver or copper ions has not been investigated yet in detail, but there are good indications (Ref. 18), that not the free silver ion, but an olefin-silver complex, containing two olefin molecules reactswith the vinyl bromide. The reaction pathway is thereby directed towards four-membered ring compounds via a template effect.

A NOVEL ROUTE TO PHENYL CATIONS

As we have shown earlier vinyl cations can react with participation of double and triple bonds to form cyclic products. As an example the 6-octyn-2-en-2-yl triflate **40** is given. This solvolyses with participation of the triple bond via the intermediate cyclic vinyl cation **41** to form the product **42** (Ref. 20).
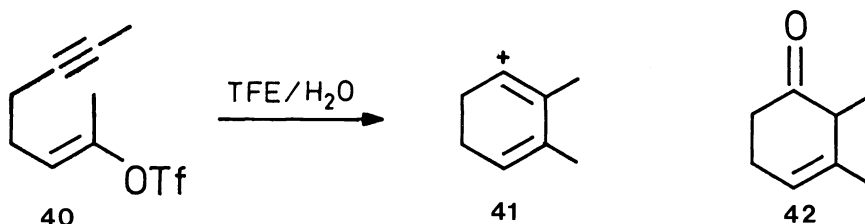
The formation of a vinyl cation with triple bond participation can be extended to 1,3-diene-5-yn-yl triflates **43** (Ref. 20). A necessary condition for participation of the triple bond in **43** is an antiposition of the triflate anion leaving group with respect to the triple bond. The appropriate anti-isomer can be easily distinguished by NMR methods from the one with a syn-arrangement of the triflate group. The triflates (Z)–**43a**, (E)–**43a** and (E)–**43b** were solvolyzed under the conditions given in Table 5 (Ref. 21).

The solyolysis products were identified by the usual methods (capillary GLC, GLC-mass spectroscopy, ^{1}H-NMR spectroscopy and by comparison with authentic samples). The product composition clearly demonstrates that the aromatic products **47a** and **47b**, **49a** and **49b** and **50** formed via the intermediate phenyl cations**44a** and **44b**, which are clearly generated by triple bond participation during the vinyl cation formation from **43a** and **43b**. This is consistent with a dependence of the formation of the aromatic products upon the stereochemistry of the triflate: Whereas from (Z)–**43a** in which the syn-stereochemistry for participation of the triple bond is not favourable, only 1.4% of the substitution product **47a** arising from the intermediate phenyl cation is formed, (E)–**43a** with the favourable anti-stereochemistry for participation of the triple bond yields the ether **47a** as a main solvolysis product. Solvolysis of (E)–**43b** in TFE also gives **47b** as the main product; the corresponding (Z)-isomer of **43b** only yields 9% of **47b**. In the solvolysis of both (E)–**43a** and (E)–**43b** in TFE the phenyl trifluoromethanesulfonates **49a** and **49b** are formed, indicating an internal return process via the intermediate phenyl cations**44a** and **44b**, respectively.

TABLE 5.   Solvolysis products of dienynyl triflates (Z)–**43a**, (E)–**43a** and (E)–**43b** (Ref. 21).

Substrate No.	Solvent	43	45	47	48	49
(Z)–**43a**[b]	100% TFE[c]	1	29.4	1.4	19.5	–
	100% C_2H_5OH[d]	1	70	–	1	–
(E)–**43a**[b]	100% TFE[c]	1	19.5	26.4	7.8	2.1
	100% C_2H_5OH[d]	52.4	18.7	6.1	–	–
(E)–**43a**[b]	TFE+H_2O[c,e] dioxane+LiBr (excess)	–	–	14.4	41.2	1
(E)–**43b**[f]	100% TFE	–	21	24.6	15.6	9.3

[a] Yield determined by gas chromatography.   [d] X = CH_2CH_3

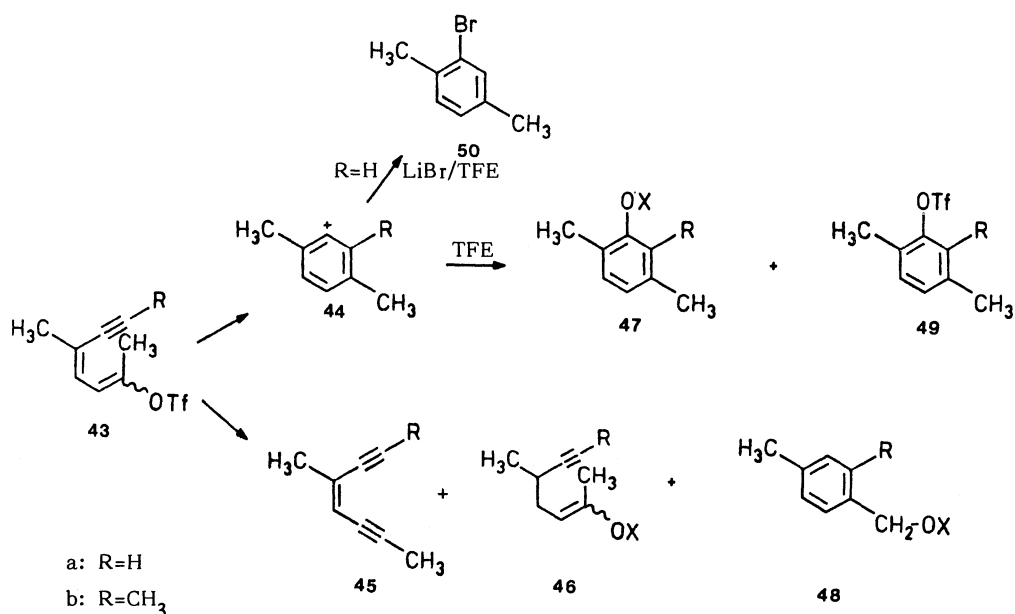[b] R=H   [e] 16.6% of the bromide **50** was also found.

[c] X = CH_2CF_3 [f] R=CH_3

The solvolysis of **43a** in TFE was also carried out with an added nucleophile, the bromide ion, to trap the intermediate phenyl cation **44a**. 16.6% of the expected bromo-p-xylene (**50**) was formed (Scheme 6).


Scheme 6

The other products listed in Table 5 are characteristic for the solvolysis of the triflates with formation of the corresponding vinyl cations. Besides cyclization the vinyl cations react via elimination to give the dienes **45a** and **45b**; substitution products **46** were not found in this case. The composition of the products reflects typical solvent effects for solvolysis reactions. In TFE a solvent of high ionizing power, the highest percentage of cyclization products are observed. The mechanism for the formation of the benzylic derivatives **48a** and **48b** is reported elsewhere (Ref. 22).

In addition to the acyclic 1,3-diene-yn-yltriflates **43** the solvolyses of the (Z)- and (E)-triflates **51** have been also investigated. The triflate (E)-**51** solvolyses in trifluoroethanol predominantely via the intermediate naphthyl cation **52** to form the naphthyl ether **53** and the naphthyl triflate **54**. Addition of an external nucleophile like bromide ion leads to the formation of 1-bromo-2,3-dimethylnaphthalene (**55**), thereby confirming the intermediate formation of the naphthyl cation **52**. The corresponding (Z)-triflate having the triflate leaving group in the syn-position to the triple bond does not solvolyze to form naphthyl derivatives, but reacts mainly with formation of elimination products (Ref. 23).
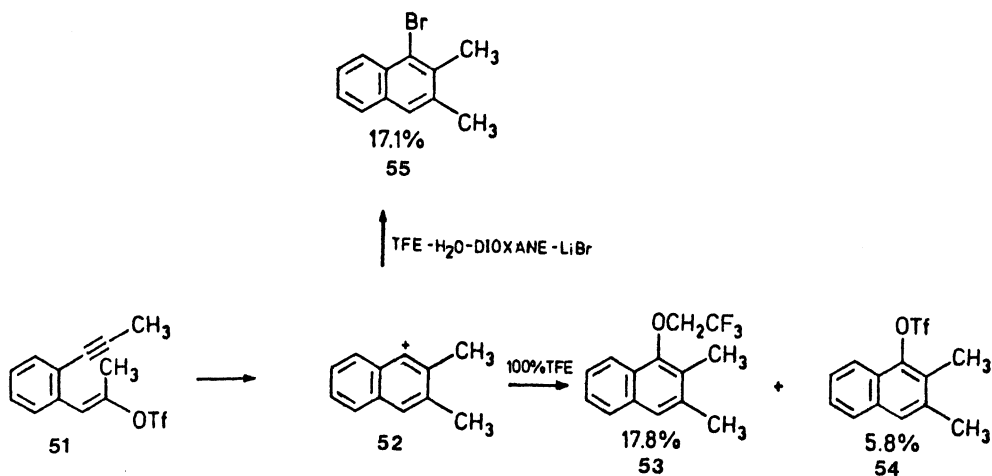
A phenyl cation can also be generated by dissociative ionization of the dienynyl bromide **56** in the gas phase. Electron impact ionization at 70 eV of **56** with loss of $Br^\cdot$ furnished a $C_6H_5^+$ ion whose collisional activation mass spectrum (CAMS) is identical in all respects with the CA-mass spectrum of a $C_6H_5^+$ ion, which for example is accessible by loss of $Br^\cdot$ from the molecular ion of bromobenzene (Ref. 24).
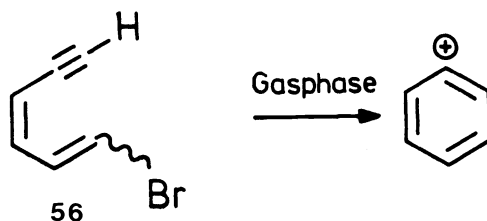
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