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Rearrangements in Vinyl Cations

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The literature data on the rearrangements of vinyl cationoid intermediates arising in the solvolysis of various vinyl derivatives and in the addition of cationoid reagents to the triple bond are examined and the differences between the rearrangements of vinyl cations and those of the "usual" saturated carbonium ions are demonstrated. The influence of the structure of vinyl cationoid intermediates on the rate and mode of rearrangements of various types (the migration of alkyl and aryl groups, shifts via the double bond and to a double bond, and higher-order shifts) are discussed. The bibliography includes 87 references.

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I. INTRODUCTION

Vinyl cations belong to the class of "hot" carbonium ions and it proved possible to detect them by NMR [1-4] as species stable in solution only in isolated instances. The chemistry of vinyl cations (VC) is therefore developing at the present time mainly on the basis of the study of the characteristics of reactions occurring under conditions most favourable for the formation of cationoid intermediates of the VC type. Either the solvolysis of vinyl derivatives containing readily removable groups such as triflate [trifluoromethanesulphonate(OTf)] or nonaflate [nonafluorobutanesulphonate (ONf)] or the addition of cationoid reagents to the triple bond are usually employed. In both cases it is better to use polar and non-nucleophilic media.

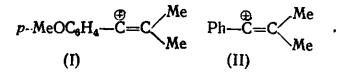
The question of the validity of the hypothesis of the intermediate formation of VC in these processes is by no means always clear, because it is sometimes difficult to exclude the possibility of alternative pathways leading to the formation of the observed products, for example, the elimination–addition or addition–elimination mechanisms in the solvolysis of vinyl derivatives or the synchronous Ad_E3 mechanism in the addition to the C≡C bond.

The choice between possible mechanisms is usually made on the basis of the study of the kinetics and stereochemistry in combination with data on the composition of the reaction products formed under various conditions. However, one of the principal criteria indicating the intermediate formation of VC is as a rule the observation of sextet rearrangements. Although, strictly speaking, this criterion does not constitute total proof, it has been used traditionally also in the more general case involving the study of the mechanisms of any reactions with possible involvement of carbonium ions as intermediates.

The characteristics of sextet rearrangements of the "usual" carbonium ions have been studied very widely and have been considered in detail in a series of monographs and reviews[5-8]. The data on the rearrangements of VC are much more scanty and limited, but in recent years numerous instances of reactions of this kind have been described and in the present review an attempt is made to survey these data†.

† Different aspects of the chemistry of VC have been examined in a series of reviews[16-23] published recently, which reflects the enhanced interest in these intermediates.

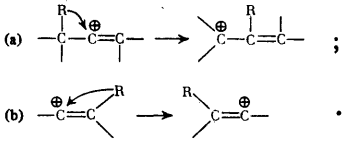
In discussing the characteristics of the rearrangements of C≡C, it is necessary to have a clear idea about their structure. At the present time this problem has still not been adequately investigated experimentally, although the available calculations in the literature[9-12] have shown that a linear structure with an *sp*-hybridised carbon atom having a positive charge is preferred for VC. This structure of VC has been confirmed[1,4] by ^{13}C and ^{1}H NMR for VC (I) and (II) in which the alkyl groups proved to be equivalent:



(I) (II)

The results of solvolytic reactions also indicate a linear structure of VC. Thus the rate of solvolysis of cycloalkenyl triflates in 50% aqueous ethanol solution at 75 °C increases with increase of ring size, while the the cyclo-octene derivative it becomes comparable to the rate solvolysis of (*E*)-1-methyl-1-propenyl triflate[13-15]. The relatively low rate of solvolysis of cyclohexenyl triflate can be explained by the impossibility of attaining a linear geometry in the vinyl-cation-like transition state in rings of this size.

The examples of rearrangements in vinyl-cationoid intermediates (VCI) available at the present time are mainly 1,2-shifts and can be divided into two large groups: (a) rearrangements with migration to the double bond leading to allyl cations and (b) rearrangements via the double bond, as a result of which one VC isomerises to another:



The less numerous rearrangements occurring as a result of higher-order shifts do not fit within the framework of this classification, because they involve simultaneously saturated and unsaturated fragments of the molecule and their usual result is the formation of a carbonium ion centre at a saturated carbon atom.

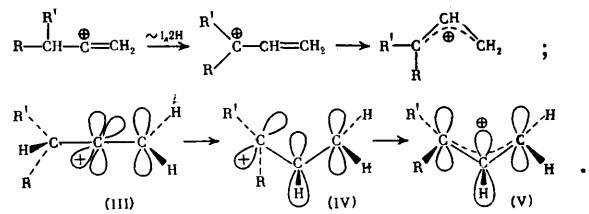
For each of the above type of rearrangements, there is a possibility of a more detailed classification based on the atoms or groups which migrate under these conditions.

II. REARRANGEMENTS WITH MIGRATION TO THE DOUBLE BOND

1. The 1,2-Hydride Shift

The hydride shifts in the chemistry of the "usual" carbonium ions are very common and usually take place extremely readily (the activation barrier to such rearrangements is frequently less than 12–16 kJ mol^{-1}). For example, the 1,2-hydride shift in the 2-butyl cation is so fast compared with the NMR time scale that even at −120 °C only a single average signal due to the CH_3 group is observed in its ^{1}H NMR spectrum[24].

The 1,2-hydride shifts in VC take place with much more difficulty and have been described for a fairly limited number of examples. This fact may appear fairly strange since this type of 1,2-shift should result in the conversion of an unstable VC to the stabilised system of the allyl cation and hence the thermodynamic driving force of such rearrangements should be fairly considerable. However, the difficulty of the 1,2-shifts in VC can be explained by considering the stereochemistry of the orbital interactions in this process. Indeed the conversion of the linear VC (III) into the planar resonance-stabilised allyl cation (V) should proceed via a non-planar transition state (or intermediate) (IV), in which resonance stabilisation is impossible and which is additionally destabilised by the presence of an orthogonal π-system:

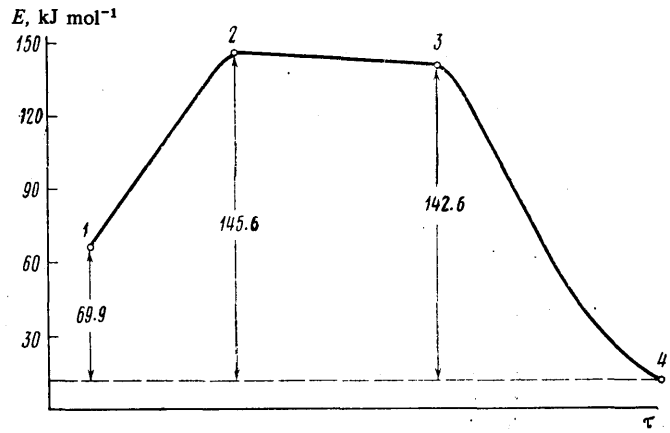


This is apparently why the activation barrier to the above process is in fact significantly higher than for the 1,2-shift in the "usual" carbonium ions.

The energetic pathway of the 1,2-hydride shift in VC, obtained[12] on the basis of the available calculations of the energies of the isomeric $C_3H_5^{\oplus}$ ions, is illustrated in the Figure.

The 1,2-hydride shifts in VC have been studied in greatest detail in connection with the protonation of alkynes in "magic" acid (FSO_3H–SbF_5). It has been found that in none of the instances investigated is it possible to observe directly (by ^{1}H NMR) the formation of VC even at low temperatures (−78 °C), although these conditions have almost always proved to be suitable for the observation of carbonium ions of other types. It has been shown that the result of the protonation of the triple bond, observed with the aid of ^{1}H NMR, is the formation of the allyl cation (produced by the unimolecular 1,2-hydride shift in the VCI) or an oligomeric product (a bimolecular process). The latter pathway is usually preferred when the reaction is carried out at low temperatures (78 °C). An increase of temperature as a rule leads to a significant increase of the yield of rearrangement products, which reflects the usual kinetics of unimolecular and bimolecular reactions.

The 1,2-hydride shift takes place most readily in VC formed from alkynes, in which there are two alkyl substituents at the α-carbon atom. The rearrangements in such alkynes take place at −20 °C. The activation barrier for such systems is lower than the value indicated in Fig.1 owing to the stabilising effect of the alkyl groups. In alkynes with only one alkyl substituent at the α-carbon atom the 1,2-hydride shifts take place at higher temperatures (7–20 °C). The protonation of alkynes without branches at the α-carbon atom is more complex and in this instance it is not possible to detect the formation of allyl cations introduced by the 1,2-hydride shift in the VC formed initially.

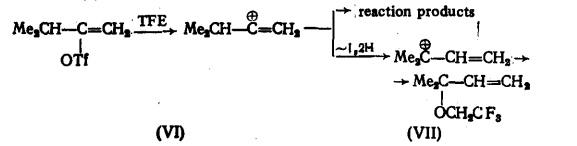


The energetic pathway of the 1,2-hydride shift in the vinyl cation:

1) $Me-\overset{\oplus}{C}=CH_2$; 2) $H_2C\overset{H}{\overset{+}{\cdots}}C=CH_2$; 3) $H_2\overset{\oplus}{C}-CH=CH_2$;

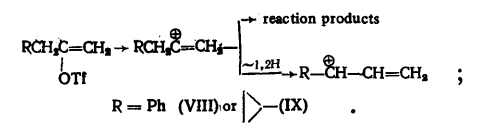
4) $H_2C\overset{CH}{\overset{+}{\cdots}}CH_2$.

The only other example in which a 1,2-hydride shift to the double bond is observed is the solvolysis of isopropylvinyl trifluoromethanesulphonate (VI) in trifluoroethanol (TFE). The ether (VII), which is believed[26] to be formed as a result of the 1,2-hydride shift in the VCI formation stage, was isolated together with the normal solvolysis products under these conditions:



However, the authors do not consider the possibility of its formation via the elimination–addition mechanism.

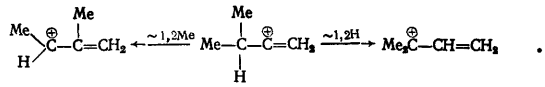
This result appears to be unexpected also because, for example, in the solvolysis of 1-benzylvinyl triflate (VIII) [27] and 1-cyclopropylmethylvinyl triflate (IX),[28] compounds which might be formed via a 1,2-hydride shift in the VCI are not detected among the products, although the presence of a stabilising substituent at the allyl carbon atom in the given systems should facilitate such a transition:



2. The 1,2-Shifts of Methyl Groups

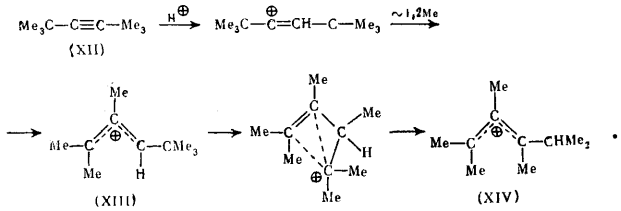
The characteristics of the 1,2-hydride shifts in VCI mentioned above, leading to an increase of the activation barrier compared with the rearrangements in the "usual" carbonium

ions, apply equally to the 1,2-shifts of methyl groups. In this instance too the number of examples is negligibly small compared with the number of studies on the 1,2-migrations in the "usual" carboniun ions. As will be seen from further exposition, the 1,2-shift of the methyl group is observed in compounds with a t-butyl substituent at the carbon atom with a positive charge. This is not surprising, since, in the presence of a hydrogen atom attached to an α-carbon atom, the hydride ion migrates, as has been observed in the protonation of alkynes[25], as a result of which the cation (X) formed is more stable than the alternative cation (XI):



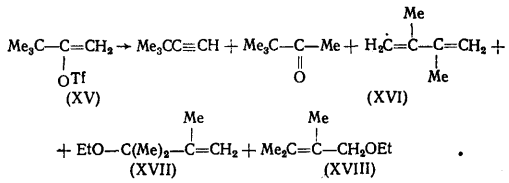
(XI) (X)

The protonation of t-butylacetylene and 2-t-butyl-1-methylacetylene at −20 °C in FSO_3H-SbF_5 leads to the formation of the corresponding allyl cations[25], which indicates the occurrence of 1,2-methyl shifts in the VCI formed initially. At a lower temperature (−78 °C) complex mixtures of oligomerisation products are formed in these reactions. However, the rearrangement involving the sterically hindered di-t-butylacetylene (XII) is observed also at −78 °C. In this instance the rearrangement is more far reaching and, instead of the signals of the allyl cation (XIII), the ^1H NMR spectrum shows signals due to the carbenium ion (XIV), which is apparently formed as a result of the rearrangement of the homoallyl cation:



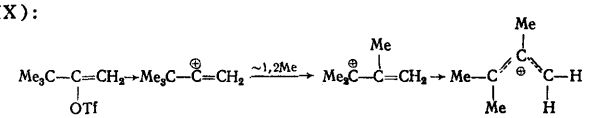
(XII) (XIII) (XIV)

The solvolysis of t-butylvinyl triflate (XV) in aqueous ethanol solution yields t-butylacetylene as the main product, but this is accompanied by the formation of 10–15% of 2,3-dimethylbutadiene (XVI) and of the rearranged alcohols and ethers (XVII) and (XVIII):[29]



(XV) (XVI) (XVII) (XVIII)

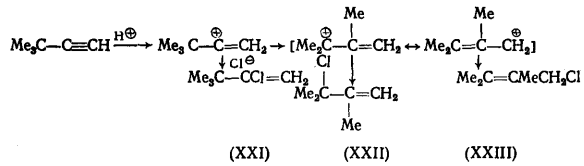
The products (XVI)–(XVIII) were obtained as a result of the 1,2-shift of the methyl group in the VC (XIX) formed initially and further transformations of the isomeric cation (XX):



(XV) (XIX) (XX)

Analogous products are formed also in the acetolysis of compound (XV). The study of this process in CH_3COOD showed that deuterium is not incorporated in the reaction products and the alternative mechanisms of the formation of these products via addition–elimination or elimination–addition processes do not therefore occur and a rearrangement in the VCI takes place[30].

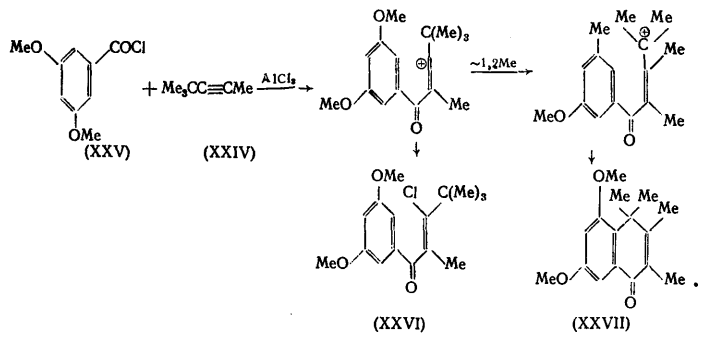
The addition of hydrogen halides to acetylenes is not usually accompanied by rearrangements[31], but in the interaction of t-butylacetylene with HCl without a solvent (the alkyne and dry HCl are mixed in a closed vessel at approximately −180 °C and the temperature is then raised to room temperature) the rearrangement products (XXII) and (XXIII) were isolated in 10–15% yield together with the normal reaction product (XXI):[32]



(XXI) (XXII) (XXIII)

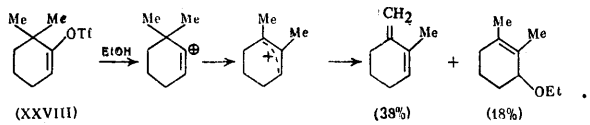
With increase of the amount of HCl to give a tenfold excess, the yield of rearranged products increases to 64%.

In the acylation of 4,4-dimethylpent-2-yne (XXIV) with 3,5-dimethoxybenzoyl chloride (XXV) in the presence of $AlCl_3$, 5–10% of the product of the 1,2-migration of the CH_3 group [compound (XXVII)] is formed together with β-chlorovinyl ketone (XXVI):[33]



(XXV) (XXIV) (XXVI) (XXVII)

The 1,2-migration of the methyl group has also been observed in the solvolysis of the cyclohexenyl triflates (XXVIII) with two methyl groups at the α-carbon atom[34]:

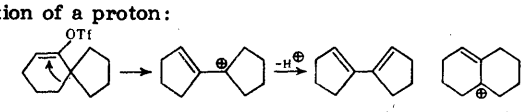


(XXVIII) (38%) (18%)

3. Rearrangements Involving a Change in the Cyclic System of Alicyclic Molecules

Most of the rearrangements involving an alteration of the skeleton of alicyclic compounds should be included in the class of rearrangements via the double bond of VC and these will be considered below.

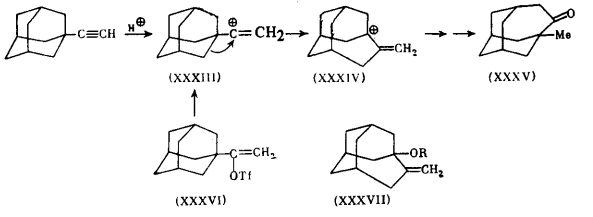
However, there are several examples which can be regarded as rearrangements with migration to the double bond. Thus the main product of the solvolysis of spiro-vinyl triflate (XXIX) in 60% aqueous ethanol or 50% aqueous TFE (in the presence of pyridine buffer) at 130 °C is the diene (XXXI). The authors[35] explain its formation by concerted ionisation and migration with the probable anchimeric participation of a bond of the cyclohexane ring in a convenient position, which leads to the formation of the carbenium ion (XXX) and the latter is converted into compound (XXXI) as a result of the elimination of a proton:



(XXIX) (XXX) (XXXI) (XXXII)

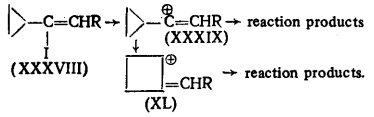
Important evidence in support of this concerted mechanism is the absence of compounds among the reaction products whose formation would have corresponded to the intermediate generation of the carbonium ion (XXXII). Its formation might have been expected by analogy with the above example of the migration of one or two geminal methyl groups in the solvolysis of compound (XXVIII). However, the virtually quantitative (>90%) yield of the diene (XXXI) shows that none of the spiroalkyl bonds of the cyclopentane ring in compound (XXIX) is involved in the migration.

Another example is the conversion of the adamantane system into the homoadamantane system. The hydration of adamantylacetylene catalyed by mercury salts takes place normally and leads to adamantyl methyl ketone[36]. However, in the protonation of adamantylacetylene with 90% H_2SO_4 in hexane at −5 °C 3-methyl-4-homoadamantanone (XXXV) is formed together with the normal product—adamantyl methyl ketone[37]:



Its formation can be explained by the rearrangement of the adamantylvinyl cation (XXXIII) to the homoadamantyl cation (XXXIV). The solvolysis of the vinyl triflate (XXXVI) confirms the proposed mechanism of the rearrangement. Depending on the conditions of the solvolysis[30], the main products are either elimination products (in 60% ethanol and acetic acid with a buffer) or rearranged products (in TFE); thus the use of a less basic solvent promotes the rearrangement, which confirms that the latter takes place via the VCI (XXXIII). It was also shown that the further transformation of the cation (XXXIV) into the final reaction products proceeds under the influence of an acid, since in the solvolysis in TFE with a buffer the main reaction products were compounds of the type of (XXXVII, R = CH_2CF_3 or H). If the CF_3SO_3H evolved in the solvolysis is not neutralised, the above compounds rearrange to compound (XXXV). It must be emphasised that the driving force of the rearrangement of the VC (XXXIII) should apparently be considerable, since the increasing strain of the system on passing from adamantane to homoadamantane does not prevent the rearrangement.

The rearrangement with participation of the bonds of a cyclic substituent is observed also in the solvolysis (noncatalysed or catalysed with silver salts) of 1-cyclopropyl-1-iodovinyl compounds of the type of (XXXVIII):[38–40]:



Despite the fact that the cyclopropane ring has a stabilising influence in the given systems on the VC (XXXIX) formed initially, the latter partly rearranges to the allylic cyclobutyl cation (XL) and up to 14% of cyclobutane derivatives were detected among the reaction products. Study of the temperature variation[39] showed that the yield of the rearranged products increases with temperature.

III. REARRANGEMENTS VIA THE DOUBLE BOND

As stated above, in the 1,2-shifts via the double bond one VCI rearranges to another. Therefore the driving force of such rearrangements is the formation of a more stable VCI. Naturally the mode and extent of such rearrangements depend significantly, apart from other factors (the nature of the solvent, the nucleophiles present in the medium, etc.), on the stabilising influence of the substituents in both the initial and the rearranged VCI.

1. The 1,2-Hydride Shift

The 1,2-hydride shift of the type under consideration should take place most readily in those cases where the initial intermediate is the primary VC (XLI), since the conversion of the latter into compound (XLII) should be a thermodynamically favoured process [according to calculations for the gas phase, compound (XLII) is more stable to the extent of 67 kJ mol^{-1} than compound (XLI)]:[12]

$$\underset{\text{(XLI)}}{MeCH=\overset{\oplus}{C}H} \rightleftarrows \underset{\text{(XLII)}}{Me\overset{\oplus}{C}=CH_2}$$

However, because of the low stability of the initial VC, the formation of this type of intermediate is unlikely and apparently occurs only in exceptional cases (see, for example, Hanack et al.[41]). Accordingly, mechanisms which do not require the intermediate formation of a primary VC are as a rule more justified in the interpretation of the results of the reactions.

For example, in the reactions of *cis*- and *trans*-β-bromostyrenes (XLIII) with $MeCO_2Ag$ in MeCOOH the formation of acetophenone as the main product (together with phenylacetylene) was observed[42]. It was also found that in the course of the reaction there is no 1,2-shift to the phenyl group and it was suggested that the hydride ion migrates in the VC:

$$\underset{\text{(XLIII)}}{Ph-{}^{14}CH=CHBr} \rightarrow Ph-{}^{14}CH=\overset{\oplus}{C}H \rightarrow Ph-{}^{14}\overset{\oplus}{C}=CH_2 \rightarrow Ph-\underset{\underset{O}{\|}}{{}^{14}C}-Me.$$

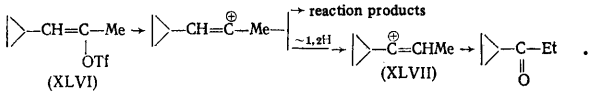
However, it was later established[43] that the successive elimination–addition mechanism is more probable for the solvolysis of both β-bromostyrenes and other similar substrates[44]. There is good reason to consider mechanisms involving VC in those cases where a secondary VC is formed initially. For example, in the solvolysis of (*E*)- and (*Z*)-1-methyl-2-phenylvinyl triflates (XLIV) the main products are an alkyne and an allene. However, they are accompanied by the formation of between 3 and 17% (depending on the conditions) of ethyl phenyl ketone (XLV), produced as a result of the 1,2-hydride shift via the double bond in the VCI:[43]

$$\underset{\text{(XLIV)}}{PhCH=\underset{\underset{Me}{|}}{C}-OTf} \rightarrow PhCH=\overset{\oplus}{C}-Me- \begin{cases} \rightarrow \text{reaction products} \\ \xrightarrow{\sim 1,2H} \underset{\text{(XLV)}}{Ph\overset{\oplus}{C}=CHMe \rightarrow Ph-\underset{\underset{O}{\|}}{C}-Et} \end{cases}.$$

Although in the given instance synchronous elimination takes place to a considerable extent (this is manifested, in particular, by the higher rate of solvolysis of the *Z*-isomer compared with the *E*-isomer), ethyl methyl ketone (XLV) is not formed as a result of the hydration of methylphenylacetylene, since the latter is not hydrated under the reaction conditions and is isolated unchanged.

An analogous 1,2-hydride shift has been observed also in the solvolysis of (*E*)- and (*Z*)-2-cyclopropyl-1-methylvinyl triflates (XLVI).[26,45] The yield of cyclopropyl ethyl ketone

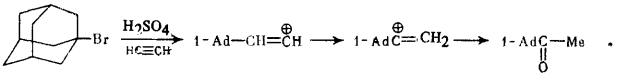
(XLVII), formed as a result of the rearrangement of the VCI, is 11–17%. In contrast to the previous case, in this instance the solvolysis via the formation of the VCI was not rigorously demonstrated, but the composition of the product and the ratio of the rates of solvolysis of the *E*- and *Z*-isomers suggest that the solvolysis does in fact proceed mainly via this mechanism:



(XLVI) (XLVII)

It is of interest that, under comparable solvolysis conditions (3 : 2 or 4 : 1 TFE–H_2O mixture at 80 °C), the yield of ethyl phenyl ketone (4.7–5.9%) is smaller by a factor greater than two than the yield of cyclopropyl ethyl ketone (11.1 to 16.9%), which is associated, according to the authors[26,43], with the greater ability of the cyclopropane ring to stabilise the α-cationic centre.

A 1,2-hydride shift via the double bond has also been suggested to account for the results of the reaction of 1-adamantyl bromide (XLVIII) with acetylene in H_2SO_4,[46,47] leading to the formation of 1-adamantyl methyl ketone (XLIX) as the main product (40%):

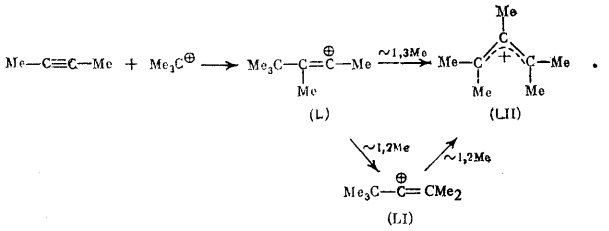


(XLVIII) (XLIX)

However, a vulnerable feature of this mechanism is undoubtedly the formation of the primary VC and the reaction probably proceeds in reality via a different pathway.

2. The 1,2-Shifts of the Methyl Groups

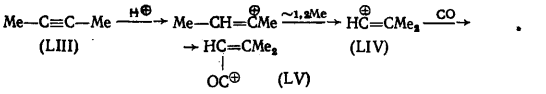
The ^1H NMR spectra of the products of the addition of the t-butyl cation (obtained via the reaction of t-C_4H_9Cl with $SbCl_5$ in SO_2) to but-2-yne showed[48] that, even at low temperatures (-75 °C), the pentamethylallyl cation (LII) is formed exclusively. It can be formed either as a result of a single 1,3-shift of the methyl group or as a result of two consecutive 1,2-shifts:



(L) (LII) (LI)

This problem was solved in the alkylation of but-2-yne by $(CD_3)_3CCl$; on the basis of the distribution of the D label, it was shown that the allyl cation (LII) is formed as a consequence of two consecutive 1,2-shifts of the CH_3 groups[48]. Thus this reaction is a unique example in which both types of rearrangements in VC are observed in succession: initially via the double bond [(L) → (LI)] and then via migration to the double bond [(LI) → (LII)]. This example also shows apparently that two consecutive 1,2-methyl shifts instead of a single 1,3-migration are preferable for VC, as for the "usual" carbonium ions.

A fairly unusual rearrangement has been observed[49] when a mixture of but-2-yne and CO was passed into the "superacid" medium ($FHSO_3$–SbF_5):



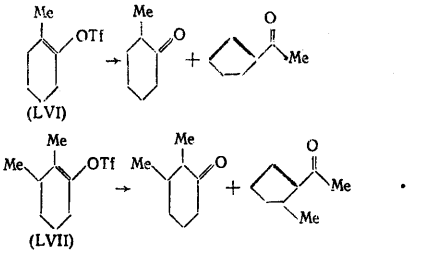
(LIII) (LIV) (LV)

The acylium ion (LV), believed[49] to be capable of formation as a result of a 1,2-shift of the CH_3 group via the double bond, was detected (by ^1H NMR) among the reaction products. The reaction is unusual, because the VC (LIII) formed initially rearranges to a less stable VC (LIV), while in all the rearrangements described above the driving force is the formation of a thermodynamically more stable VC. It is appropriate to mention here that the carbonylation of the "usual" carbonium ions always leads to the formation of thermodynamically more stable isomers[50]. In the explanation of the course of the above reaction, the authors[49] attribute to SbF_5 a specific role in the formation of complexes with alkynes, which, however, appears to be unlikely.

3. Rearrangements Associated with a Change in the Cyclic System of Alicyclic Molecules

The rearrangements of cyclic VC are characterised by a series of features due primarily to the fact that the mode and extent of the rearrangements are determined not only by the greater thermodynamic stability of the rearranged ion but also by the structure (ring size) of the entire alicyclic molecule.

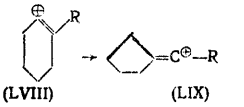
The solvolysis of methyl-substituted cyclohexenyl triflates (LVI) and (LVII) yields a mixture of approximately equal amounts of the rearranged and non-rearranged products[13]:



(LVI)

(LVII)

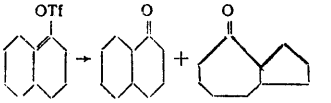
At first sight these results appear to be fairly strange, since a linear geometry is preferable for VC and the complete conversion of the VC (LVIII) into the VC (LIX) might have been expected:



(LVIII) (LIX)

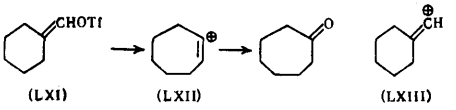
However, this transition is apparently prevented by the increasing strain in the methylenecyclopentane system compared with the cyclohexenyl system. It is also possible that cyclohexanone derivatives are not formed via VC but as a result of the dissociation of the S–O bond[51].

A much smaller degree of rearrangement is observed[13] in the solvolysis of the bicyclic vinyl triflate (LX):



(LX) (93%) (7%)

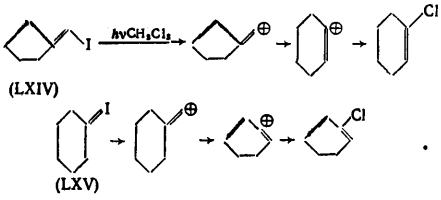
The rearrangements described above occur only in systems having a substituent at the β-carbon atom of the vinyl group. For the cations (LVIII, R=H), the rearrangement is hardly observed, because it would lead to the formation of very unstable primary VC of the type of (LIX, R=H), which, as stated above, is unlikely under the solvolysis conditions. The data on the solvolysis of the vinyl triflate (LXI), which results in the formation of 95% of cyclohexanone and 2.5% of formylcyclohexane, are consistent with these ideas:



(LXI) (LXII) (LXIII)

Cycloheptanone is probably formed via a mechanism involving concerted ionisation and the migration of an alkyl group, leading to the intermediate cycloheptenyl VC (LXII).[35] These results show that, despite the preferred linear configuration of VC, the bent secondary VC (LXII) is more stable than the linear primary VC (LXIII); hence it is clear how significantly the size of the VCI ring influences the mode and degree of the rearrangement.

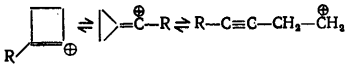
Rearrangements of a similar kind have been observed in studies of the photochemical transformations of vinyl halides which are believed to proceed via a stage involving the heterolysis of a carbon–halogen bond with formation of VC. Thus the photolysis of the vinyl iodides (LXIV) and (LXV) in methylene chloride results in the formation of considerable amounts of 1-chlorocyclohexene and 1-chlorocycloheptene respectively; this is believed[52] to occur as a result of a rearrangement via the double bond of the initial primary VC to the secondary VC, which subsequently abstract a chloride ion from the solvent molecule:



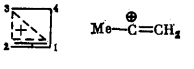
(LXIV)

(LXV)

Interesting examples of reversible transformations of the VCI, occurring as 1,2-shifts via the double bond, have been described by Hanack and coworkers[41,51,53], who investigated the solvolysis of cyclobutenyl nonaflates, bromomethylenecyclopropanes, and but-3-yn-1-ol derivatives. It was found that the composition of the products obtained is very insensitive to the nature of the substrate, which is consistent with the following mechanism of the transformation of carbonium ion intermediates:



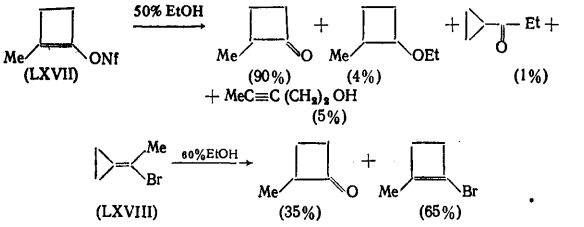
Bearing in mind that a linear geometry is preferable for the VC, the assumption that these transformations involve the cyclobutenyl cation, for which this type of geometry is impossible, appears fairly strange. However, it has been suggested[51] that the positive charge in the cyclobutenyl cation is delocalised over $C_{(2)}$ and $C_{(3)}$ as a result of the overlap of the vacant *p* orbital of the VC and the σ orbital of the $C_{(2)}$–$C_{(3)}$ bond:



(LXVI) (XLII)

The possibility of the formation of this non-classical structure (LXVI) has been confirmed by calculations[51] showing that its stability is comparable to that of the linear VC (LXII). The mode and degree of the rearrangements in the systems under consideration depend on the ability of the substituent R to stabilise the positive charge. Thus the only product of the solvolysis of cyclopropylidenemethyl bromide in the 1 : 1 water–ethanol mixture was cyclobutanone[53]. The same ketone proved to be the main product of the solvolysis of cyclobutenyl nonaflate[51]. On the basis of these data as well as calculations, the authors concluded that the cyclobutenyl cation is more stable than the cyclopropylidenemethyl cation.

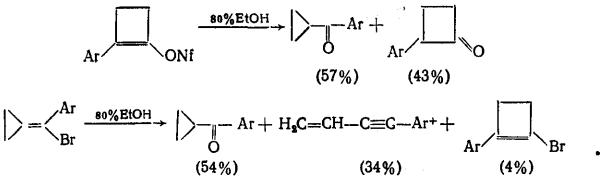
It is noteworthy that in these examples and those described above the carbonium ion mechanism has been fairly reliably demonstrated for solvolytic reactions of this kind. The absence of an addition–elimination process has been demonstrated by the independence of the solvolysis rate constant on the pH of the medium; furthermore, for certain reactions in labelled solvents, no incorporation of the isotope label was observed. In some cases[51,54] the ionic mechanism of the reactions was demonstrated by adding to the reaction mixture salts with an anion different from that of the leaving group. Under these conditions, both the initial and rearranged compounds containing the anion of the added salt were isolated; this demonstrates that the rearrangements proceed via the intermediate formation of ion pairs. The introduction of the methyl group in the 2-position of the cyclobutenyl ring exerts an additional stabilising effect on the cyclobutenyl cation formed, as shown by the considerable increase of the rate of solvolysis. The formation of cyclobutane derivatives as the main products in the solvolysis of 2-methylcyclobutenyl nonaflate (LXVII) and bromoethylidenecyclopropane (LXVIII) is believed[41,51] to show that the 2-methylcyclobutenyl cation is much more stable than the corresponding cyclopropylidene VC:



(LXVII) (90%) (4%) (1%) (5%)

(LXVIII) (35%) (65%)

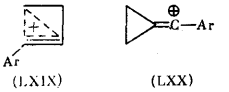
The introduction of an aromatic substituent (a phenyl or anisyl group) in compounds (LXVII) and (LXVIII) instead of the CH_3 group alters significantly the composition of the products formed (cyclopropene derivatives constitute more than 50% of the mixture[51,55]):



(57%) (43%)

(54%) (34%) (4%)

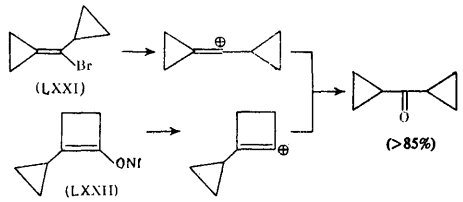
Thus the stabilising influence of the aromatic substituent on the cyclobutenyl cation (LXIX) is very insignificant:



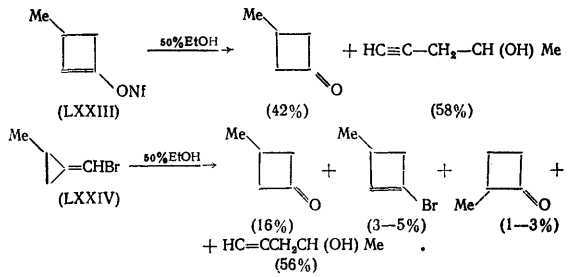
(LXIX) (LXX)

This is also indicated by the rate constants for the solvolysis of 2-arylcyclobutenyl nonaflates, which increase little compared with the rate constant for the unsubstituted derivative.

On the other hand, the VC (LXX) is stabilised significantly by an aromatic substituent. The stabilisation of this species by the cyclopropane ring is even greater, which is reflected in the composition of the solvolysis products of the cyclopropylcyclopropylidene bromide (LXXI) [41] or 2-cyclopropylcyclobutenyl nonaflate (LXXII): [51]



The main product of the solvolysis of these compounds in ethanol is dicyclopropylketone. The solvolysis of 3-methylcyclobutenyl nonaflate (LXXIII) leads to a mixture of 3-methylcyclobutanone and pent-1-yn-4-ol.[51] Derivatives of cyclobutane and the same alcohol have been isolated in the solvolysis of the *E*- and *Z*-isomers of 2-methylcyclopropylidenemethyl bromides (LXXIV),[56] both isomers giving rise to the same mixtures of products:



Thus in the given instances the 3-methylcyclobutenyl cation is more stable than the 2-methylcyclopropylidene cation.

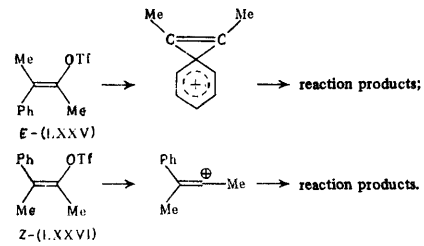
4. The 1,2-Shifts of Aryl Groups

The migration of aryl groups has been studied in greatest detail among the rearrangements of the VCI. This is quite natural because aryl-substituted VC in fact belongs to the most stable intermediates and the characteristics of the reactivity of these carbonium ions can be most conveniently studied on these models.

The usual method of synthesising VC of this type is solvolysis of various arylvinyl compounds; the study of the kinetics of this reaction and of data for the compositions of the products made it possible to elucidate a number of features relating to the migration of aryl groups via the double bond.

One of the principal problems in this connection is whether or not the migrating group is involved in the transition state of the heterolysis or whether the initial ionisation leads to a non-rearranged VC. Evidently in the general case the answer to this question depends to the greatest extent on the structure of the initial substances and particularly on their configuration. This has been studied in very great detail [57,58] in relation to the solvolysis of the *E*- and *Z*-isomers of 3-phenyl-2-but-2-enyl triflates (LXXV) and (LXXVI). The solvolysis of the *Z*-isomer in 60% aqueous ethanol gives rise to 33.5% of 3-phenyl-2-butanone and 66.5% of allene, while the *E*-isomer produces 82% of the ketone and only 18% of the allene; the rate of solvolysis of the *E*-isomer is twenty times higher than that of the *Z*-isomer.

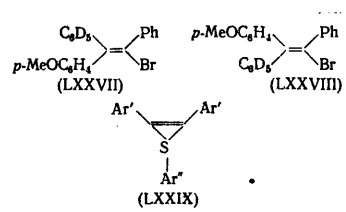
The solvolysis of these compounds in absolute TFE established the dependence of the mode of reaction on the stereochemistry of the initial compounds. To account for the different rates of reaction, the differences between the products, and their stereochemistries (the solvolysis in TFE yields the *E*-isomers in both cases), it has been suggested [57] that the *E*-isomer reacts preferentially if not exclusively with participation of the β-phenyl group and the formation of a bridged ethylidenephenonium ion as an intermediate. The *Z*-isomer yields initially a linear VC, which gives rise to a considerable amount of allene after the elimination of the proton. The formation of the *trans*-adduct in the solvolysis of the *E*-isomer in TFE confirms the formation of a bridged intermediate during the solvolysis, while it is believed [57] that in the case of the *Z*-isomer the VC forms an ion pair with the leaving group, which leads to a *trans*-adduct in the reaction with the solvent:



This mechanism was also confirmed in a study of the reactions with isotopically-labelled compounds (α- and β-CD_3 groups). The *E*-isomer then gives rise to compounds with a virtually complete redistribution of the D label, which was to be expected for the formation of an intermediate bridged carbenium ion, while in the reaction with the *Z*-isomer the degree of redistribution of the label is much smaller.

Further confirmation of the proposed mechanism was obtained in the study of the β-isotope effect (α-CD_3 group). It was found that the β-effect in the *Z*-isomer is very large (k_H/k_D = 1.47), while that for the *E*-isomer is smaller (k_H/k_D = 1.16). This shows that a linear VC with a positive charge on the α-carbon atom is formed from the *Z*-isomer, while in the case of the *E*-isomer the positive charge on the VCI is to a large extent delocalised over the benzene ring, which leads to a lower value of the isotope effect. This example clearly demonstrates that, depending on the configuration of the arylvinyl compounds, the latter can react with or without the involvement of the β-phenyl group.

On passing from the α-alkyl- to the α-aryl-vinyl systems, the stabilising effect of the α-aryl group on the vinyl cationoid centre produced exerts a significant influence on the mode of reaction; this leads to reactions in such systems via open-chain linear VC without the participation of the β-aryl groups. Thus the kinetics, stereochemistry, and degree of the rearrangement in the reactions of the vinyl bromides (LXXVII) and (LXXVIII) clearly show that the β-aryl groups are not involved in the heterolysis of the bonds [59]:



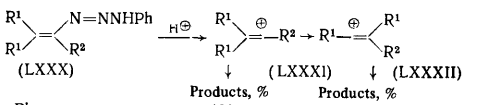
Linear VC are formed analogously from α-anisyl-substituted systems [60]. Numerous data on the solvolysis of β-arylthiovinyl derivatives have shown that the heterolysis of their

bonds proceeds with participation of the β-substituents and with the intermediate formation of thi-irenium ions of the type of (LXXIX).[61]

The degree of the rearrangement caused by the 1,2-shift of the aryl groups via the double bond depends on many factors: the structure of the initial vinyl compound, the method of generation of the VC, the solvents employed, and the nature of the migrating group.

The most significant properties of the solvents for the rearrangements are their nucleophilicity and ionising capacity. It has been suggested[60] that, in solvents with a high dielectric constant, the stability and lifetime of the carbonium ions increase. In highly nucleophilic solvents the rate of reaction of carbonium ions with the solvent increases and there is a corresponding decrease of the yield of rearrangement products. For all the migrations of aryl groups investigated, the best solvent promoting the rearrangements proved to be TFE, which has a high ionising capacity and a low nucleophilicity. In 60% ethanol, which has a higher dielectric constant and is more nucleophilic, the yield of rearrangement products is much lower. Acetic acid occupies an intermediate place between the above solvents. All the remaining factors influencing the degree of rearrangement are to some extent related. However, the decisive factors are of course the structure and stereochemistry of the initial vinyl derivative, because the ease of formation of the VCI in solvolysis, its stability, and hence the tendency towards rearrangements or reactions with the solvent depend on them.

The same VCI can arise in different reactions—in the solvolysis of arylvinyl bromides and arylvinyl triflates and in the interaction of arylvinyltriazenes with acids. Comparative studies[62,63] have shown that in certain cases the degree of the rearrangement depends significantly on the source of the VCI. For example, the solvolysis of the triflate $(Ph)_2C{=}C.(OTf)Me$ in 80% EtOH leads to the formation of rearrangement products, while the triflate $(Ph)_2C{=}CHOTf$ is solvolysed very slowly and the rearrangement products are not formed[30]. Formally, the same VC can be generated via the reaction of arylvinyltriazenes (LXXX) with an acid; data on these reactions are compiled below[62,63] (Scheme 1)



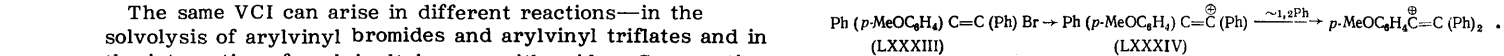
(LXXX) → (LXXXI) ↓ (LXXXII)

	Products, % (LXXXI)	Products, % (LXXXII)
(a) $R^1 = R^2 = Ph$	100	0
(b) $R^1 = n\text{-}MeC_6H_4$, $R^2 = Ph$	80	20
(c) R^1 Ph, $R^2 = Me$	5	86
(d) $R^1 = Ph$, $R^2 = H$	0	90
(e) $R^1 = R^2 = p\text{-}MeOC_6H_4$	68	38

The degree of the rearrangement in symmetrically substituted triazenes (LXXX, a and e) was determined[64] in compounds labelled with ^{13}C or ^{14}C as the vinyl carbon atoms. It is seen from the results presented that the VC (LXXXIc), generated both by the solvolysis of the triflate and by the reaction of a triazene with an acid, rearranges almost wholely to the VC (LXXXIIc). In contrast to these results, the VC (LXXXId) formed in the reaction of triazene also rearranges wholely, but no rearrangement products were detected in the solvolysis of the triflate. This difference in the course of the reaction can apparently be accounted for by the impossibility of the formation of the primary VCI (LXXXId) under the conditions of the solvolysis reaction, as a result of which the solvolysis proceeds via an elimination–addition mechanism.

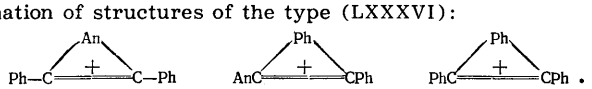
Other examples indicating the dependence of the degree of rearrangement on the mode of generation of the VC have been obtained in the study of degenerate rearrangements in the VC (LXXXI, a and e) (in systems with labelled vinyl carbon atoms). The reaction of the triazene (LXXXe) with acetic acid results in the formation of 38% of the rearranged acetate. The reaction of trianisylvinyl bromide with silver acetate in acetic acid leads to the formation of 20% of rearrangement products[64], i.e. the yield of the latter diminishes. In contrast to this, the triazene (LXXXa) does not give rise to rearrangement products, while the solvolysis of triphenyl triflate in acetic acid[65] or the interaction of triphenylvinyl bromide with silver acetate in acetic acid[67] lead to the formation of 7% of rearrangement products, i.e. under solvolytic conditions a higher degree of rearrangement is observed. These results can be explained by the different degrees of involvement of the ion pairs in the reaction; whereas in the first instance (the trianisylvinyl cation) the rearrangement proceeds in the VCI formation stage, the formation of rearranged products in the solvolysis of triphenylvinyl compounds takes place in the ion-pair formation stage.

The available data on the solvolysis of various triarylvinyl compounds[60] make it possible to consider the problem of the relative migratory capacities[23] of aryl groups, particularly phenyl and anisyl groups, in rearrangements via the double bond. In this respect one of the most interesting examples is the solvolysis of 2-anisyl-1,2-diphenylvinyl bromides (LXXXIII), since in the resulting VC (LXXXIV) there is a possibility of a 1,2-shift of the phenyl group and of a degenerate rearrangement associated with the migration of the anisyl group (the degree of rearrangement was determined in the solvolysis of 2-anisyl-2-pentadeuterophenyl-1-phenylvinyl bromides[67]):



(LXXXIII) (LXXXIV)

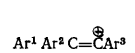
The migratory capacity of the anisyl group relative to that of the phenyl group, from competing migrations in the VC (LXXXIV), proved to be 76 for 60% ethanol and 120 for acetic acid. These data demonstrate the difference between the energies of the transition states for the two rearrangements, since the energies of the ground states are the same. Thus the formation of bridged structures of type (LXXXV) with the anisyl group in the transition state is preferable to the formation of structures of the type (LXXXVI):



(LXXXV) (LXXXVI) (LXXXVII)

This is also indicated by a comparison of the 1,2-shift of the anisyl group described above with the 1,2-shift of the phenyl group in the solvolysis of triphenylvinyl triflate. It has been shown[60] that the migratory capacity of the anisyl group in acetic acid is 82 times greater than that of the phenyl group, i.e. in this instance the anisyl group in the transition state (LXXXV) stabilises the positive charge more effectively than the phenyl group in compound (LXXXVII). The degree and mode of the 1,2-shifts of the aryl groups are significantly influenced also by groups not involved in the migration but are linked directly to the atom from which the migrating group departs and to the atom to which it becomes attached. Under these conditions, the stronger stabilising influence of the anisyl group, compared with the phenyl group, on the carbonium ion centre is most significant.

For all the combinations of the substitution of vinyl atoms by phenyl or anisyl groups investigated in the solvolysis of triarylvinyl derivatives, it has been found that the degree of migration to the α-phenyl-substituted centre (Ar^3 = Ph) in VC of the type of (LXXXVIII) is greater than the degree of migration to the α-anisyl-substituted centre ($Ar^3 = p\text{-}MeOC_6H_4$):



(LXXXVIII)

On the other hand, the rearrangements of the α-anisyl-substituted VC with formation of an α-phenyl-substituted VC have not been observed. The rearrangements of VC with Ar^1 or Ar^2 = *p*-$MeOC_6H_4$, leading to the formation of VC in which one of the substituents is the phenyl group, are also preferable to the corresponding degenerate rearrangements. It follows from the examples considered that the following transformation is most favourable:

$$(p\text{-}MeOC_6H_4)_2C{=}\overset{\oplus}{C}Ph \xrightarrow{\sim 1,2\,An} p\text{-}MeOC_6H_4C^{\oplus}{=}C(Ph)C_6H_4OMe\text{-}p\ .$$

On the other hand, the degenerate migration of the phenyl group between two anisyl-substituted centres is least favourable:

$$An^*(Ph)C{=}\overset{\oplus}{C}An \rightarrow An^*\overset{\oplus}{C}{=}C(An)Ph\ ;\quad An = p\text{-}MeOC_6H_4\ .$$

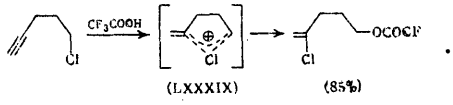
Comparison of the relative capacities for 1,2-migration of the phenyl and anisyl groups in saturated and unsaturated systems[23] shows that in both cases the anisyl group migrates more readily. The only exception has been found in the case of the deamination of 1,2,2-triarylethylamines[68], where a smaller degree of migration was observed for the β-anisyl group compared with the β-phenyl group. In the analogous transformations of phenyltriazenes in reactions with acids, the greater relative migratory capacity of the anisyl group was observed as usual.

IV. HIGHER-ORDER SHIFTS IN VINYL CATIONS

An extremely limited number of examples of such transformations in VCI are available and apparently, as in the case of the "usual" carbonium ions[69], the higher-order shifts are not characteristic of the VCI. In particular, it has been observed earlier that, instead of the 1,3-shift, two consecutive 1,2-migrations of the methyl group take place in the VC (L).[48] Depending on the nature of the migrating group, all the examples of the higher-order shifts described can be divided into two groups: (1) halogen shifts and (2) hydride ion shifts.

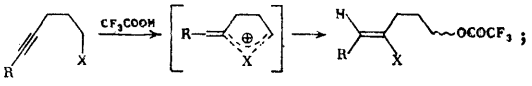
1. The Halogen Shifts

An unusal rearrangement with a 1,4-shift of chlorine in a VC was observed for the first time by Peterson and coworkers[70,71]. They obtained 2-chloropent-4-enyl trifluoroacetate by the reaction of 5-chloropentyne with trifluoroacetic acid. It is apparently formed via a mechanism involving the synchronous protonation of the triple bond and a shift of the halogen via an intermediate state of the chloronium ion type (LXXXIX) with subsequent attack by CF_3CO_2H:



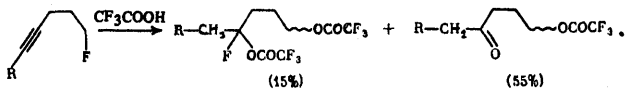
(LXXXIX) (85%)

Interestingly, in contrast to the acetylene derivative, 5-chloropentene gives only 0.6% of the product involving the migration of chlorine. This can be explained by the different degrees of formation of the chloronium ions. It was shown later[72] that the interaction of other halogen-containing acetylene derivatives with analogous structures (5-bromo- and 5-iodo-pentynes, 6-chloro- and 6-iodo-hex-2-ynes) with trifluoroacetic acid also involves a 1,4-shift of the halogen atom:



X = Cl, Br or I.

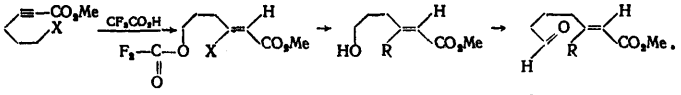
Next it was observed[72] that the interaction of γ-fluoroalkynes with trifluoroacetic acid results in the formation, together with rearranged products, of 15% of a bisadduct corresponding to the fairly unusual 1,4-shift of the fluorine in the VC (similar shifts have not been observed in the chemistry of the "usual" carbonium ions):



(15%) (55%)

The structure of the products obtained shows that exclusive *trans*-addition of the proton and halogen to the triple bond takes place[72].

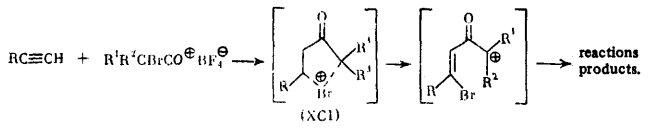
This stereospecific mode of the rearrangement has been used[73] to obtain the aldehyde (XC), which serves as an intermediate in the synthesis of the juvenile hormone:



(XC)

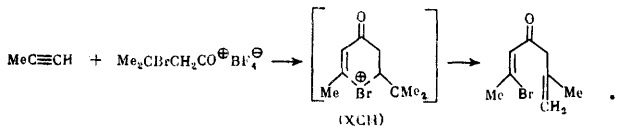
It was found that in the methyl ester of 6-iodohex-2-ynoic acid the 1,4-shift of iodine takes place quantitatively on refluxing for 50 h with trifluoroacetic acid. In contrast to this, the 6-chloroderivative rearranges much more slowly and, after heating the reaction mixture for eight days at 130 °C, only 30% of the rearranged ester and 60–65% of the initial ester were isolated. Thus the esters of acetylenecarboxylic acids rearrange at much lower rates than the alkylacetylenes described above, which is probably associated with the deactivating effect of the methoxycarbonyl group.

The migration of the bromine atom has also been observed in the acylation of alkynes by bromoacylium cationoid reagents[74,75]. In this case the reaction evidently proceeds as the coupled *cis*-addition of the acylium cation and the halide anion to the triple bond. A characteristic feature of the reaction is that the source of the bromide anion is the acylium residue and the final result of the process is a 1,4-shift of the bromine atom. The structure of the final products suggests that in these reactions there apparently arises an intermediate of the type of the five-membered bromonium ion (XCI), the opening of the ring of which actually leads to the formation of β-bromovinyl ketones with a Z-configuration of the double bond:



(XCI)

The interaction of alkynes with β-bromoisovaleryl tetrafluoroborate also leads to the formation of β-bromovinyl ketones[76]. Apparently in this instance a six-membered bromonium ion (XCII) is formed as an intermediate:



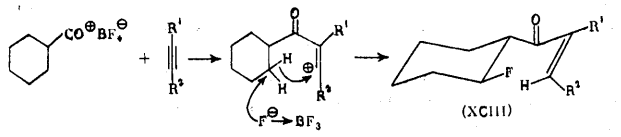
(XCII)

2. The Shift of the Hydride Ion

Higher-order hydride shifts constitute a fairly rare phenomenon in the thoroughly investigated chemistry of the "usual" carbonium ions, *trans*-annular reactions involving

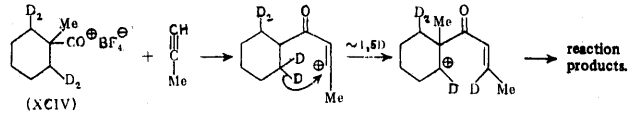
rings of medium size constituting an exception[69]. Direct and quantitative data on the 1,3-, 1,4-, and 1,5-hydride shifts are available only for 2,4-dimethyl-2-pentyl, 2,5-dimethyl-2-hexyl-, and 2,6-dimethyl-2-heptyl cations[77]. Here it is of interest to note that the lowest activation energy (25–29 kJ mol^{-1}) is required for the 1,5-hydride shift. The recently discovered new intramolecular 1,5-hydride shift reaction involving VCI is of undoubted interest in this connection.

In the acylation of alkynes with cyclohexanoyl tetrafluoroborate[78], fluoroketones of the type of compound (XCIII) were obtained as the main products:



(XCIII)

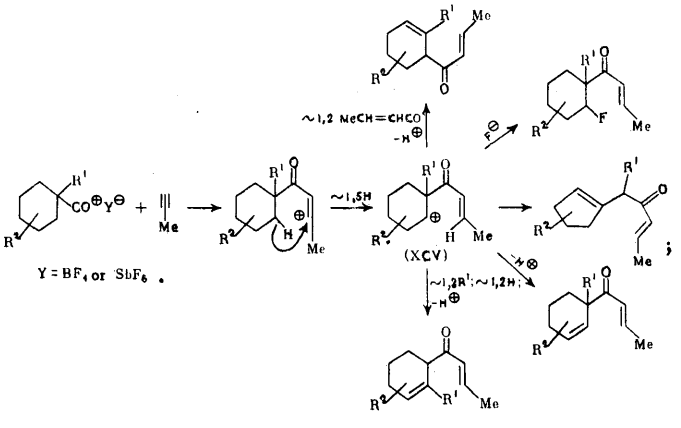
The structure of these compounds (the *E*-configuration of the double bond) suggested that they are formed via an intramolecular 1,5-hydride shift. To demonstrate this hypothesis, Kanishchev et al.[79] used as the acylating agent 1-methyl-2,2,6,6-tetradeuterocyclohexanoyl tetrafluorborate (XCIV):



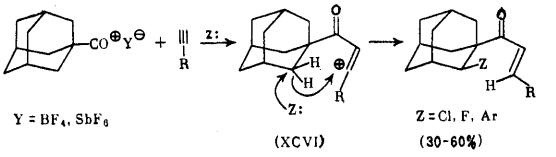
(XCIV)

A careful study of the ^{1}H NMR and mass spectra of the reaction products showed that at the β-carbon atom of the side chain there is only a deuterium atom (>95%) and they are therefore formed exclusively via an intramolecular 1,5-hydride shift. It is of interest to note that the hydrogen atoms of the C–H σ-bond of the CH_3 group of the cyclohexane ring do not participate in this reaction; this has also been demonstrated by an experiment in which the protons of the methyl group were replaced by deuterium.

Further study of the acylation of alkynes showed[81–84] that the observed 1,5-hydride shift is a common process in these reactions when aliphatic cycloacylium salts are used as acylating agents. It has been found that this type of transformation takes place most readily for the equatorial position of the carbonyl group in the cyclohexane ring of the initial reactant. A direct result of the 1,5-hydride shift under consideration is the formation of an aliphatic cyclocarbonium ion (XCV); the nature of the final reaction products is determined by the specific features of the structure and stereochemistry of the cyclic skeleton and also by the nature of the nucleophiles present in the medium. In a general form the list of processes observed in these reactions can be represented schematically as follows:



The 1,5-hydride shift takes place particularly effectively in the acylation of alkynes by acylium salts derived from adamantane-1-carboxylic acid[81–84] because in this case the VC (XCVI) formed has six equivalent C–H σ-bonds involving the β-carbon atoms:

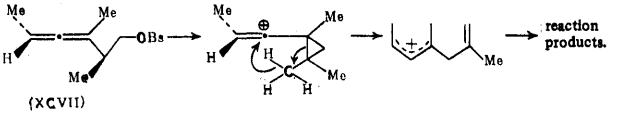


(XCVI) (30-60%)

It is readily seen that in all cases the outcome of the reaction is the introduction of a functional group into the aliphatic cyclic residue. The preparative usefulness of these reactions was demonstrated for the formation of a series of 1,2-disubstituted adamantanes, which are difficult to obtain.

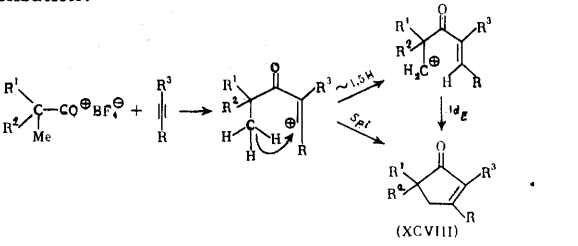
Only in the examples of the 1,5-hydride shift described above were the transformations of VCI of this kind rigorously demonstrated. In all other cases the occurrence of higher-order hydride shifts is one of the postulated pathways followed in the transformations of the VC into the final reaction products. For example, in the protonation of branched alkylacetylenes[25] in superacid media the authors do not rule out the possibility of a 1,5-hydride shift in the VC formed, although there are other possible reaction pathways.

The 1,4-hydride shift has been postulated[85] to account for the formation of nonatrienes in the solvolysis of 2,2,3-trimethylhexa-3,4-dienylbromobenzenesulphonates (XCVII):



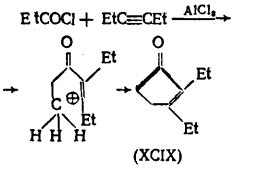
(XCVII)

In contrast to the acylation of alkynes by aliphatic cycloacylium salts described above, the analogous reactions with cationoid reagents derived from branched aliphatic acids lead to alkylcyclopentenones (XCVII).[86] They are formed via the attack on the β-CH bond of the acylating agent by the cationoid centre, ring closure occurring either via a mechanism involving direct electrophilic substitution (S_Ei) or via a stage in which there is a 1,5-hydride shift with subsequent Ad_E cyclisation:



(XCVIII)

2,3-Diethylcyclopent-2-enone (XCIX) is apparently formed via an analogous mechanism (in small amounts) in the acylation of hex-3-yne with propionyl chloride[87]:



(XCIX)

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The data examined above show that sextet rearrangements are just as characteristic of VC as of carbonium ions of other types. The features of VC rearrangements have now been systematically investigated only for the 1,2-migrations of aryl groups. In the majority of cases the result of the investigation has been merely the demonstration of the occurrence of the rearrangement and the elucidation of the general structural features determining its feasibility. There are not yet experimental data characterising quantitatively VC rearrangements. At the same time, the available results show that the transformations of VC are not only of theoretical interest but can also be used for synthetic purposes. An example of useful synthetic processes of this kind is provided by cyclisation (the formation of cyclopentenones), the 1,4-shift of the halogen in the series of ω-halogenoalkynes, the 1,5-hydride shifts in the acylation of alkynes, and finally the generation of allyl cations from alkynes.

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