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Alkynylcarbenium ions and related unsaturated cations

S M Lukyanov, A V Koblik, L A Muradyan

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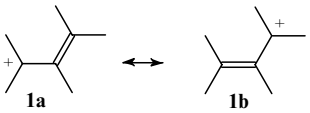
Abstract. Published data on carbenium ions containing C≡C bonds both directly conjugated with the carbenium centre and separated from it are surveyed and described systematically. Ammonium, diazonium, iminium, phosphonium and iodonium cations containing alkynyl groups, which can be regarded as heteroanalogues of alkynylcarbenium ions, are also considered. The bibliography includes 283 references.

I. Introduction

The chemistry of unsaturated carbenium ions is constantly attracting the attention of researchers. The range of objects containing unsaturated carbenium ions is fairly broad: they vary from stable salts used as reagents with unique properties to extremely reactive intermediates the stability of which is comparable to that of the methyl cation.

Unsaturated carbocations with a variety of structures are known. However, all of them can be classified as two main types: (1) cations with a tricoordinated carbenium centre (trisubstituted ions) and (2) cations with a dicoordinated carbenium centre (disubstituted ions). In the former type of cations, the multiple bond is located in the α-position in relation to the positively charged atom (or is farther removed from it along the chain), whereas in the latter type of cations, an atom forming the multiple bond acts as the carbenium centre.

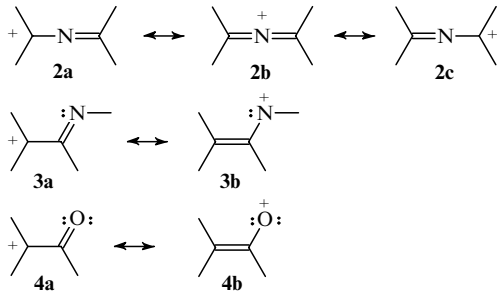
The first type of unsaturated cations comprises allyl cations **1**[1–7] including functionally substituted ones[8,9] and their heteroanalogues — 2-azaallenium ions **2**,[10–15] iminocarbenium ions **3**[16,17] and α-oxocarbenium ions **4**.[17–21]



1a **1b**

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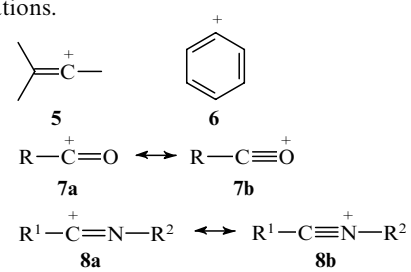


2a **2b** **2c**

3a **3b**

4a **4b**

The second type includes vinyl (**5**)[22–27] and phenyl (**6**)[17,26–29] cations as well as acylium (**7**)[2,26,30] and nitrilium (**8**)[26,31,32] cations.

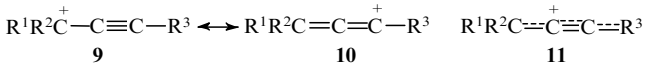


5 **6**

7a **7b**

8a **8b**

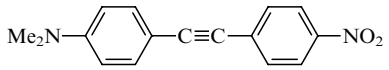
The species, which arise when a carbenium centre is generated near a triple carbon – carbon bond, occupy a special place among unsaturated carbocations. They can be related to either of the two types mentioned above, because in some cases, these species behave as destabilised (compared to the dimethylvinyl- and even ethyldimethyl-carbenium) tertiary cations (alkynylcarbenium ions **9**),[17] whereas in some other cases, they behave as vinyl ions stabilised by conjugation (allenyl ions **10**).[23]



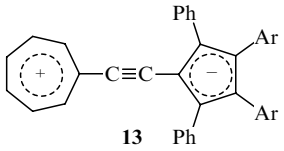
9 **10** **11**

It is obvious that in reality, the charge in the three-carbon chain is substantially delocalised, the degree of delocalisation and, hence, the structure and the behaviour of the cations **11** being dependent on the nature of the substituents R^1, R^2 and R^3 and the reaction medium. These cations have been considered in numerous studies, the results of which have not yet been surveyed. The stabilised species **10** are discussed in several reviews devoted to vinyl cations.[22,23,26,33] However, in our opinion, it is more correct

to regard them as acetylene derivatives in which the triple bond is activated by a cationic substituent. This approach has been proposed in studies [34, 35] dealing with the reactions of acetylene derivatives with nucleophiles. The use of acetylene derivatives with cationic substituents proved to be more efficient than the introduction of neutral electron-withdrawing groups [36–38] or the use of acetylene derivatives of the push–pull type (for example, compounds **12** and **13** [39, 40]).



12

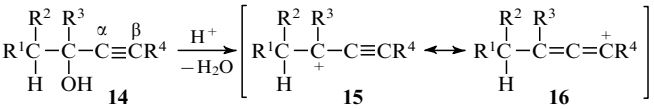


13

In this review we consider the ions **11** as alkynylcarbenium ions the properties of which are determined by the degree to which the multiple bond in these species retains the nature of a triple carbon–carbon bond.

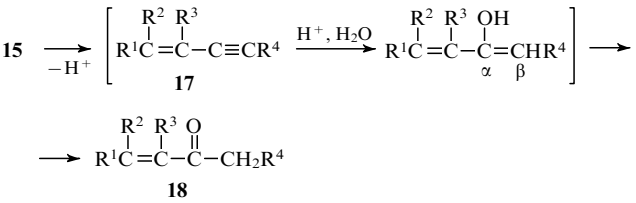
II. Alkynyl carbocations in transformations of acetylene derivatives

Alkynylcarbenium ions have been postulated as intermediates in acid-catalysed transformations of functionally substituted acetylene derivatives. First of all, this refers to the Meyer–Schuster and Rupe rearrangements (see a review [41] and studies [42–44]). Long before alkynylcarbocations were detected experimentally (see Section III), it had been concluded that acid-catalysed propargyl rearrangements [45–47] can occur *via* the intermediate formation of carbocations the structure of which allows realisation of two reaction pathways.[48] These pathways usually compete, the predominance of either of them being determined by the structure of the initial α-hydroxyacetylene **14**.



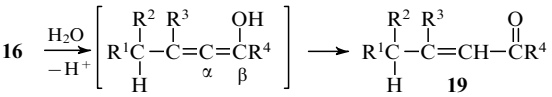
14 **15** **16**

the Rupe rearrangement



17 **18**

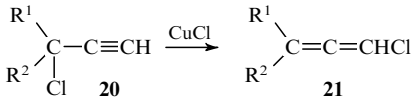
the Meyer–Schuster rearrangement



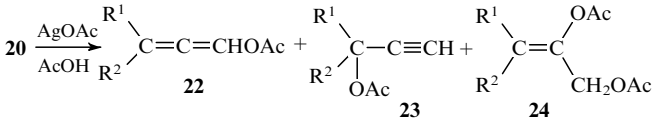
19

In both cases, α,β-unsaturated carbonyl compounds **18** and **19** are formed. The main difference between these two routes is determined by the carbon atom in the acetylenic fragment which is hydrated and, hence, forms the carbonyl group. The Rupe rearrangement occurs *via* alkynylcarbenium intermediates **15**, which are capable of being deprotonated to enynes **17**. Protonation of the β-carbon atom in the enyne **17** with the addition of water to the α-carbon atom is energetically the most favourable route. However, when the cationic intermediate is stabilised by, for example, aryl groups, participation of the allenyl cation **16** in the reaction becomes more favourable. This cation is hydrated at the β-carbon atom of the acetylenic fragment (the Meyer–Schuster rearrangement).

Other functional derivatives of acetylene also can enter into this type of rearrangement. α-Chlorinated alkynes **20** are converted into allene compounds **21** or **22**, depending on the reaction conditions.[48, 49] In the latter case, the reaction also gives products **23** and **24**.[49]

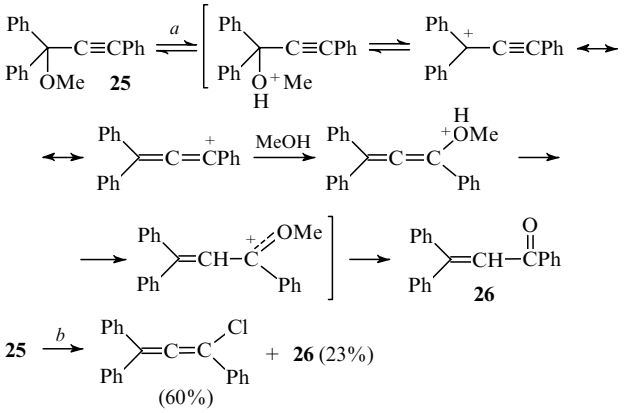


20 **21**



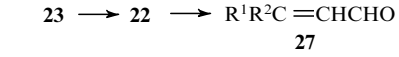
22 **23** **24**

3-Methoxy-1,3,3-triphenylprop-1-yne **25** rearranges under various conditions, and the structure of the rearrangement products implies that the reaction occurs predominantly *via* the most stable cationic intermediates.[50]



(*a*) MeOH, 100% H_2SO_4; (*b*) HCl.

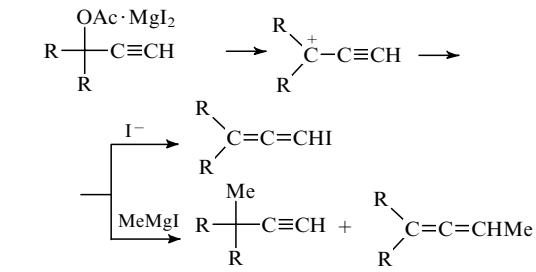
In the presence of copper and silver salts, the acetates of tertiary alkynols **23** are converted exclusively into α,β-unsaturated aldehydes **27**.[46]



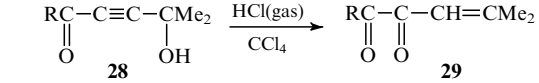
27

R^1 = Me: R^2 = $(CH_2)_2CH{=}CMe_2$, $(CH_2)_2C(Me){=}CMe_2$;
R^1, R^2 = $(CH_2)_4$, $(CH_2)_5$.

It has been suggested that alkynyl carbocations can arise even under Grignard reaction conditions.[51]



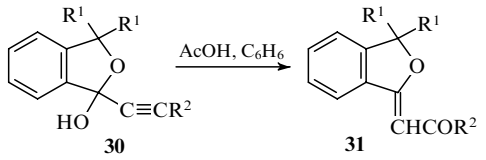
When hydroxy ketones of the acetylene series **28** react with dry HCl in CCl_4, they undergo an unusual rearrangement to give vinyl-substituted α,β-diketones **29**.[52]



28 **29**

R = Me, Et, Pr^i.

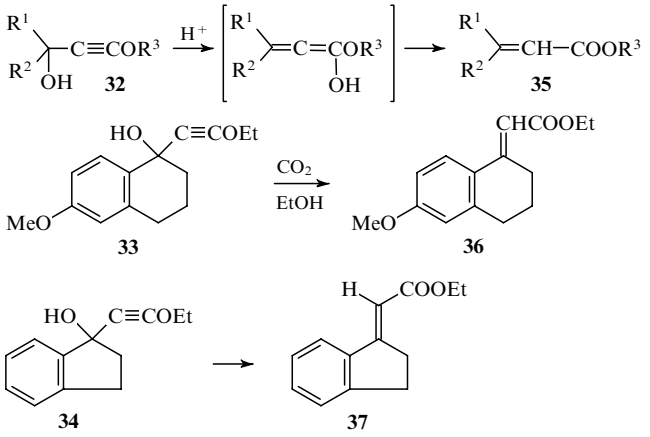
A series of studies describe[53–57] the transformations of 1-ethynyl-1-hydroxyphthalans **30** yielding the corresponding α,β-unsaturated ketones **31**.



30 **31**

R^1 = Me, Ph; R^2 = Me, Bu^t, Ph, 4-MeC_6H_4.

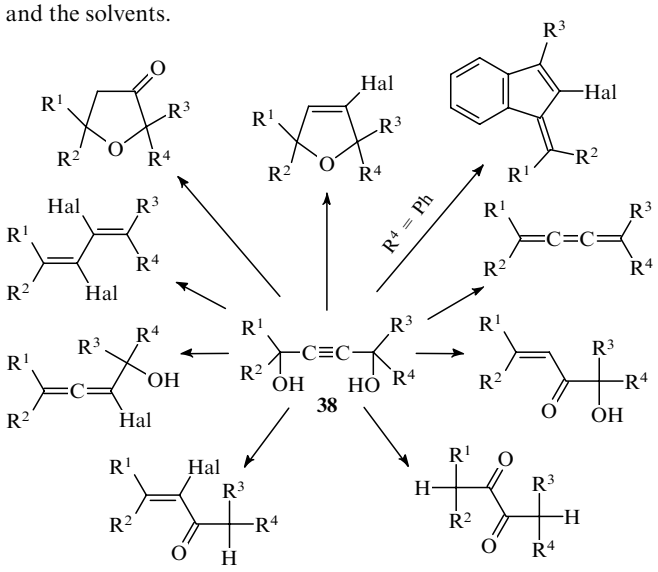
Alkoxyalkynols **32**–**34** are converted into α,β-unsaturated esters **35**–**37** under mild conditions.[58–60]



32 **35** **33** **36** **34** **37**

Four possible mechanisms, including those involving alkynylcarbenium ions, have been discussed for these transformations.[59] It has been noted that none of the schemes provides a satisfactory explanation for the formation of the *cis*-isomers of the compounds **36** and **37**, which possess higher energies than the corresponding *trans*-isomers.

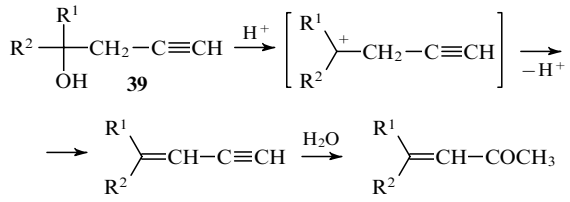
Acid-catalysed transformations of a large series of symmetrical and asymmetrical alkynediols **38** have been described in detail.[61] The pathway of these reactions, which occur presumably with participation of alkynylcarbenium ions, depends on the structure of the substrates and the nature of the acid catalysts and the solvents.



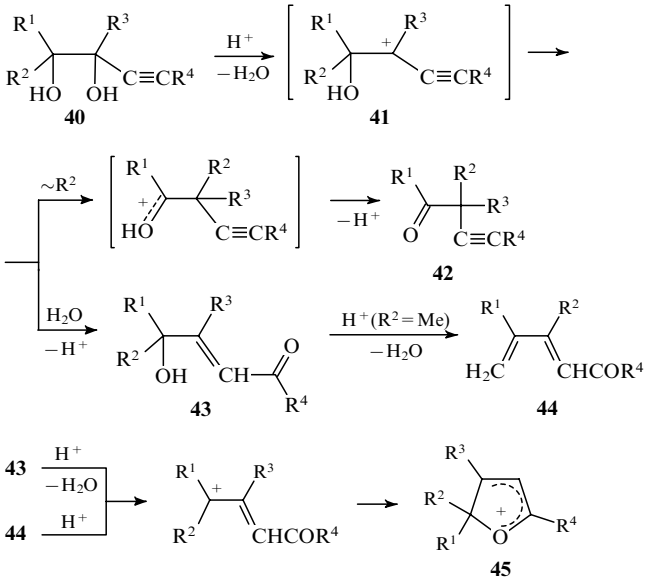
38

R^1–R^4 = Me, Et, Pr^i, Bu^i, Bu^t, Ph, 4-MeC_6H_4, PhCO, 2-pyridyl, $(CH_2)_5$; Hal = Cl, Br, I;
Acid catalyst: H_2SO_4, HCl, HBr, HI, HI–I_2, AcCl, HCOOH;
Solvent: THF, EtOH, AcOH, Me_2CO, CCl_4, AcOH–dioxane.

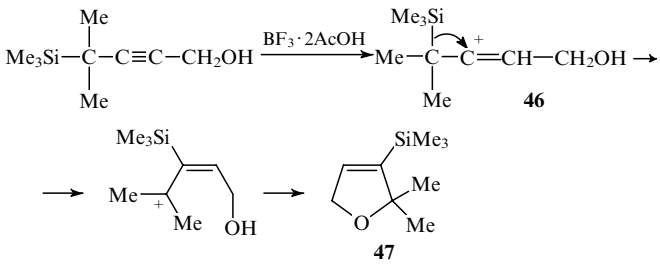
The structures of the products formed in these transformations reflect the typical reactions of carbenium intermediates,[2] namely, deprotonation, addition of nucleophiles, alkyl migrations and electrophilic aromatic substitution.[61] The same typical reactions are observed in many other cases. Thus tertiary β-alkynols **39** undergo the Rupe rearrangement.[41]



On treatment with dilute H_2SO_4, bitertiary 1,2-diols of the acetylene series **40** undergo not only the Meyer–Schuster rearrangement yielding enones **43** (or subsequent dehydration to dienones **44**) but also the pinacolic rearrangement to give alkynones **42**. Undoubtedly, this process occurs *via* the alkynyl carbocations **41**. The transformation of the compounds **40** affords as well stable dihydrofurylium salts **45**.[62,63]

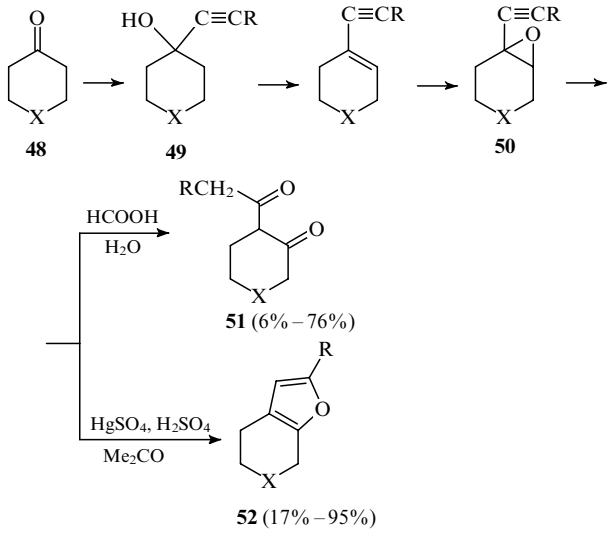


The use of the Meyer–Schuster and Rupe rearrangements, accompanied by sextet rearrangements with group migrations and ring transformations, for the synthesis of compounds that are difficult to prepare by other methods has been described in a review.[41] These transformations are possible when tertiary or, at least, secondary alkynyl carbocationic intermediates are fairly stable. In this connection, the formation of the vinylic cation **46**, which rearranges to give dihydrofuran **47**, deserves attention.[64]



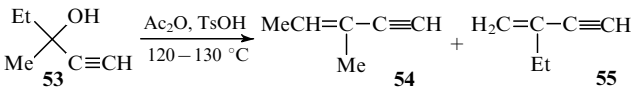
46 **47**

Based on dehydration of hydroxyacetylenes **49**, an interesting preparative approach has been developed for the transformation of alicyclic ketones **48** into diketones **51** and furans **52**.[65,66]

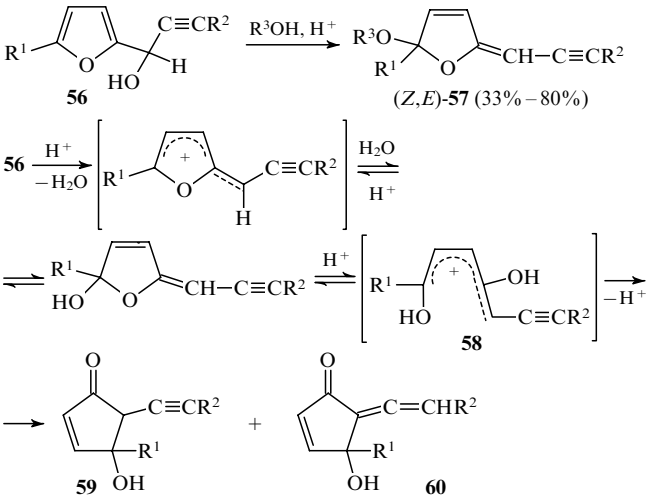


R = Me, Ph, 3,4-$(MeO)_2C_6H_3$, 4-$NO_2C_6H_4$; X = CH_2, CHMe, CHPh, CPh_2 (**51**, **52**);
R = 4-$MeOC_6H_4$, 2,4-$(NO_2)_2C_6H_3$; X = SO_2, NTs, NCO_2Et (**52**).

Tertiary alcohols of the acetylene series **53** have been used to synthesise enynes **54** and **55**.[67]



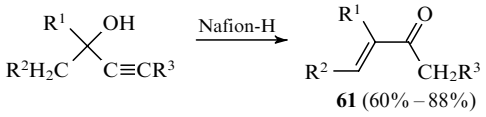
Dehydration of secondary alkynols of the general formula **56** occurring on treatment with various acidic reagents (HCl, CF_3COOH, polyphosphoric acid) affords unusual enyne furan derivatives **57**.[68–72]



R^1 = H, Me: R^2 = H, Pr, Bu, C_5H_{11}, C_6H_{13}, CH_2OMe, C≡CPh, Ph; R^3 = Et, Bu^t.

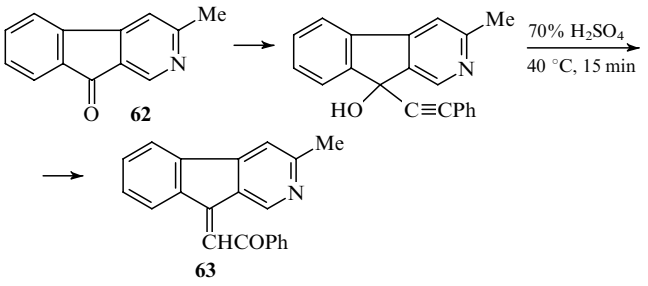
On heating in aqueous dioxane (60 °C) in the presence of toluene-*p*-sulfonic acid, the alcohols **56** recyclise to cyclopentenones **59**, **60**, which can serve as valuable starting compounds for the synthesis of prostanoids.[72] In early experiments, the yields of these products were very low (~10%), due to substantial resinification of the reaction mixtures; however, later, the yields were brought to 80% as a result of stabilisation of the intermediate alkynyl carbocations by complex formation (see Section V).

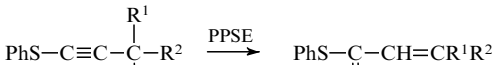
The Rupe rearrangement in the presence of the solid superacid 'Nafion-H' has been proposed as an improved method for the synthesis of alicyclic and linear α,β-unsaturated ketones **61** [73] (see also Ref. 74).



R^1 = Me, Et; R^2 = Me; R^1, R^2 = $(CH_2)_n$, n = 3–6; R^3 = H, Me.

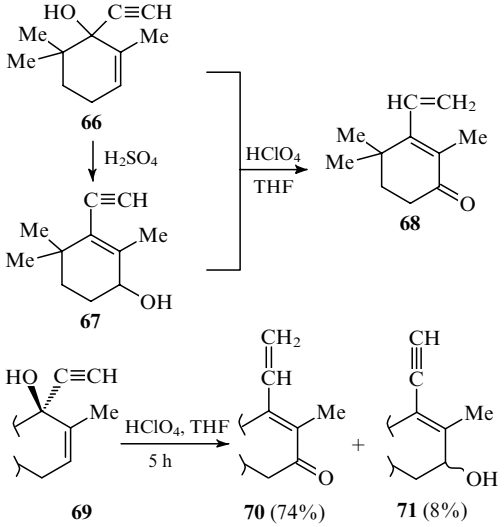
The Meyer–Schuster rearrangement has been used to prepare fulvenes **63** (which are intermediates in the synthesis of spiro compounds) based on 3-methyl-2-azafluorenone **62**.[75] A new method for the preparation of *S*-phenyl thioesters **65** consists in the reaction of phenylthio-substituted alkynols **64** with the trimethylsilyl ester of polyphosphoric acid.[76]



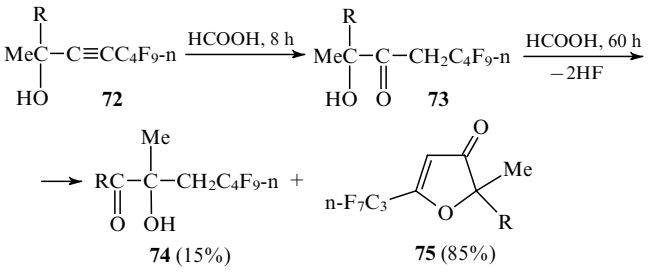


R^1 = Et, Pr^i, Bu, Bu^t, $PhCH_2CH_2$, $BuCH_2$, PrCH=CH, PhCH=CH, BuC≡C; R^2 = Bu; R^1, R^2 = $(CH_2)_n$, n = 4–6.
PPSE is the trimethylsilyl ester of polyphosphoric acid.

The specific structure of the initial hydroxyacetylene may result in an unusual route of the propargyl rearrangement. Thus treatment of ethynyl-containing alcohols **66**, **67** and **69** with a 35% solution of $HClO_4$ in THF gave rise to dienones **68** and **70**, which are difficult to prepare by other methods and which are used in the synthesis of di- and tri-terpenoids.[77]

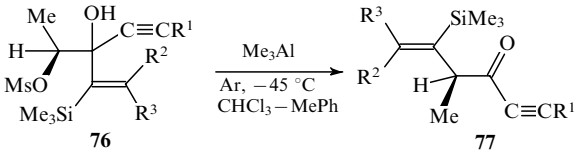


Perfluorobutyl-substituted alkynols **72** have been found [78] to behave unusually under the Rupe reaction conditions: dehydration does not occur at all; nevertheless, a carbonyl group appears at the α-carbon atom of the multiple bond. The α-hydroxy ketones **73** thus formed are converted into a mixture of hydroxy ketones **74** and furanones **75** upon prolonged (60 h) refluxing in HCOOH as a result of the acyloin rearrangement involving the perfluorobutyl group.



R = Me, Et.

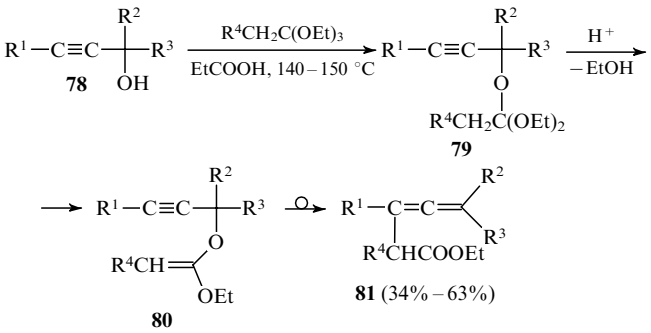
Mention should be made of the unusual pinacolic rearrangement of 1,2-glycol derivatives of the acetylene series **76**, which gives rise to α,β-unsaturated alkynones **77**. These compounds are used as chiral synthons in syntheses of biological active compounds.[79]



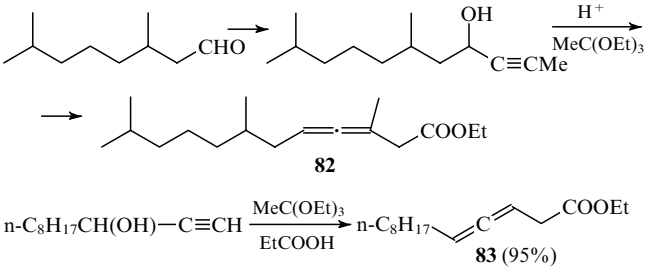
R^1 = Ph, Bu^tMe_2Si, $Ph(CH_2)_3$; R^2 = H, Bu, $PhCH_2OCH_2$; R^3 = H, Bu.

This stereospecific 1,2-rearrangement occurs due to the fact that the ability of the ethynyl substituent for migration to the carbenium centre is much lower than that of the alkenyl substituent activated by the Me_3Si group.[79]

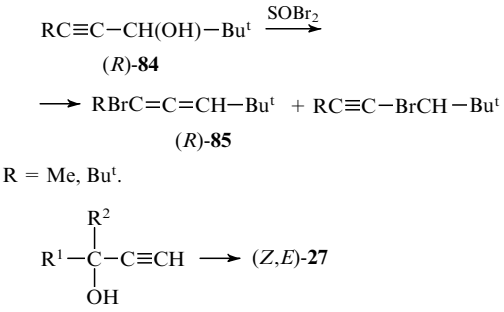
Acid-catalysed esterification of alcohols **78** resulting in the formation of mixed orthoesters **79** and the subsequent Claisen rearrangement of ketene acetal **80** afford allene esters **81**.[80] This type of transformation of orthoesters is known[81] to involve cationic intermediates. These reactions have been used to synthesise compounds **82** and **83**, analogues of juvenile hormones[82] and sex pheromones[83] of insects.



R^1 = H, Me; R^2,R^3 = H, Me, Pr, $(CH_2)_5$; R^4 = H, Me.



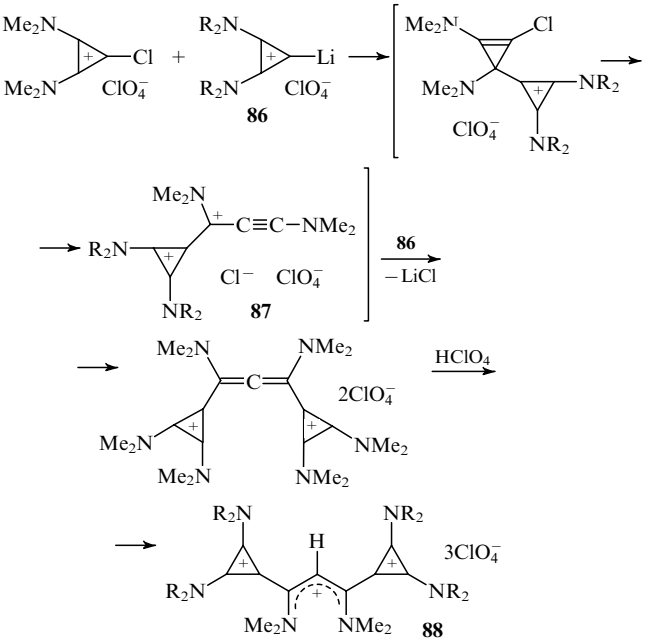
The Meyer–Schuster rearrangement initiated by $SOBr_2$ has been used to carry out stereospecific synthesis of chiral 1,3-disubstituted bromoallenes (*R*)-**85** from alkynols (*R*)-**84**[84] and to synthesise the α,β-unsaturated aldehydes **27** in the presence of polyvanadiumorganosiloxanes.[85,86]



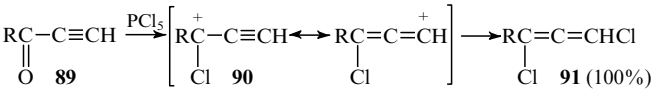
R = Me, Bu^t.

R^1 = H, Me; R^2 = 4-$Pr^iC_6H_4$, 4-$Bu^tC_6H_4$, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2,4-$Me_2C_6H_3$.

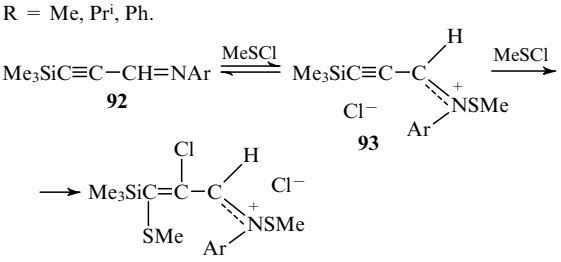
A reaction of cyclopropenylium salts which is accompanied by rearrangement with cyclopropene ring opening and gives alkynylcarbenium dications **87** has been described;[87] the dications **87** were converted into tricarbenium ions **88** stabilised by electron-donating substituents. The principle of coupling of positively charged building blocks used here seems promising for the synthesis of extended polycationic systems consisting of allyl-cationic and/or cyclopropenylium fragments stabilised by electron-donating groups.



Treatment of ethynyl ketones **89** with PCl_5 affords 1,3-dichloroallenes **91** *via* intermediate chloro(ethynyl)carbenium ions **90**.[88] Participation of ethynyliminium ions **93** has also been assumed in the transformations of azomethines of the acetylene series **92**.[89]

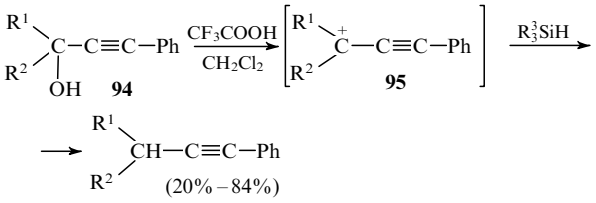


R = Me, Pr^i, Ph.



Ar = 2-MeC_6H_4, 4-ClC_6H_4.

Ionic hydrogenation of alkynols **94** (treatment with trialkylsilanes in the presence of trifluoroacetic acid) involves reduction of the hydroxyl group.[90] The mechanism proposed for this reaction includes transformation of the alcohol into carbocation **95**, which adds the hydride ion detached from the silane.[91]

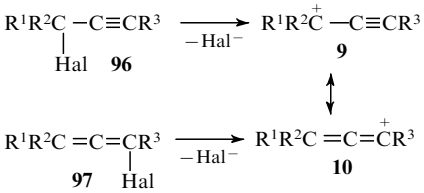


R^1 = Me, Et, Ph; R^2 = H, Me, Et, Pr^i, Bu^t; R^3 = Me, Et, Bu, Ph.

In the greater part of the publications listed above, the formation of alkynylcarbenium ions was merely postulated based on the general considerations about the mechanisms of acid-catalysed propargyl rearrangements and transformations of functional derivatives. However, alkynylcarbenium ions have ceased to be hypothetical species long ago. They have been repeatedly detected by spectroscopy (Section III); numerous reliable examples of stable alkynylcarbenium salts have now been described (Section V).

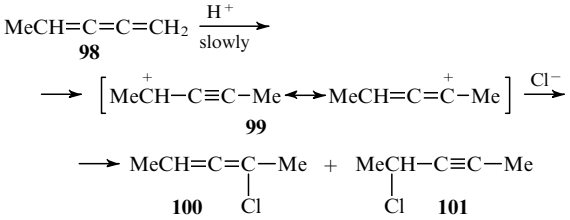
III. Spectroscopic studies of alkynyl carbocations

The first attempts to detect experimentally alkynylcarbenium ions were based on the study of the kinetics of solvolysis. The few studies devoted to this topic are surveyed in several publications.[33,92,93] However, they provided only kinetic evidence for the participation of carbocationic intermediates in solvolysis but gave no information about the structure of these species. It has been noted that the allenyl cations **10** are contributing structures in relation to the the propargyl cations **9** and that the ions in question can be generated by solvolysis of both haloalkynes **96** and haloallenes **97**.

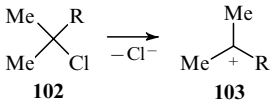


In general, the experimental data obtained for the solvolysis of both series of derivatives under a variety of conditions indicate that these reactions follow the S_N1 mechanism and that the halides **96** react much faster than the corresponding allenyl isomers **97**.[92–95]

Attempts to elucidate the nature of unsaturated cationic intermediates have also been made in studies dealing with electrophilic addition to cumulenes. Thus, it has been found that hydrochlorination of penta-1,2,3-triene **98** in aqueous ethanol gives 1,2- and 1,4-addition products (**100** and **101**, respectively) in 1 : 4 ratio, whereas in a 4 : 1 sulfolane–CH_2Cl_2 mixture, the ratio of these products is 1 : 1.[93]

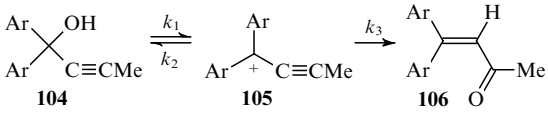


The relative stability of the ethynyl carbocations with respect to the stabilities of secondary, tertiary and allylic cations can be derived based on the rates of solvolysis of the series of derivatives **102**. The results obtained indicate that substituents R can stabilise the cationic intermediate **103** (the rate of solvolysis for R = H was taken to be unity).[17]



R	H	C≡CH	CH_2CH_3	$CH=CH_2$
k_{rel}	1	10^2	10^4	3.4×10^6

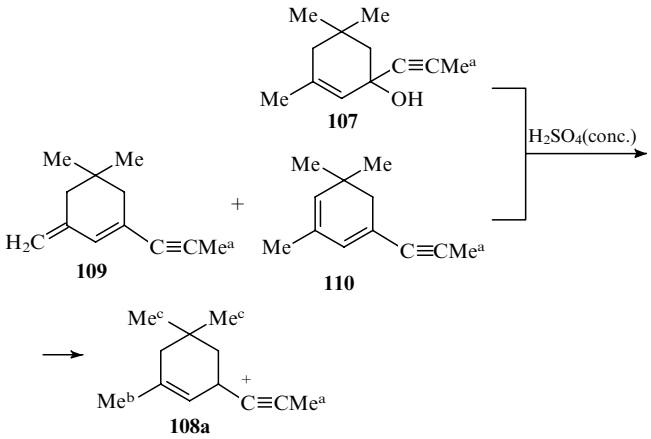
More definite information about the structure of the unsaturated cations in question can be obtained by NMR spectroscopy. The first direct observation of alkynyl carbocations **105** was reported by Richey *et al.*[95] in 1965. These cations aroused particular interest due to the fact that they could be regarded as a sort of vinylic cations (see Section I). The ^1H NMR spectrum of the solution resulting from extraction with CCl_4 of the product formed upon careful addition of 1,1-di(*p*-methoxyphenyl)but-2-yn-1-ol **104** to concentrated H_2SO_4 proved the formation of the cations **105** under these conditions.



Ar = 4-$MeOC_6H_4$.

Dilution of this solution by water or aqueous alkali results in the recovered initial alcohol **104** together with a minor amount of the rearranged product **106** (*i.e.* $k_2 \gg k_3$). The signal for the methyl protons of the propynyl fragment (δ = 2.6 ppm) in the cation **105** is substantially shifted downfield in relation to this signal for the initial alcohol **104** (δ = 1.87 ppm); this is due to the substantial charge delocalisation between the tertiary carbenium centre and the multiple bond.

It was shown in the same study[95] that the cation **108a** is generated both from alcohol **107** and from a mixture of dienynes **109** and **110**; this was proved by the data of ^1H NMR spectra in which the signals for the methyl protons at the ends of the unsaturated chain (Me^a, Me^b) almost coincide.



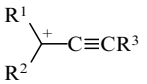
Compound	Chemical shift, δ /ppm		
	Me^a	Me^b	Me^c
107	1.78		
108a	2.65	2.76	1.10
109	1.93		
110	1.93		

A large series of ethynyl- and propynyl-carbenium ions **9a–h**, **105** and **108a,b** have been obtained by mixing solutions of the corresponding tertiary alcohols in liquid SO_2 with a solution of

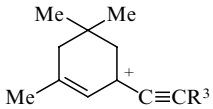
Table 1. Chemical shifts of the protons of substituent R^3 in the ^1H NMR spectra of ethynyl- and propenylcarbenium ions.[96]

Compound	R^1	R^2	R^3	$\delta(R^3)$ /ppm	$\Delta\delta$
9a			Me	2.47	0.63
9b	Ph	Ph	Me	2.88	1.06
9c	Ph	Me	Me	2.94	1.12
9d	$MeC\equiv C-$	$MeC\equiv C-$	Me	2.76	0.89
9e			H	5.58	3.35
9f	4-$MeOC_6H_4$	4-$MeOC_6H_4$	H	5.70	3.05
9g	Ph	Ph	H	6.96	4.35
9h	Ph	Me	H	7.24	4.76
105	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Me	2.60	0.73
108a	–	–	Me	2.63	0.85
108b	–	–	H	6.32	4.00

antimony pentafluoride in fluorosulfonic acid (the ratio $SbF_5:FSO_3H = 1:3$ by volume) at -78 °C. Table 1 presents the ^1H NMR spectra of these mixtures recorded at -60 °C.[96]



9a–h, 105



108a,b

The chemical shifts of the methyl group protons in the compounds **9a–d**, **105** and **108a** and the ethyne protons in **9e–h**, **108b** as well as the downfield shifts of these signals ($\Delta\delta$) with respect to the signals of the corresponding protons in the initial alcohols point to substantial deficiency of the electron density on the carbon atoms of the acetylenic fragment. This deficiency becomes more pronounced as the carbenium ions become less stable, *i.e.* the ability of the substituents at the tertiary carbenium centre to delocalise the charge decreases.

More comprehensive data on the ^1H NMR spectra of the above cations and some other alkynyl carbocations can be found in reviews.[33,97]

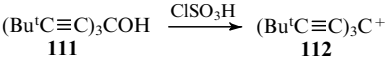
Olah *et al.*[98] attempted to generate alkynylcarbenium ions by treating tertiary alkynyl chlorides with SbF_5 or a solution of SbF_5 in SO_2. However, these experiments were unsuccessful due to the large amount of side products. Therefore, the researchers[98] used again the corresponding tertiary alcohols, which were treated as described in the study cited above.[96] As a result, they recorded the ^1H NMR spectra of the cations **9b** and **9i–n** (Table 2).

Table 2. Chemical shifts of methyl group protons in the cations **9b**, **i–n**.[98]

Compound	R^1	R^2	R^3	δ/ ppm
9b	Ph	Ph	Me	2.88
9i	Ph	Ph	Ph	–
9j	Ph	Me	Ph	3.14
9k	Me	Me	Ph	3.39
9l	Me^a	Me^a	Me^b	3.67(a), 3.13(b)
9m	Me^a	4-$Me^bC_6H_4$	Me^c	3.05(a), 2.45(b), 2.59(c)
9n		Me^a	Ph	3.11(a), 2.82–3.00(b, c)

Several conclusions were drawn from analysis of the ^1H NMR spectra of these cations.[98] Thus the downfield shift of the signal of the protons of the methyl group bound to the tertiary carbenium centre increases in the sequence **9m** < **9n** < **9j** < **9k** < **9l**, *i.e.* following the decrease in charge delocalisation by the other two substituents. The positive charge in the ion **9l** ($\delta^{Me} = 3.67$ ppm) is markedly redistributed, with respect to that in the *tert*-butyl cation ($\delta^{Me} = 4.35$ ppm),[99] with participation of the propynyl fragment; this is also manifested as a downfield shift of the signal of the methyl protons in the cation **9l**. Nevertheless, an alkynyl group is unable to delocalise the charge efficiently (at least, as efficiently as does the vinyl group), because the attempts to generate alkynyl carbocations from the secondary alcohols $RCH(OH)C\equiv CPh$ (R = Ph, Me) failed.[99] Under the conditions reported, instantaneous polymerisation occurred even at -60 °C.

The alkynoyl cations $RC\equiv C-C^+=O$ (R = H, Me, Ph) are quite stable; for these species, ^1H and ^{13}C NMR spectra have been recorded[100] and substantial charge delocalisation over the conjugation chain has been demonstrated. Tris(*tert*-butylethynyl)methanol **111** readily reacts with strong acids even at room temperature. However, a satisfactory ^1H NMR spectrum of cation **112** was obtained only upon cooling a solution of the alcohol **111** in chlorosulfonic acid below 3 °C. The spectrum exhibits a singlet with $\delta = 1.86$ ppm due to the *tert*-butyl group protons (note for comparison that the protons of the alkyl group in the initial alcohol **111** are responsible for a signal with $\delta = 1.70$ ppm).[101]

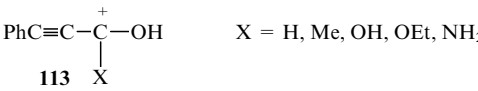


111 **112**

It is of interest that bright colouring of acidic solutions of tris(alkynyl)methanols was mentioned in publications back in the 1920s (see Ref. 101 and references therein).

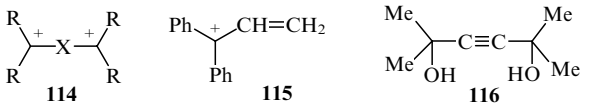
The alkynyldihydroxycarbenium ions $RC\equiv C-C^+(OH)_2$ (R = H, Me, Ph) arising upon protonation of the corresponding propiolic acids by FSO_3H in liquid SO_2 (-78 °C) or in SO_2ClF (-120 °C) have been detected by NMR spectroscopy.[102]

A fairly comprehensive study of the ^{13}C NMR spectra of a series of phenylethynylcarbenium ions (together with benzyl- and naphthylcarbenium cations) has been reported by Olah *et al.*[103] They analysed in detail the degree of positive charge delocalisation as a function of the nature of the substituents at the carbenium centre. In particular, the ^{13}C NMR spectra of protonated carbonyl compounds **113** were discussed.

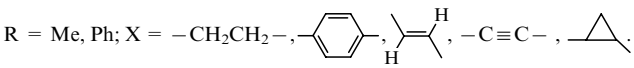


113

Olah *et al.*[104] have analysed the ability of an alkynyl group to delocalise positive charge in comparison with this property of other groups. This was done using a series of carbenium dications **114** generated from the corresponding diols or dihalo-derivatives on treatment with FSO_3H, SbF_5-FSO_3H or SbF_5-SO_2ClF.



114 **115** **116**

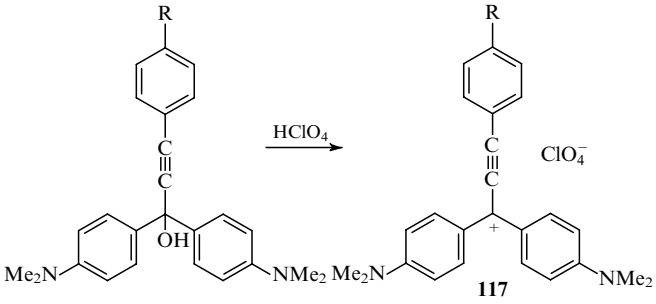


According to the data of ^1H and ^{13}C NMR spectra, *para*-phenylene and cyclopropyl groups possess the best capacity for charge delocalisation. The $-CH=CH-$ group occupies an intermediate position, and the $-C\equiv C-$ group exhibits the poorest charge delocalisation capacity. In the tetraphenyl-substituted dications **114** (R = Ph), the charge is mainly concentrated on the carbenium centres and also in the *ortho*- and *para*-positions of the terminal phenyl groups.[104]

The ^{13}C NMR spectra of dications of the type **114** were compared with those of the diphenylpropynylcarbenium (**9b**) and diphenylallyl (**115**) cations.[100,104] The relationship between the chemical shifts of the carbon atoms implies that in symmetrical dications **114** (R = Ph, X = $-CH=CH-$, $-C\equiv C-$), the charge is delocalised to a lesser extent than in the corresponding ions **115** and **9b**. When the initial alcohol molecule contains no electron-

releasing groups attached to the potential carbenium centre and capable of charge delocalisation, dications of the type **114** (R = Me) are not formed. Attempts to ionise 2,5-dimethylhex-3-yne-2,5-diol **116** result in a complex mixture of carbocations. As has already been mentioned, systems of this sort (**38**, Section II) readily undergo various types of isomerisation such as the Rupe and Meyer–Schuster rearrangements.

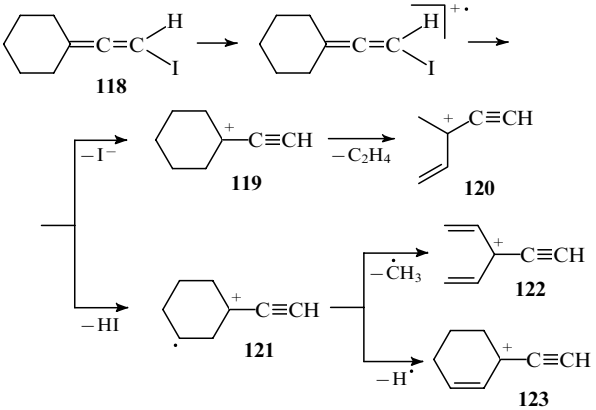
Other spectroscopic methods have also been used to study alkynylcarbenium ions. Stable alkynylcarbenium salts have been characterised by IR spectroscopy (Section V). Electronic spectroscopy has been used to detect cationic intermediates and to measure their lifetimes.[33,95] The dependence of the electronic spectra of cations **117** on the nature of the substituent in the arylethynyl fragment has been studied in order to develop new ethynyl analogues of triphenylmethane dyes, which intensely absorb light in the region 700–800 nm.[105]



R = H, Cl, NO_2, MeO, NMe_2.

It has been found that introduction of a triple carbon–carbon bond in the structure of a triarylmethane dye makes this cationic species planar, because one of the aryl groups moves away from the trigonal unit; this is accompanied by a strong bathochromic shift of the absorption band to the visible region of the spectrum. In addition to the decrease in the steric strain between the *ortho*-hydrogen atoms in the aryl groups, it becomes possible to influence the electron density distribution over the whole cation by varying the nature of substituent R.

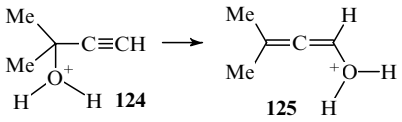
Degradation of the molecular ions of allene hydrocarbons has been proposed to give the propargyl cation ($HC\equiv C-CH_2^+$).[7] The most intense peaks (about 100%) in the mass spectrum of iodoallene **118** are the peaks of fragment ions with m/z 107, 91, 79 to which structures of the ethynylcarbenium ions **119**, **122** and **120**, respectively, were assigned.[106]



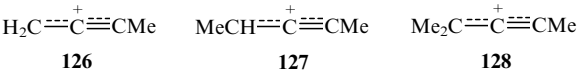
The use of various spectroscopic techniques for identification of alkynylcarbenium ions is discussed in Section V using particular synthetic examples.

IV. Quantum-chemical calculations

The mechanism of the Meyer–Schuster rearrangement has been studied theoretically using *ab initio* calculations for *O*-protonated 3-methylbut-1-yn-3-ol **124** and the product of its rearrangement, 3-methylbuta-1,2-dien-1-ol **125**. Based on the results of these calculations, it was concluded that the transition state of the **124** → **125** rearrangement is a complex consisting of a carbocation and a water molecule acting as the migrating species.[107]



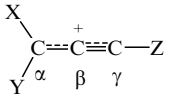
To rationalise the predominant 1,4-addition to penta-1,2,3-triene **98**, which could not be explained based merely on the data of ^1H and ^{13}C NMR spectra of alkynyl carbocations (Section III), *ab initio* calculations of the charge distribution in three cations (**126**–**128**) have been performed.[93]



126 **127** **128**

The calculations showed that in these three cations, the charge is mostly concentrated on the propargyl sp^2-hybridised centre. As the number of methyl groups in the cations **126**–**128** increases, nucleophilic attack at this position becomes more favourable.[93] Since the stability of alkynyl carbocations is insufficient for them to be directly observed by spectroscopic methods (Section III), it is difficult to follow the variation of the stability of these species over a wide range of structures starting from the simplest one and to estimate the contributions of the resonance structures **9** and **10** as functions of the degree of substitution.

Valuable information on the geometrical parameters of a series of alkynylcarbenium ions **129** and charge distribution in these species found by *ab initio* calculations has been reported by Dorado *et al.*[108]



129

X, Y, Z = H, Me, F, NH_2.

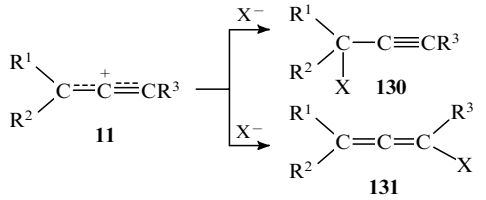
For cations **129**, the lengths of the $C_\alpha-C_\beta$, $C_\beta-C_\gamma$, $C_\alpha-X$, $C_\alpha-Y$ and $C_\gamma-Z$ bonds, bond angles and the relative energies have been calculated. In general, it was noted that the propargyl form **9** predominates in those cases where the substituent X, substituent Y or both of them either withdraw σ-electrons from the C_α atom or donate π-electrons to the unsaturated fragment. Conversely, the same effects of the substituent Z increase the contribution of the allenyl structure **10**. These effects are especially pronounced for fluorinated cations.

The change in the ratio of the $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ bond lengths (and, correspondingly, in the bond orders) depending on the number and positions of substituents in cations **129** presents particular interest. Upon introduction of any substituent other than hydrogen (Me, F, NH_2) to the C_γ atom, the $C_\alpha-C_\beta$ bond becomes shorter, while the $C_\beta-C_\gamma$ bond becomes longer than the corresponding bonds in the cation **129** in which X = Y = Z = H. Conversely, accumulation of substituents at C_α causes the opposite tendency. The average $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ bond lengths for trisubstituted cations have been determined. For X = Y = Z = Me, these values are 1.381 and 1.204 Å, and for X = Y = Z = F, they are 1.399 and 1.196 Å, respectively. Thus, introduction of substituents into the C_α position makes the $C_\alpha-C_\beta$ bond 'more single' and the $C_\beta-C_\gamma$ bond 'more triple'. The values for charge distribution determined in the study cited [108] are consistent with the fact found by Olah *et al.* [100] that the positive charge on the C_α atom is approximately twice as large as that on the C_γ atom.

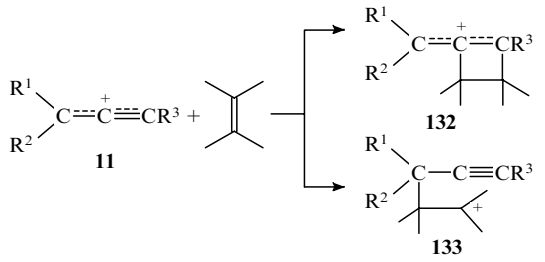
A detailed theoretical study of a series of alkynylcarbenium ions including the unsubstituted propargyl cation and methyl- and phenyl-substituted ions of the type **129** has been reported by Mayr *et al.*[109] As in the previous publication,[108] *ab initio* calculations for

the bond lengths, charge distributions and stabilisation energies for methyl- and phenyl-substituted allenyl cations were carried out. The bond lengths calculated by the two groups of researchers [108, 109] and the conclusions based on them virtually coincide. Thus the $C_\alpha-C_\beta$ bond in the nonsubstituted propargyl cation (**129**, X = Y = Z = H) (1.360 Å) is somewhat shorter than the length of the single C–C bond in propyne (1.484 Å) but longer than the double C=C bond in allene (1.288 Å); at the same time, the $C_\beta-C_\gamma$ bond in this cation (1.215 Å) is longer than the triple bond in propyne (1.170 Å) but shorter than the double bond in allene. Phenyl substituents at the tertiary C_α atom elongate the $C_\alpha-C_\beta$ bond and simultaneously shorten the $C_\beta-C_\gamma$ bond more substantially than methyl substituents.

The calculations performed [109] made it possible to predict the reactivity of the alkynyl carbocations **11** with respect to nucleophilic reagents. The propargyl structure **9** is responsible for the addition to C_α and the allenyl form **10** provides the attack at C_γ. Hard nucleophiles add predominantly to the C_α position, because the positive charge on this atom is always greater than that on the C_γ atom; therefore, under conditions of kinetic control, propargyl derivatives **130** are mostly formed. The formation of allenyl derivatives **131** can be explained by assuming thermodynamic control of the addition.



Soft π-nucleophiles should also add predominantly to the C_α atom, because, according to the results of calculations, this site is characterised by the highest LUMO coefficients.[109]



However, as substituents R^1-R^3 stabilising the cations **11** are introduced in the molecule, the addition to the $C_\beta-C_\gamma$ moiety becomes more and more pronounced, because these substituents stabilise intermediate **132** but not **133**. The formation of the allylic cations **132** can be demonstrated by reactions of alkynylcarbenium ions with alkenes and dienes (the Diels–Alder reaction).

V. Synthetic applications of alkynyl carbocations

The first systematic studies on the possibility of practical application of alkynylcarbenium ions as reactive intermediates for building various cyclic and polyfunctional systems were carried out in the late 1970s and the early 1980s by a group of German scientists headed by Mayr.[110] Alkenes and dienes of various structures were used as nucleophilic substrates.

1. Reactions of alkynyl carbocations with unsaturated compounds

The alkynylcarbenium (allenyl) cations **11** are ambident electrophilic species. Five variants of the addition of unsaturated substrates (alkenes **134** and 1,3-dienes **135** both linear and cyclic) can be conceived theoretically. Figure 1 shows the structures of cationic adducts **A**–**Q** arising upon the reaction of the ions **11** with unsaturated substrates. The carbon atoms of the substrates **11**, **134** and **135** participating in the formation of new covalent bonds are designated by letters. The alkenes **134** and the 1,3-dienes

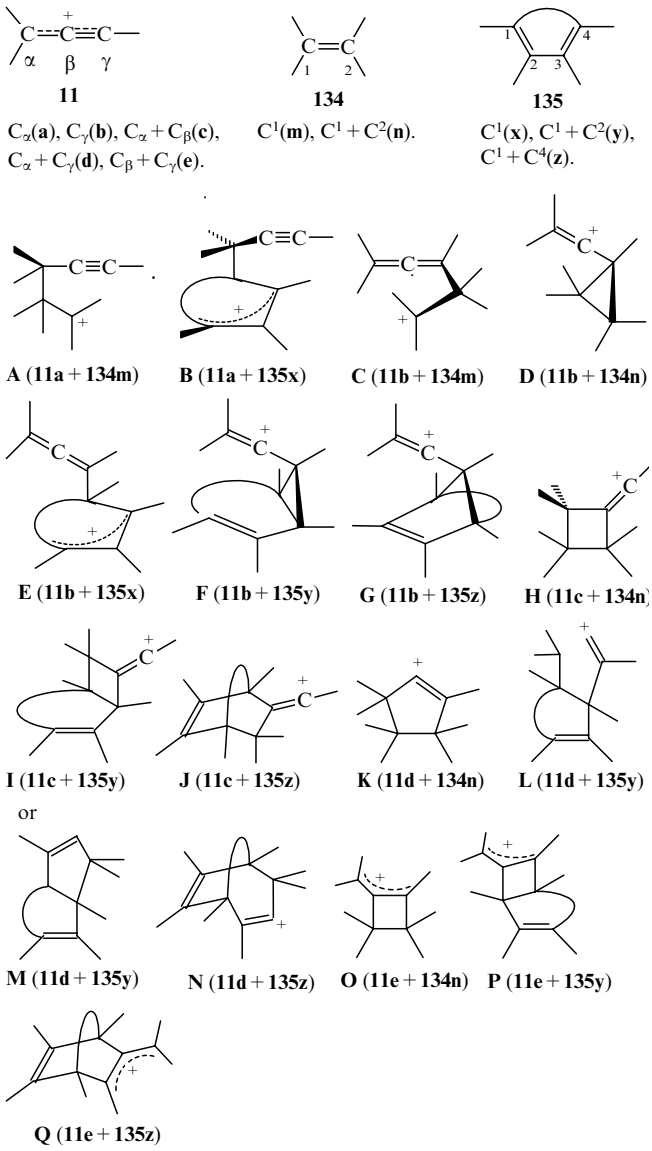
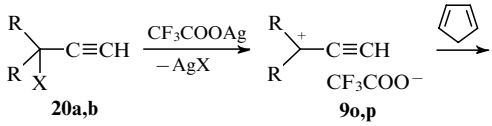


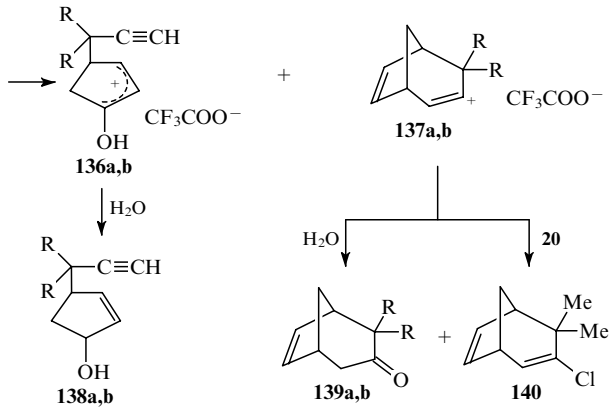
Figure 1. Variants of cycloaddition of alkynylcarbenium ions to alkenes and dienes. The letters designate the fragments of molecules formed upon the reaction.

135 are considered to be symmetrical, *i.e.* positions C(1) and C(2) in the substrate **134** and positions C(1) and C(4), C(2) and C(3) in the substrate **135** are equivalent.

The addition of alkynyl carbocations of the type **11** to the alkenes **134** and the dienes **135** can yield linear carbenium ions (**A**, **C**) or allylic (**B**, **E**, **O**, **P**, **Q**) or vinylic (**D**, **F**, **G**, **H**, **I**–**N**) cations.

The reactions of alkynyl carbocations with cyclopentadiene (CPD) have been studied most comprehensively.[110–116] The ions were generated by treatment of the corresponding halides with silver trifluoroacetate in pentane in the presence of CPD.[110] After hydrolysis of the reaction mixture, obtained from 3-bromopropyne **20a**, with aqueous ammonia, 4-(prop-2-ynyl)cyclopent-2-en-1-ol **138a** was isolated as the major product containing a slight amount of bicyclic ketone **139a**. Under the same conditions, the transformation of 3-chloro-3-methylbut-1-yne **20b** gave three products **138b**, **139b** and **140** in nearly equal amounts.[110, 113]

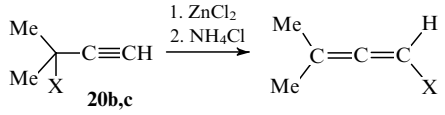




R = H(**9o**, **20a**), Me(**9p**, **20b**); X = Cl, Br.

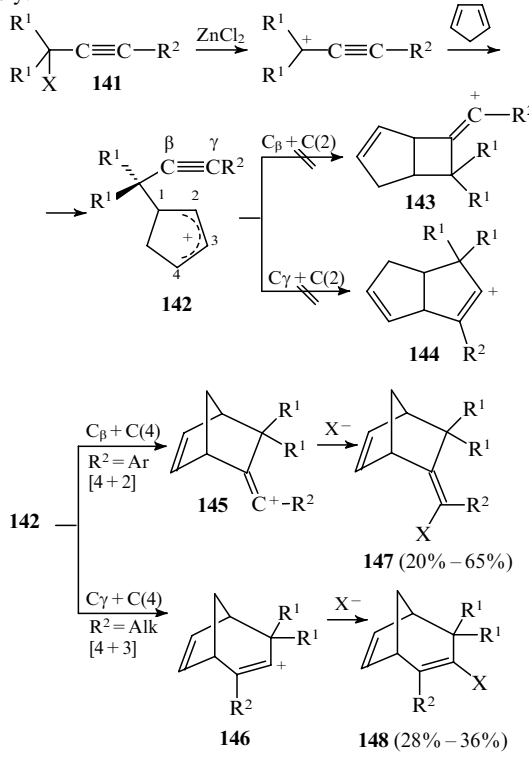
Since cyclopentadiene is highly sensitive to acidic reagents, in more recent studies,[111,112] the researchers employed a milder catalyst, namely, the efficient homogeneous catalytic system $ZnCl_2-Et_2O-CH_2Cl_2$, which is formed upon dissolution of zinc chloride (1 mole) in diethyl ether (1.5 moles) and dilution of the resulting solution with dichloromethane.[113]

It has been noted[110] that the reaction route depends on the structure of the alkynylcarbenium ion. The reaction conditions are also fairly significant. In the presence of an ethereal solution of $ZnCl_2$, the halides **20b**,**c** mentioned above do not react with CPD but instead, they are converted into allenyl halides.[113]



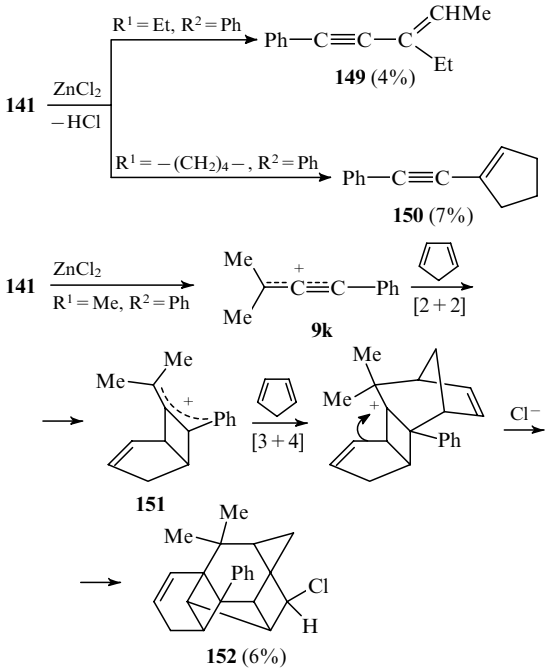
X = Cl (**20b**), Br (**20c**).

Trisubstituted haloacetylenes **141** react with CPD to give products of [4 + 2]- and [4 + 3]-cycloaddition **147** and **148**, respectively.[111,113]

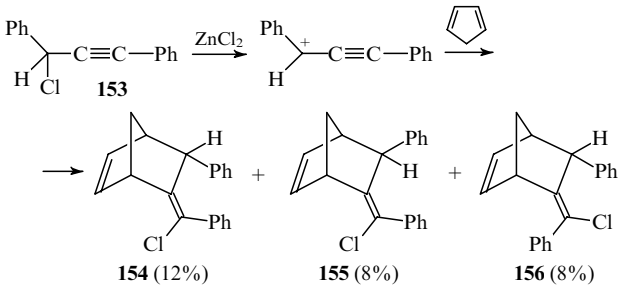


R^1 = Me, Et, $(CH_2)_4$; R^2 = Me, Et, Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4; X = Cl, Br.

In some cases, side products, enynes **149** and **150**, have been isolated from the reaction mixtures. Apparently, these compounds result from dehydrochlorination of the initial haloacetylenes **141**. Another side product, compound **152**, forms upon the addition of two CPD molecules to the dimethyl-(phenylethynyl)carbenium ion **9k**.[112,113] It is assumed that [2 + 2]-cycloaddition of the ethynyl fragment of the ion **9k** to one of the C = C bonds in CPD giving allylic cation **151** also occurs to a small extent. This cation is sufficiently stable, so that it has time to add one more CPD molecule. The subsequent rearrangements of the cations give the compound **152**.

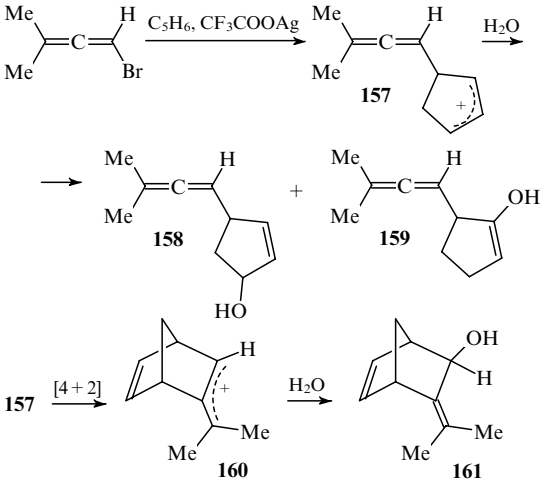


The reaction of 3-chloro-1,3-diphenylpropyne **153** with CPD gives three isomeric products of [4 + 2]-cycloaddition **154**–**156** in a total yield of 28%.[113]



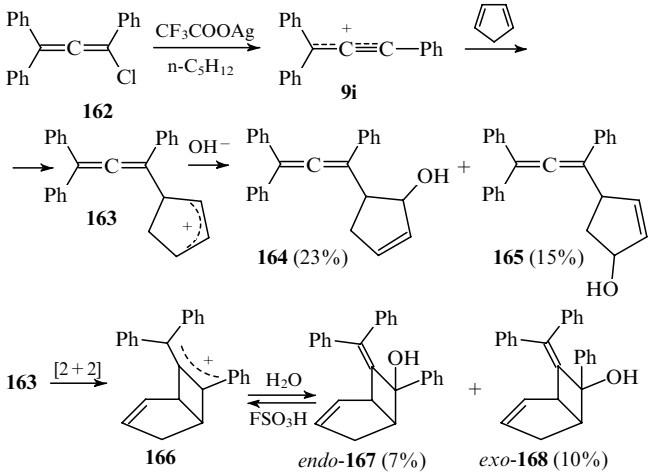
The structures of the products **147**, **148** and **154**–**156** formed in these transformations indicate that the addition of CPD to alkynyl carbocations having geminal substituents (or a phenyl group at the secondary carbenium centre) involves the sp^2 carbon atom (C_α) and one of the *sp* atoms (C_β or C_γ). This can give only the vinylic cations **143**–**146** (Fig. 1, ions **I**, **J**, **L**, **N**). Allylic cations of the types **P** and **Q** (Fig. 1), which are energetically more favourable, are not formed. Of the four possible routes of transformation of the cations **142**, only two are realised, namely those in which the ions **145** and **146** are formed intermediately. This is due to the fact that, according to calculations,[113] the bicyclic vinylic cations **143** and **144** are characterised by much higher energies. It is noteworthy that the alternative pathway to the vinylic halides **147** consisting in the isomerisation of the initial haloalkynes **141** to haloallenes followed by their reaction with CPD has been rejected,[113] because it was found that 1-halo-3-methylbuta-1,2-dienes do not react with CPD under these conditions.

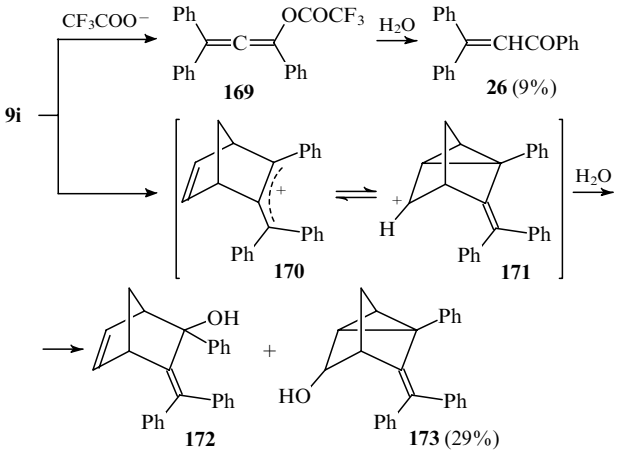
As has already been noted (Section III), not only functional acetylene derivatives but also the corresponding allene derivatives can serve as the precursors of the alkynyl carbocations **11**. In fact, the reaction of cyclopentadiene with 1-bromo-3-methylbuta-1,2-diene in the presence of silver trifluoroacetate affords a mixture of polymers from which allenylcyclopentenols **158** and **159** (ratio 83 : 17, total yield ~15%) and traces of the compounds **138b** and **161** were isolated.[113]



Thus, 3-chloro-3-methylbut-1-yne **20** and isomeric bromoallene react with CPD under the same conditions to give absolutely different products. Although in the latter case, the yields of the reaction products are too low for reliable conclusions to be made, it should be noted that the CPD molecule adds to that carbon atom in the alkenylcarbenium ion precursor from which the halogen atom is eliminated. In all probability, this situation is due to the very low stability of ethynyldimethyl carbocations of the type **9** with a terminal triple bond.

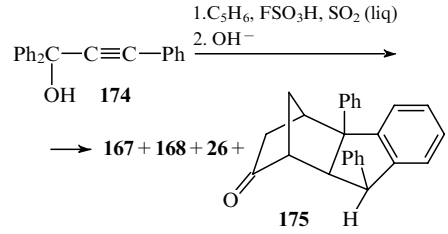
Alkynyl carbocations with three aryl substituents are much more stable (see also Sections III and IV). The attempts to generate triphenylethynyl carbocations by treatment of chlorotriphenylallene **162** with the $ZnCl_2 - Et_2O - CH_2Cl_2$ catalytic system resulted in complex product mixtures of an unknown composition. Therefore, silver trifluoroacetate was used, which ensured that transformations of the cationic intermediates were irreversible, because the cations were bound by the trifluoroacetate anions.[114,115] Treatment of a mixture of chlorotriphenylallene **162**, CPD and CF_3COOAg in pentane with an alcoholic solution of KOH gave a mixture of the compounds **26**, **164**, **166**, **167**, **172** and **173** in a total yield of 95%.



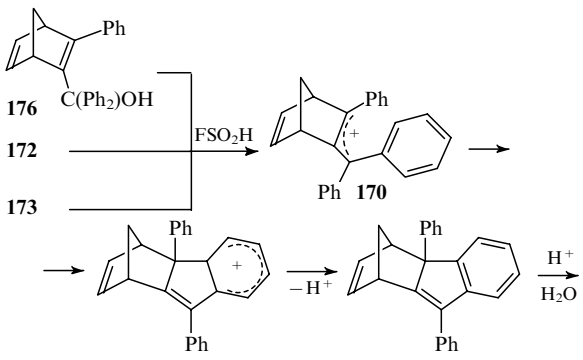


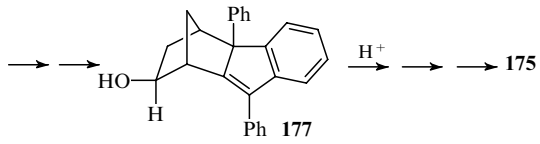
However, it can be seen from the above scheme that only 9% of the alkynyl carbocations **9i** are bound by trifluoroacetate anions yielding the α,β-unsaturated ketone **26** as the final product. The prevailing process is addition of CPD to the cation **9i**. It was shown in special experiments[114,115] that the tertiary alcohol **172** rearranges to the secondary alcohol **173** on treatment with toluene-*p*-sulfonic acid. Nevertheless, according to ^1H NMR spectroscopy, dissolution of allenylcyclopentenol **164** and the tertiary alcohol **167** in a mixture of FSO_3H and liquid SO_2 at −70 °C affords only the bicyclic vinylic cation **166**. Thus, the allylic cations **170** are intermediates on the pathway to the alcohols **172** and **173**, while the cations **163** react with CPD to give the ions **166**. These results led the investigators to the conclusion that the [2 + 2]-cycloadditions **9i** → **163**, **9i** → **166** are stepwise processes, whereas the [4 + 2]-cycloaddition **9i** → **170** is a concerted process.

The addition of CPD to the terminal *sp*-hybridised carbon atom in the cation **9i** might be a result of the structure of the initial chloroallene **162**. However, when phenyl-substituted alkynol **174** was made to react with CPD in the presence of fluorosulfonic acid, compounds **167** and **168** were obtained as the major products after hydrolysis of the reaction mixture (the ratio **167** : **168** : **26** : **175** = 9 : 4 : 4 : 3, total yield ~35%).[114,116]

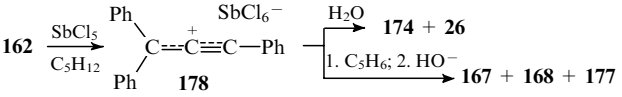


The tricyclic ketone **175** is formed in a high yield on treatment of the alcohols **172** and **173** or specially synthesised compound **176** with acids. A mechanism for this process was proposed, which includes electrocyclic ring closure in the cationic intermediate **170** and acid-catalysed rearrangements of compound **177**.[114,116]





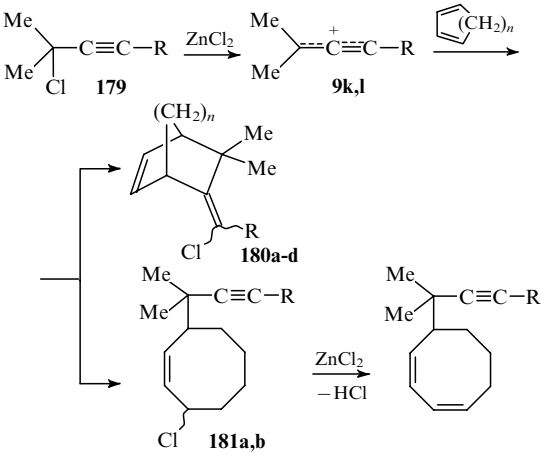
Treatment of chlorotriphenylallene **162** with $SbCl_5$ affords dark-red crystals of hexachloroantimonate **178**. Hydrolysis of this salt gives rise to a mixture of the alcohol **174** and the ketone **26** in 11 : 14 ratio. The reaction of the salt **178** with CPD (liquid SO_2, −30 °C) and subsequent alkaline hydrolysis yields the products **167**, **168** and **177** described above in a ratio of 4 : 5 : 1 (total yield ~30%).[116]



Thus, the data presented here permit the conclusion that the triphenyl-substituted ethynyl carbocation **9i** always adds a CPD molecule at the terminal *sp*-hybridised carbon atom, irrespective of the nature of the preceding compound. The cycloaddition involves only the C_β and C_γ atoms, *i.e.* only allylic cations **166** and **170** (type **P** and **Q** cations, see Fig. 1) are generated.

Unlike cyclopentadiene, which enters into both [2 + 4]- and [3 + 4]-cycloaddition reactions with dialkyl-substituted alkynyl carbocations,[111, 113] cyclohexadiene and cycloheptadiene react only according to the [2 + 4]-cycloaddition pattern in the presence of $ZnCl_2$, and cyclooctadiene gives only 1,4-addition products **181a**,**b** (Scheme 1).[117, 118]

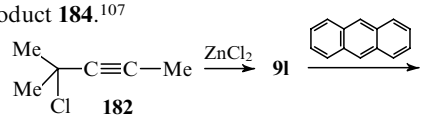
Scheme 1

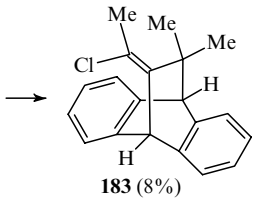


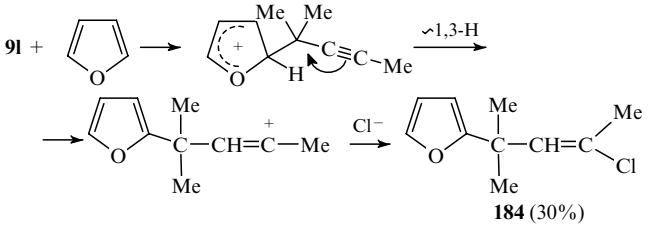
Compound	R	*n*	*E*/*Z*	Yield (%)
180a	Me	2	1 : 1	22
180b	Ph	2	only *E*	54
180c	Me	3	1 : 1	22
180d	Ph	3	only *E*	50
181a	Me	4	–	10
181b	Ph	4	–	29

This difference in the behaviour of alicyclic 1,3-dienes is due to different energies of both the corresponding cationic intermediates and the final products, which result from different degrees of strain in the rings.

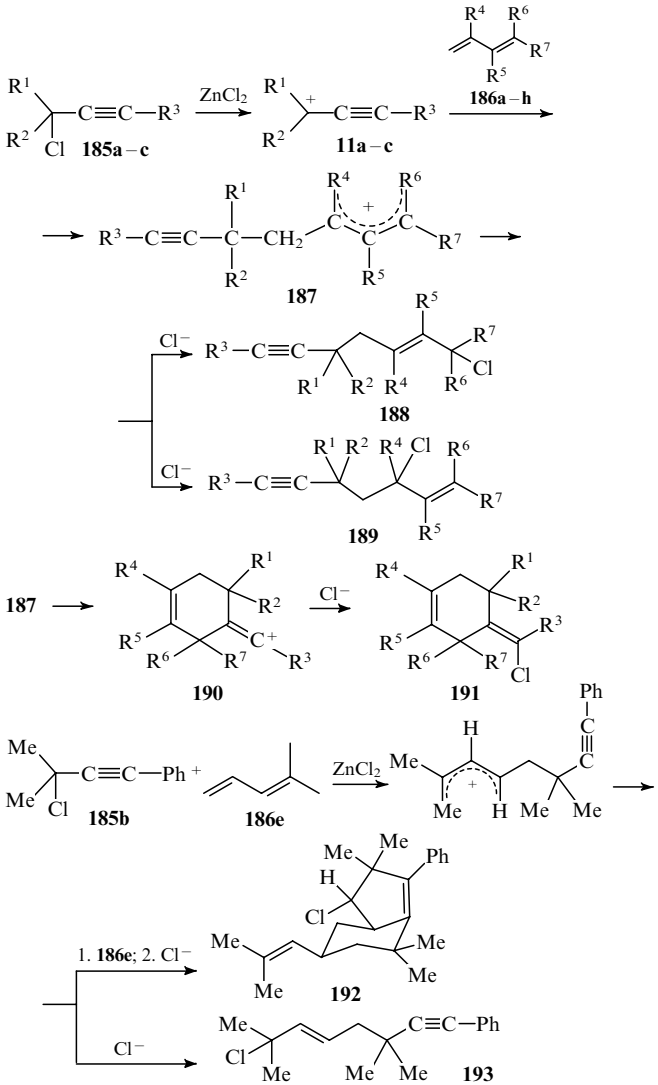
The reaction of 4-chloro-4-methylbut-2-yne **182** with anthracene in the presence of $ZnCl_2$ gives rise to the product resulting formally from [4 + 2]-cycloaddition to the isomeric chloroallene **183**.[107] The reaction of furan with the same cation yields acyclic product **184**.[107]







The addition of linear 1,3-dienes **186a**–**g** and 1,2-dimethylenecyclohexane **186h** to the propynylcarbenium ions **11a**–**c** in the presence of the $ZnCl_2$–Et_2O–CH_2Cl_2 system occurs only at the sp^2-hybridised carbon atom and gives linear allylic cations **187**. Subsequent transformations of the cations **187** are largely determined by the structures of both reactants.[119, 120]

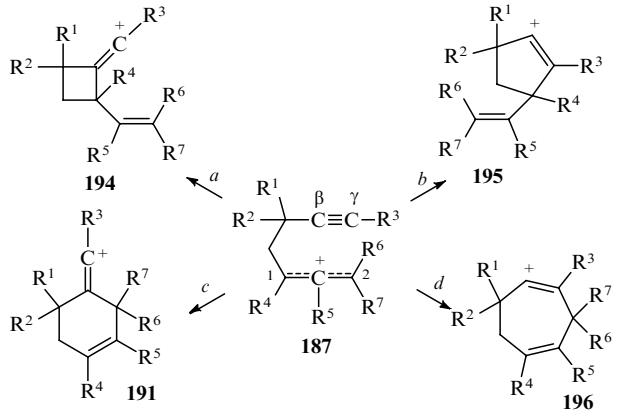


$R^1 = R^2 = R^3 = Me$ (**185a**, **11a**); $R^1 = R^2 = Me$, $R^3 = Ph$ (**185b**, **11b**); $R^1 = R^3 = Ph$; $R^2 = H$ (**185c**, **11c**); $R^4 = R^5 = R^6 = R^7$ (**186a**); $R^4 = Me$, $R^5 = R^6 = R^7 = H$ (**186b**); $R^4 = R^5 = R^6 = H$, $R^7 = Me$ (**186c**); $R^4 = R^5 = Me$, $R^6 = R^7 = H$ (**186d**); $R^4 = R^5 = H$, $R^6 = R^7 = Me$ (**186e**); $R^4 = R^7 = Me$, $R^5 = R^6 = H$ (**186f**); $R^4 = R^6 = R^7 = Me$, $R^5 = H$ (**186g**); $R^4 - R^5 = (CH_2)_4$, $R^6 = R^7 = H$ (**186h**).

Most often, allyl chlorides **188**, which are thermodynamically more stable than their isomers **189**, are formed as the major products of these reactions. Upon the reactions of the chlorides **185a**,**b** with buta-1,3-diene **186a** and the reaction of chloride **185c** with penta-1,3-diene **186c**, isomeric allyl chlorides **189** were also isolated (the **188** : **189** ratios were 4 : 1, 1 : 1 or 2 : 1, respectively). Cyclic vinyl chlorides **191** were the only products formed upon the reaction of the chloride **185b** with 1,2-dimethylenecyclohexane **186h** and the reaction of **185c** with the diene **186f**. It should be noted that the formation of six-membered cyclic vinyl halides **191** is of special interest, because the allyl-cation intermediates **187** are alkynylcarbenium ions in which the triple carbon – carbon bond is separated from the carbenium centre by one methylene unit (see Section VI).

It was shown [119, 120] that dimethylpropargyl chloride **185c** does not add to buta-1,3-diene **186a** or isoprene **186b**. When the chloride **185a** is made to react with the diene **186e** or the chloride **185b** reacts with the dienes **186e**,**f**,**g**, the reaction mixtures polymerise. Only the reaction of the chloride **185b** with the diene **186e** did give bicyclic diene **192** (yield 23%) which resulted from the addition of two molecules of the diene **186e** to the cation **11b**.

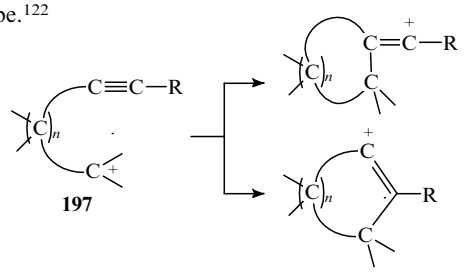
Four cyclisation pathways can, in principle, be conceived for the alkynylallylic cations **187**: those leading to four- (*a*), five- (*b*), six- (*c*) and seven-membered (*d*) vinylic cations.



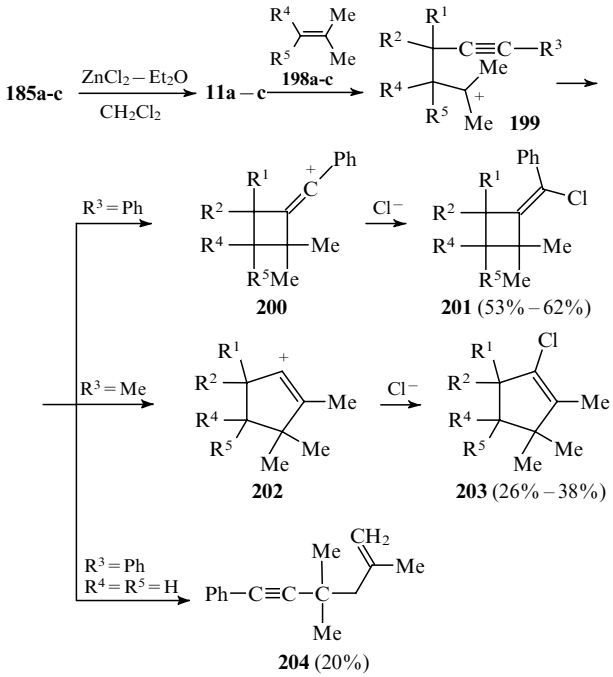
(*a*) $C_\beta + C_1$; (*b*) $C_\gamma + C_1$; (*c*) $C_\beta + C_2$; (*d*) $C_\gamma + C_2$.

Obviously, pathways *a* and *b* are energetically unfavourable, because **194** contains a strained four-membered ring, and in **195**, the geometry of the vinyl cationic fragment differs substantially from the linear geometry inherent to it.[120] The latter statement is also true for the isomer **196**. Only the cation **191** in which the carbenium centre is exocyclic and is stabilised by the neighbouring phenyl substituent is energetically favourable. This is especially clearly seen for the diene **186h**, which reacts with the chloride **185b** yielding the species **187** [R^4, $R^5 = (CH_2)_4$] the geometry of which is rigidly fixed by the cyclohexane ring.

Considerable synthetic and theoretical interest is aroused by rearrangements of alkynylcarbenium ions **197** in which the multiple bond and the carbenium centre are separated by one or more sp^3-hybridised carbon atoms. π-Cyclisation of cations of the type **197**, where $n = 1$ (homopropargyl rearrangement [22–24, 26, 27, 121]) and $n = 3$ (see Ref. 22, for more details, see Section VI) is a well-known reaction. The reactions of alkynyl carbocations with dienes described above are examples of cyclisation of cations of the type **197** with $n = 2$; the reactions with alkenes also belong to this type.[122]



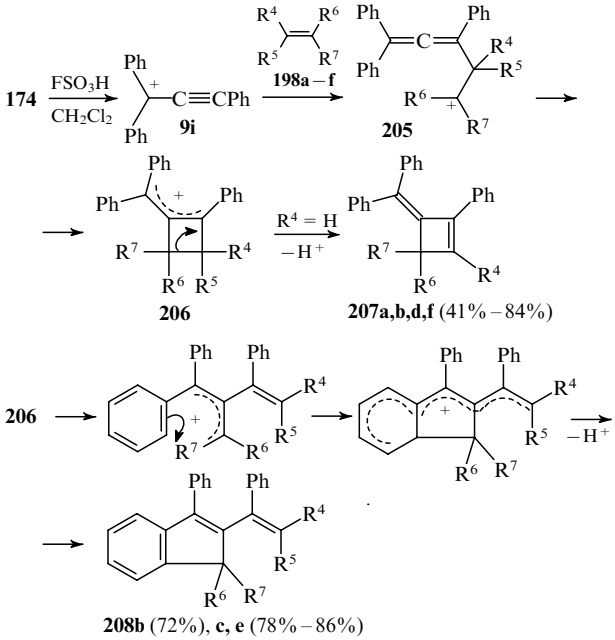
Chlorobenzylidenecyclobutanes **201** and chlorocyclopentenes **203** are formed upon [2 + 4]- or [3 + 4]-cycloaddition of the alkynyl carbocations **11a**–**e** to alkenes **198a**–**c**.[122]



$R^4 = R^5 = H$ (**198a**); $R^4 = H$, $R^5 = Me$ (**198b**); $R^4 = R^5 = Me$ (**198c**).

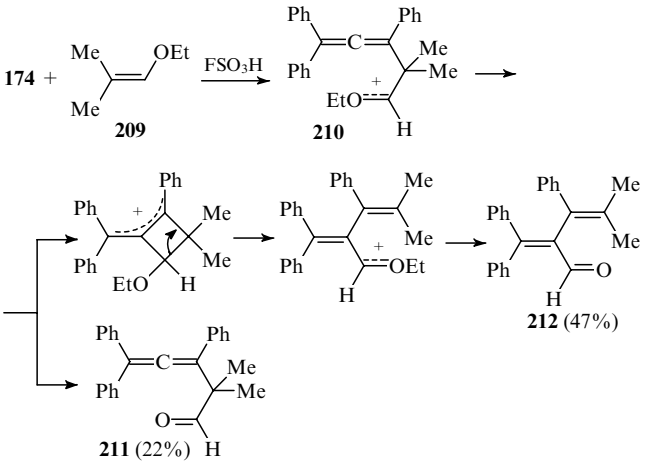
A stepwise mechanism with participation of carbocationic intermediate **199** was proposed for this reaction. The formation of this intermediate was proved by the isolation of enynes having mainly structure **204** as side products. The two routes for cyclisation of the intermediates **199** are determined by the stabilising influence of the phenyl substituent, which is attached directly to the vinylcarbenium centre in structure **200**. When the molecule contains no phenyl substituent, the reaction affords product **202** having a less strained structure.[122]

The reaction of the triphenyl-substituted cation **9i** with alkenes follows a fundamentally different pathway [123] leading to [2 + 2]-cycloaddition products.



208b (72%), **c, e** (78% – 86%)

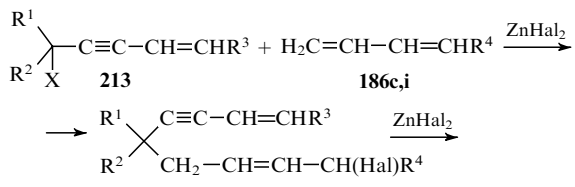
$R^4 = R^5 = H$, $R^6 = R^7 = Me$ (**a**); $R^4 = H$, $R^5 = R^6 = R^7 = Me$ (**b**);
$R^4 = R^5 = R^6 = R^7 = Me$ (**c**); $R^4 = H$, $R^5 = R^6 = Me$, $R^7 = H$ (**d**);
$R^4 = R^5 = H$, $R^6 = Ph$, $R^7 = Me$ (**e**); $R^6 = Me$, $R^4 - R^7 = (CH_2)_4$ (**f**).

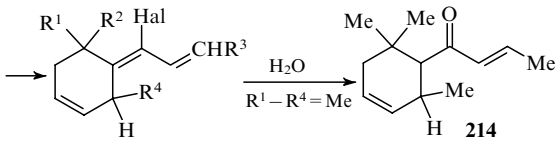


The alkenes **198a**,**b**,**d**,**f** are converted into methylenecyclobutenes **207a**,**b**,**d**,**f**, while in the case of tetramethylethylene **198c**, α-methylstyrene **198e** and trimethylethylene **198b** (with excess FSO_3H), fast electrocyclic opening of the four-membered ring occurs, resulting in the formation of bicyclic structures **208b**,**c**,**e**. When the alcohol **174** reacts with vinyl ether **209**, some of the arising ethoxycarbenium ions **210** undergo dealkylation, typical of this type of species,[124] to give aldehyde **211**. However, most of the ions **210** have time to cyclise yielding a new ethoxycarbenium ion, which is converted into aldehyde **212**.

Turning back to Fig. 1, which shows all the possible variants of cationic intermediates, one can conclude that the studies described above have provided experimental evidence for the formation of eleven of these ions, namely, **A** (**199**), **B** (**136**, **142**, **187**), **C** (**205**, **210**), **E** (**157**, **163**), **H** (**200**), **J** (**145**, **191**), **K** (**202**), **N** (**137**, **146**), **O** (**206**), **P** (**166**) and **Q** (**160**, **170**). Cyclopropylvinyl cations (**D**, **F**) have been reported [22, 23, 97] to be quite stable. As regards structures (**G**, **I**, **L** and **M**), they are energetically so unfavourable that their formation is considered [113] to be doubtful irrespective of the structure of the initial compounds and reaction conditions. It is obvious that the increase in the stability of the ion **11** upon introduction of two aryl substituents to the sp^2-carbenium centre increases the contribution of the alkynylcarbenium structure **9**. This is consistent with the data obtained by spectroscopy and quantum-chemical calculations (see Sections III, IV), which indicate that the $C_\alpha-C_\beta$ bond in the cations **129** is elongated, while the $C_\beta-C_\gamma$ bond is shortened. The attack on these cations by nucleophilic agents is mainly directed at the *sp*-carbon atom remote from the cationic centre, as in acetylene derivatives activated by electron-withdrawing substituents, while cycloaddition follows the [2+2] pattern involving the two *sp*-carbon atoms.

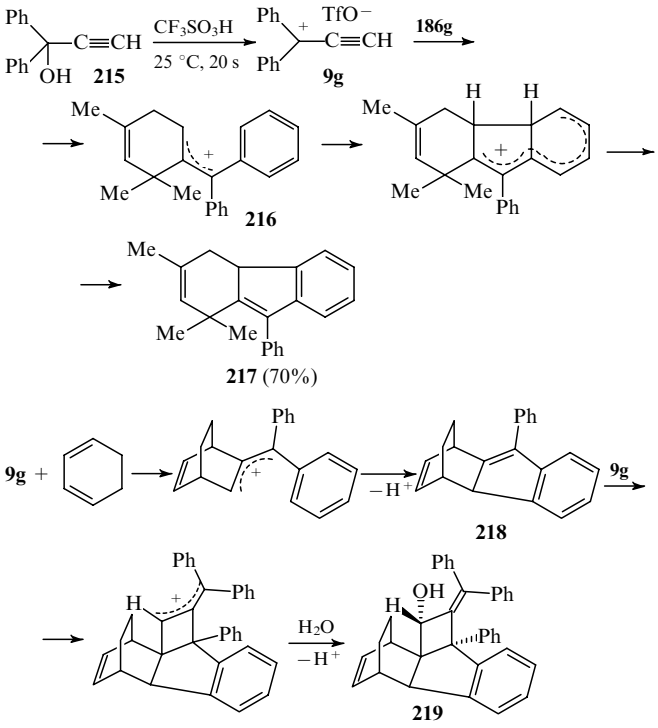
Conversely, the introduction of substituents, able to delocalise positive charge, into the acetylenic fragments results in the predominance of the allenyl form of the cation **10** and causes the nucleophile to attack the sp^2-carbon atom. It has been shown above for phenylethynylcarbenium ions (**9i**–**k**, **n**, **117**, **132**, **142**) that a similar influence can be exerted by the vinyl group. Thus the reaction of halogenated enynes **213** with buta-1,3-dienes **186c**,**i** in the presence of a homogeneous catalytic system, $ZnHal_2-Et_2O-CH_2Cl_2$ (Hal = Cl, Br), affords alkenylidenecyclohexenes.[125] A valuable product formed in this reaction is the perfume δ-damascone **214**.





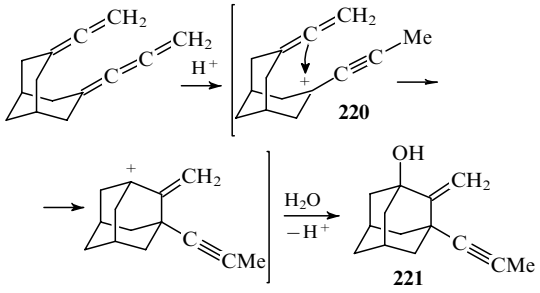
R^1, R^2, R^3, R^4 = Me, Et; Hal = Cl, Br.

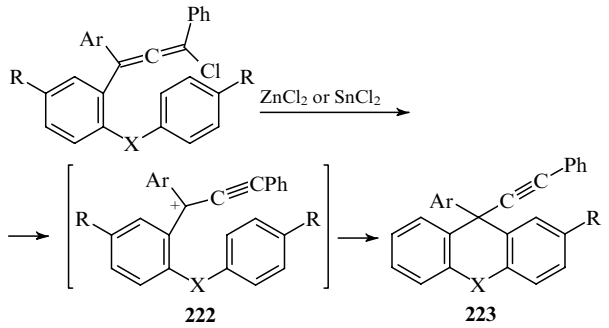
Similarly to allylic cations, alkynylcarbenium ions can act as efficient dienophiles in low-temperature Diels–Alder reactions.[126] Thus the reaction of 1,1-diphenylprop-2-yn-1-ol **215** with 2,4-dimethylpenta-1,3-diene **186g** gave tricyclic compound **217** in 70% yield.[126] Presumably, this product is formed in two successive cyclisations *via* the ethynyl carbocation **9g** and the cyclic allylic cation **216** (corresponding to structure **Q**, see Fig. 1). However, the reaction of the cation **9g** with cyclohexadiene does not stop at the stage of formation of the 1 : 1 tricyclic adduct **218**. This adduct undergoes one more [2+2]-cycloaddition to give alcohol **219** (the total yield after 20 s at 25 °C is 80%). The proposed reaction scheme was confirmed by isolation of the compound **218** (yield 62%) from this reaction carried out with a tenfold excess of cyclohexadiene and its subsequent transformation into the final product **219** under the same conditions.[126]



Neither styrene nor the indene derivative **217** reacts with the cation **9g** under the described conditions. The high reactivity of the compound **218** was explained [126] by the strained character of the double bond in the five-membered ring.[126]

Cyclisation of alkynylcarbenium ions **220** and **222** was used to prepare alkynyl derivatives of adamantane **221** [127] and fused heterocycles **223**.[128]



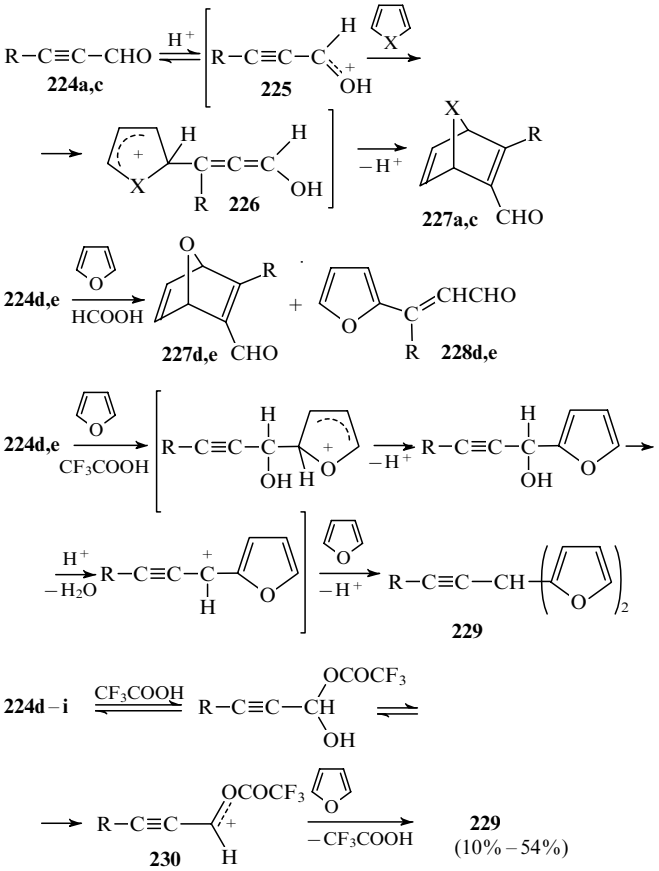


222 **223**

X = O, S, NMe, NPh.

The participation of the sp^2-hybridised carbenium atom in the cyclisation is due to the fact that the greatest charge is concentrated on this atom and also to the geometry of the intermediate **222**, which hampers the attack of the *sp*-hybridised carbon atom.

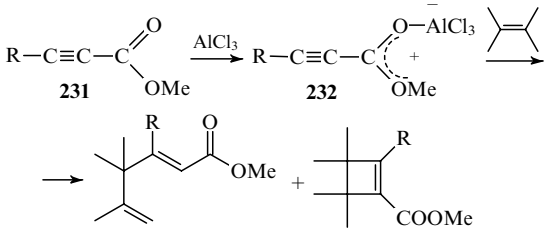
Heteroatoms (O, S, N) adjacent to a carbenium centre are known to exert a stabilising influence on carbocations.[124] In the presence of acids (HCOOH, CF_3COOH), aldehydes of the acetylene series **224** are converted into alkynylhydroxycarbenium ions **225**, which can react with cyclic dienes according to three pathways: (1) the Diels–Alder reaction giving cycloaddition product **227**, (2) nucleophilic addition of the C≡C bond to the diene molecule giving compounds of the type **228** and (3) the Michael condensation of two furan molecules with one aldehyde molecule [129, 130] affording alkynes **229**.



R = CHO (**a**), $(EtO)_2CH$ (**b**), COOEt (**c**), $CONMe_2$ (**d**), CN (**e**), H (**f**), Bu (**g**), Ph (**h**, 54%), 4-ClC_6H_4 (**i**, 20%).

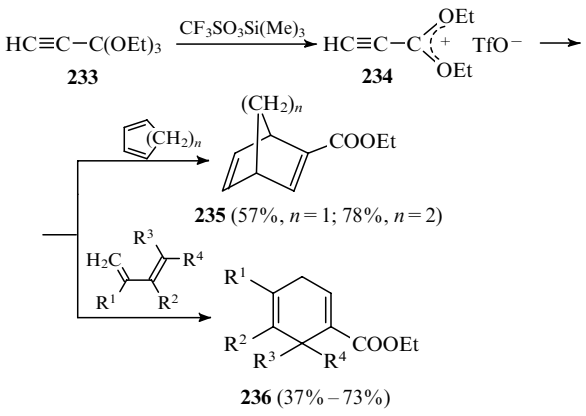
It has been shown [129, 130] that cyclopentadiene and cyclohexa-1,3-diene react with the aldehydes **224a**,**c** to give only cycloaddition products **227a**,**c** in high yields. The reactions of anthracene and diphenylfulvene with the same aldehydes **224a**,**c** give rise to mixtures of compounds **227** and **228** in which the Diels–Alder reaction products predominate. The third pathway, which is similar to the known reaction of aldehydes with dimedone,[131] occurs only for the aldehydes **224d**,**e**,**g**–**i**. The products **229h**,**i** were obtained in only moderate yields (20% and 55%, respectively). The route of the reaction of the aldehydes **224** with furan depends on the nature of the acid used. For example, the aldehydes **224d**,**e** react with furan in the presence of HCOOH giving rise to mixtures of the compounds **227d**,**e** and **228d**,**e**. In the presence of CF_3COOH, no cycloaddition products **227** are formed; instead, mixtures of compounds **228** and **229** are produced. This difference in the reaction pathways is due to the fact that in trifluoroacetic acid, which is stronger than formic acid (p*K*a 0.23 for CF_3COOH and p*K*a 3.75 for HCOOH [132]), acyloxycarbenium ions **230** can be formed, which are less stable than the hydroxycarbenium ions **225**.[32] As a result, the diene adds to the sp^2-hybridised atom of the alkynyl carbocation.

The addition of acetylenic esters **231** to alkenes is catalysed by Lewis acids and occurs either as nucleophilic addition at the triple bond or as [2 + 2]-cycloaddition.[133, 134] The reaction presumably involves the intermediate formation of complexes **232**, which can be regarded as stabilised [124] dialkoxycarbenium ions.



R = H, Cl, COOMe.

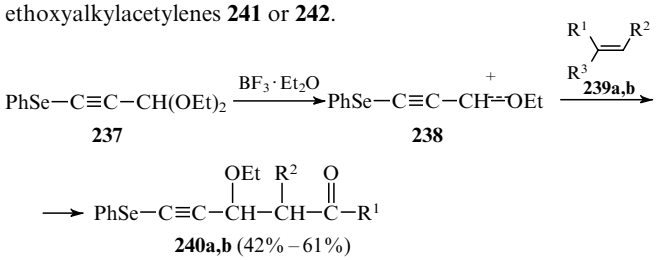
True ethynyldialkoxycarbenium ions **234** generated, for example, from orthoester **233** proved, as expected, to be extremely reactive dienophiles.[135] They add to dienes at low temperatures (0 to −78 °C) to give cyclic products **235** or **236** in good yields. These examples demonstrate successful application of alkyl propiolates in Diels–Alder reactions.[135]



235 (57%, *n* = 1; 78%, *n* = 2)

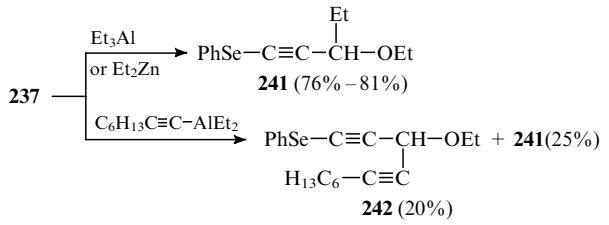
236 (37%–73%)

Ionisation of acetals of the acetylene series having a phenylselenyl substituent (**237**) affords alkoxycarbenium cations **238**, which add silyl ethers of enols **239a**,**b** at the carboxonium fragment.[136] The alkylation of the acetals **237** with organoaluminium or organozinc compounds occurs in a similar way giving rise to ethoxyalkylacetylenes **241** or **242**.

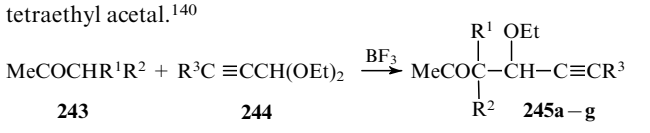


240a,b (42%–61%)

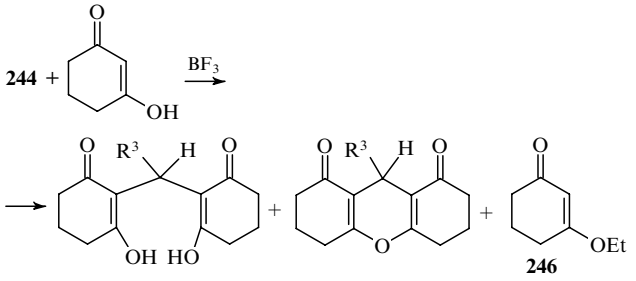
R^1–R^2 = $(CH_2)_4$, R^3 = $OSiMe_3$ (**a**); R^1 = Ph, R^2 = H, R^3 = $OSiMe_3$ (**b**).



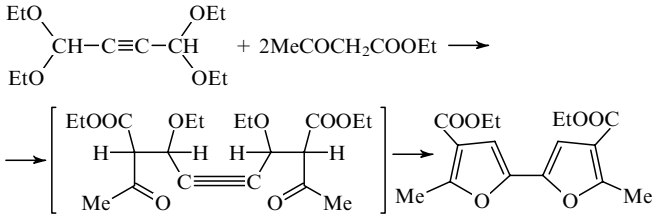
A series of studies devoted to reactions of acetals of acetylenic aldehydes with CH acids in the presence of boron trifluoride etherate deserve attention.[137–140] Acetone, methyl ethyl ketone,[137] ethyl acetoacetate, methyl acetoacetate,[138,140] acetylacetone and cyclohexane-1,3-dione[139] have been used as substrates in the reactions with alkynal acetals **244** and butynedial tetraethyl acetal.[140]



Compound	R^1	R^2	R^3	Yield (%)
245a	H	H	H	71
245b	H	Me	H	26
245c	H	CO_2Et	H	75
245d	H	CO_2Et	Ph	75
245e	H	COMe	H	37
245f	Me	CO_2Me	H	18
245g	Me	CO_2Me	Ph	18

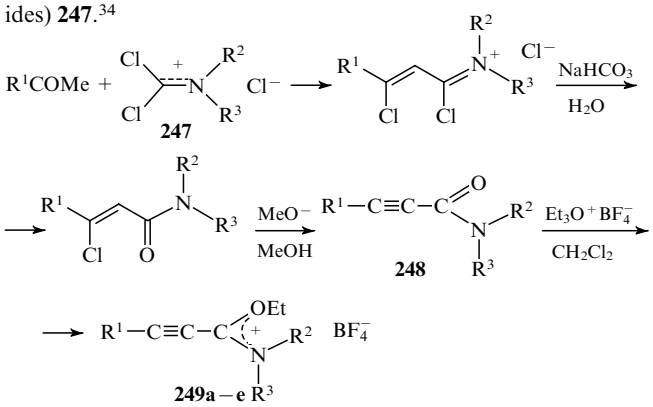


R^3 = H, Ph.



The researchers cited claim[137–140] that in these reactions, acetals are not converted into alkoxycarbenium ions like **238** and propose at least six hypothetical schemes with four- and six-centre cyclic transition states. However, none of the schemes consider the role of the catalyst, boron trifluoride etherate. In addition, in our opinion, some of the observations made by the authors rather attest to the participation of alkoxycarbocations. Thus alkynal diethyl acetals are converted into ethoxycyclohexenone **246**, and dimethyl acetals give the corresponding methoxy derivative. When a mixture of acetals is used, a mixture of methoxy- and ethoxy-cyclohexenones is formed.

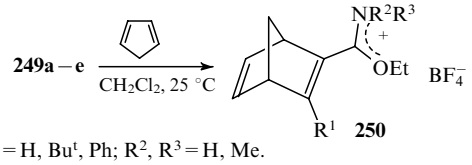
The idea of activating acetylene derivatives by cationic substituents attached directly to the triple bond has found synthetic implementation in cycloaddition reactions involving iminium derivatives of the acetylene series. Viehe *et al.*[34,141] have developed a method for the synthesis and studied the properties of ethynyl-substituted amidium salts **249** unknown previously. These salts proved to be substantially more efficient dienophiles than other acetylene derivatives activated by electron-withdrawing substituents. The salts **249** were prepared by *O*-alkylation of the amides **248** synthesised using the Viehe salts (phosgene iminium chlorides) **247**.[34]



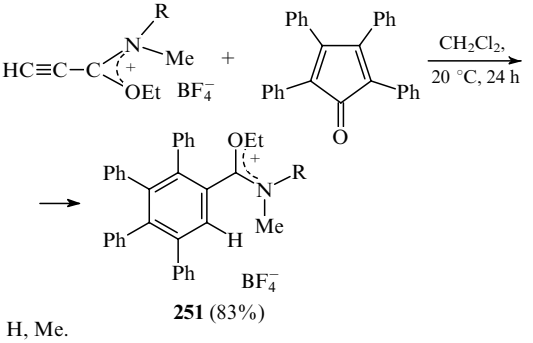
R^1 = Ph, R^2 = R^3 = Me (**a**); R^1 = Bu^t, R^2 = R^3 = Me (**b**); R^1 = H: R^2 = R^3 = Me (**c**); R^2 = H, R^3 = Me (**d**); R^2 = R^3 = H (**e**).

The amidium salts **249** remain unchanged in air and are much more stable than their dialkoxycarbenium heteroanalogues **234**. A systematic study of their ^{13}C NMR spectra showed that the carbon–carbon triple bond is substantially polarised; this decreases the energy demands and considerably facilitates the Diels–Alder and 1,3-dipolar cycloaddition reactions.

The salts **249a–e** readily react with cyclopentadiene at room temperature according to the [4 + 2]-cycloaddition pattern to give stable salts **250**. The reaction of the ethynyl-substituted salts **249c,d** with tetraphenylcyclopentadienone under the same conditions gives rise to polysubstituted benzene derivatives resulting from aromatisation of the adduct **251** formed initially.[34]

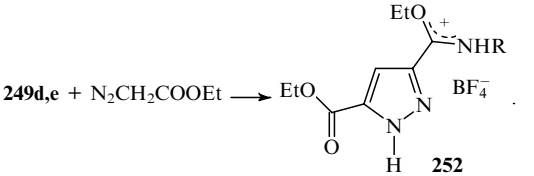


R^1 = H, Bu^t, Ph; R^2, R^3 = H, Me.

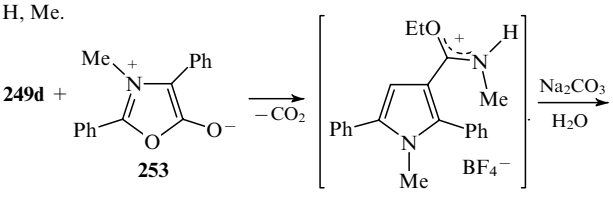


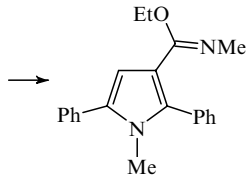
R = H, Me.

The ethynylcarbenium salts **249d,e** readily enter into 1,3-dipolar cycloaddition at room temperature. Thus the reaction with ethyl diazoacetate yields pyrazole derivatives **252**, and the addition of the salt **249d** to the azomethine 1,3-dipolar fragment of munchnone **253** opens up the way to imidates of the pyrrole series.[34]

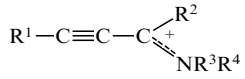


R = H, Me.



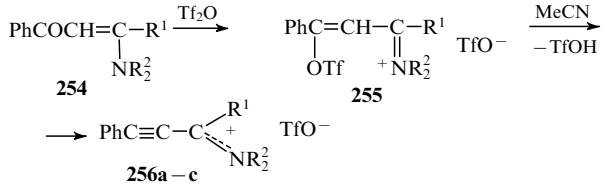


Among the alkynes containing resonance-stabilised cationic substituents, the best known are those containing a propyniminium fragment of the general formula



R^1 = H, Alk, Ar; R^2 = H, Alk, Ar, NR^3R^4, OR^5, SR^5, Hal; R^3, R^4 = H, Alk, $(CH_2)_2O(CH_2)_2$.

These are propynyliminium (R^2 = H, Alk, Ar), propynylamidinium ($R^2 = NR^3R^4$) and propynylamidium (**249**) ions.[142] The propynyliminium ions **256** can be prepared by treatment of easily accessible enaminones **254** with trifluoromethanesulfonic anhydride.[142]



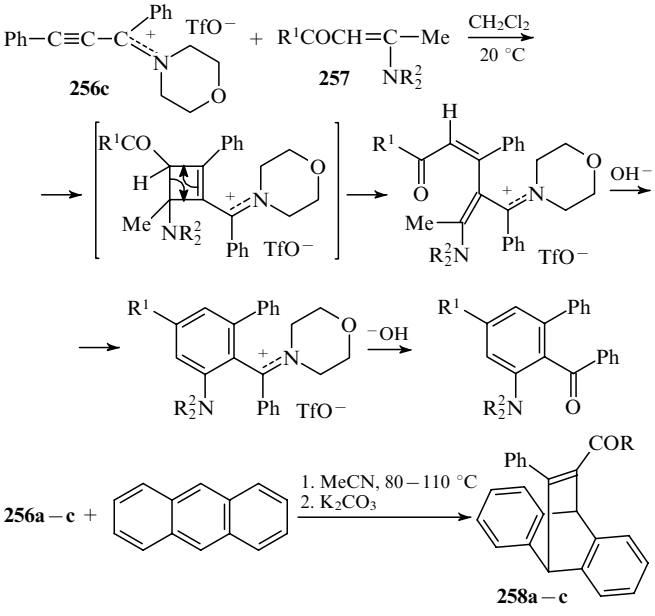
254 **255** **256a–c**

R^1 = H (**a**), Me (**b**), Ph (**c**); R^2 = Me, $(CH_2)_2O(CH_2)_2$; Tf = CF_3SO_3.

Elimination of TfOH from the iminium triflate **255** is carried out either thermally or in the presence of a tertiary amine. This procedure is suitable only for the aroyl-substituted enamines, because enamines containing an aliphatic substituent in the acyl fragment are deprotonated to give diene amines of the type $R^1C(NR^2_2)=CH-C(OTf)=CR^3_2$.

The IR spectra of the salts **256** exhibit intense absorption bands in the region of 2190–2200 (C≡C) and 1590–1630 (C=N) cm^{-1}. The ^{13}C NMR spectra of these triflates have been studied.[142]

Propynyliminium salts similar to **256** react with enaminones **257** according to the [2+2]-cycloaddition pattern and with diphenylisobenzofuran and anthracene according to the [2+4]-cycloaddition scheme.[142]



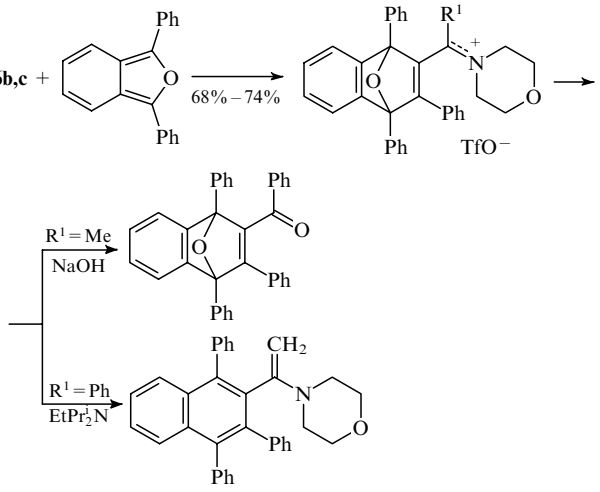
256c **257**

256a–c +

258a–c

R = H (**a**), Me (**b**), Ph (**c**).

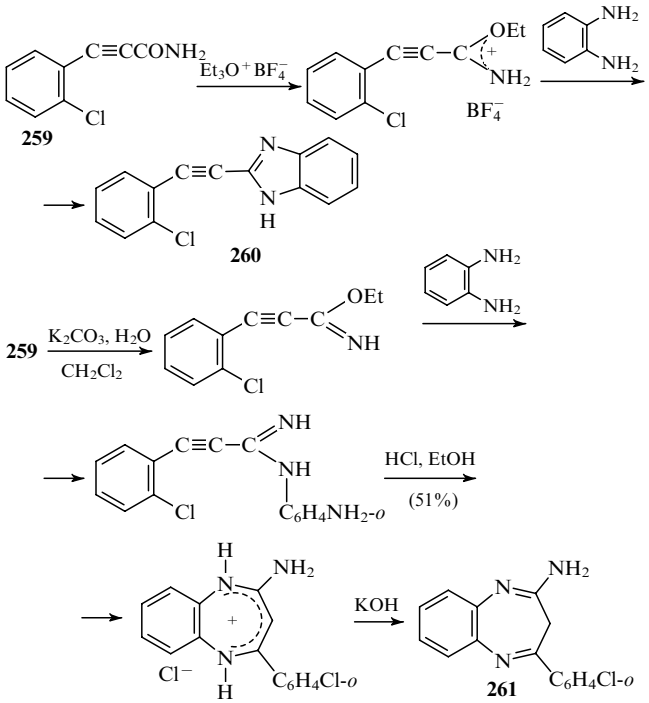
256b,c +



The propynylamidium salts **249** form no cycloaddition products with anthracene.[34] In turn, the propynyliminium salts **256** do not react with tetraphenylcyclopentadienone.[142]

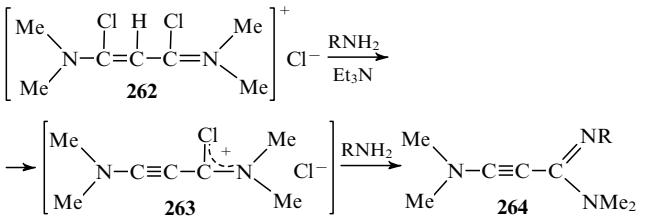
2. Reactions of alkynyl carbocations with nucleophiles

The propynylamidium cation arising upon *O*-alkylation of the amide **259** has been used to prepare 2-(2-chlorophenylethynyl)-benzimidazole **260** and 2-amino-3*H*-1,5-benzodiazepine **261**.[143]



259 **260** **261**

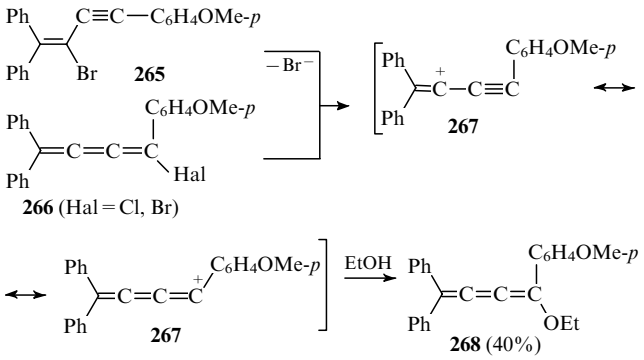
Treatment of 1,3-dichlorotrimethinecyanine **262** with aliphatic amines gives ynamine amidines **264** *via* unstable chloriminium cations **263**.[144]



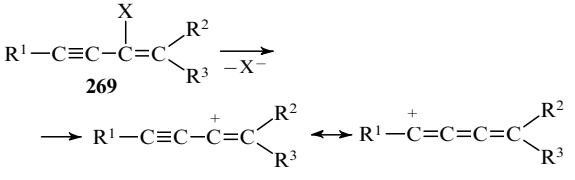
262 **263** **264**

Methods for generation and properties of another type of alkynyl carbocations — alkynylvinyl cations **267** — were simultaneously described by Japanese[145] and German[146] scientists, working independently. The former researchers[145] studied sol-

volysis of 2-bromo enyne **265** and 1-halobuta-1,2,3-triene **266** in aqueous ethanol. Ethoxycumulene **268** was detected in the reaction mixtures.

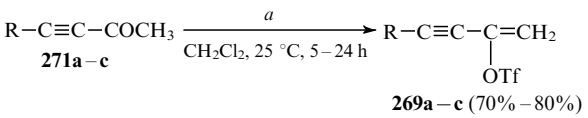


Unlike the well-known ethynylvinyl derivatives with terminal functional groups,[147] the isomeric 1-alkynylvinyl compounds of the type **269** have been little studied.

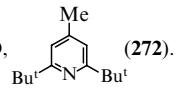


X = OR, SR, NR_2.

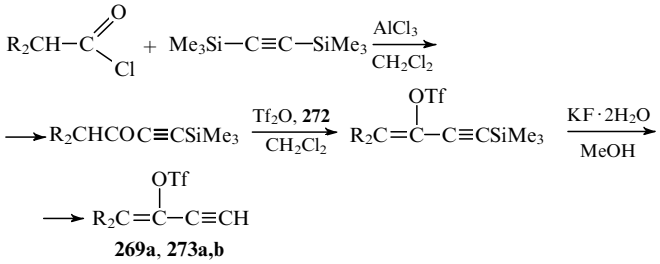
Hanack *et al.*[146] proposed a method for the synthesis of alkynyl triflates **269**, which can serve as the precursors of α-alkynylvinyl cations of the general form **270**. The method consists in treatment of ketones of the acetylene series **271a–c** with trifluoromethanesulfonic anhydride in the presence of a non-nucleophilic sterically hindered base, 2,6-di-*tert*-butyl-4-methylpyridine **272**.



R = H (**a**), Me (**b**), Bu^t (**c**).

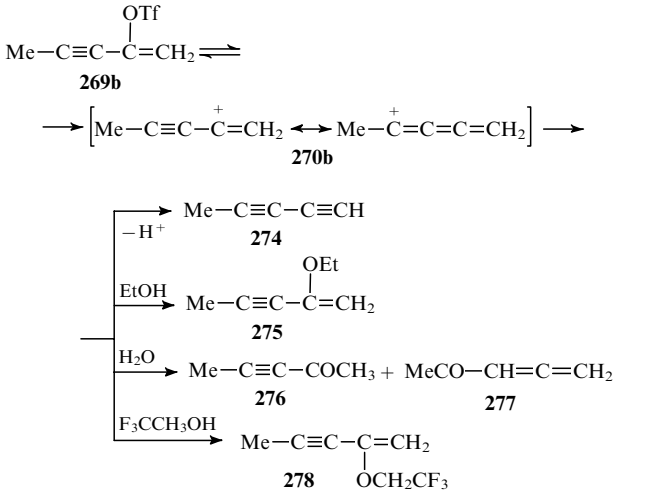
(*a*) Tf_2O,  (**272**).

A somewhat different approach, based on silylated ethynyl ketones, has been proposed by Stang *et al.*[148] These compounds are converted into ethynylvinyl triflates **269a** and **273a,b** upon successive treatment with trifluoromethanesulfonic anhydride in the presence of the base (**272**) and with potassium fluoride in methanol.



R = H (**269a**), Me (**273a**), Ph (**273b**).

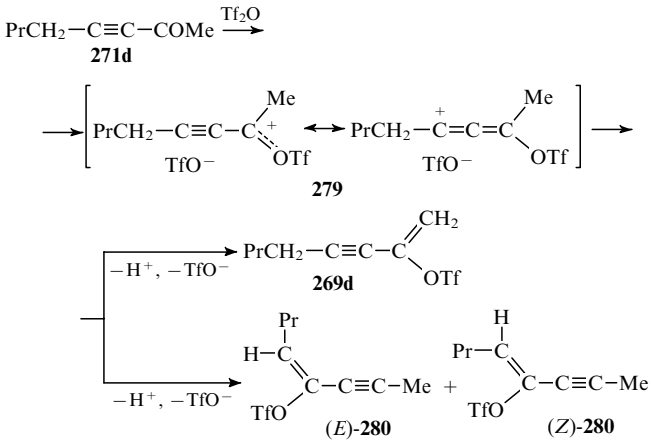
The reaction mixtures resulting from solvolysis of the triflate **269b** in 80% aqueous ethanol and 80% trifluoroethanol have been found to contain products **274–278** the formation of which has been explained by the participation of the cationic intermediate **270b**.[146]



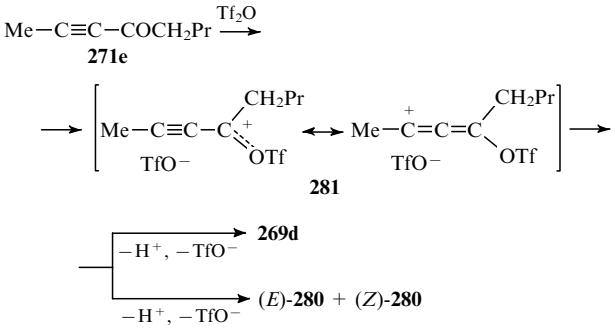
Alcohol	Yelds of solvolysis products (%)				
	274	**275**	**276**	**277**	**278**
EtOH	30	15	4	3	0
CF_3CH_2OH	24	0	20	0	28

The composition of the products of solvolysis depends on the alcohol used. These results imply that the cation **270b** reacts mainly in the form of the alkynylvinyl cation. This is consistent with kinetic measurements. It was shown[146] that the propynylvinyl triflate **269b** is solvolysed in 50% aqueous ethanol 70 times faster than the triflate $MeC(OTf)=CH_2$ and 35 times faster than the triflate $PrC(OTf)=CH_2$;[146] this points to a stabilising influence of the ethynyl fragment on the neighbouring vinyl cationic centre.

The above synthesis of 1-(1-alkynyl)vinyl triflates **269** from ethynyl ketones **271**[146] involves intermediate formation of alkynylacyloxycarbenium cations **279**, **281**. The route of their deprotonation to the final products **269** depends on the nature of the substituents R^1 and R^2.[149] It was shown that only in the case of the acetylenic ketones **271a–c**, does the reaction occur unambiguously to give the compounds **269a–c**. The alkynyl ketones **271d** and **271e** form complex mixtures of products. Thus the the ketone **271d** gave the expected triflate **269d** in 70%–75% yield. In addition, the reaction mixture contained the isomeric triflate **280** (25%–30%, the ratio $E:Z = 1:1$).

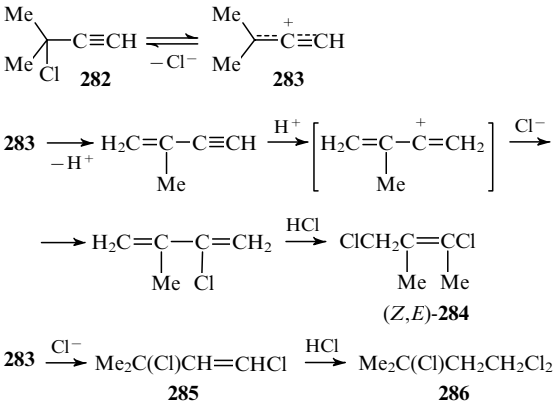


Treatment of the ketone **271e** with trifluoromethanesulfonic anhydride affords mainly the triflate **280** (85%–90%, the ratio $E:Z = 1:1$) and only 10%–15% of the triflate **269d**.



It can be seen from the above scheme that in both cases, the major reaction products result from deprotonation of the intermediates in the alkynyl carbocation form **279**, **281**.

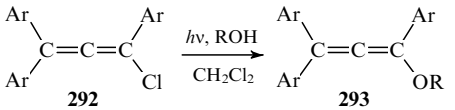
The addition of anhydrous HCl to 3-chloro-3-methylbut-1-yne **282** affords 16 reaction products. The main products are (*E*)-1,3-dichloro-3-methylbut-1-ene **285**, 1,1,3-trichloro-3-methylbutane **286** and (*Z*)- and (*E*)-1,3-dichloro-2-methylbut-2-ene **284**. The intermediate formation of dimethylethynyl carbocation **283** was postulated.[150]



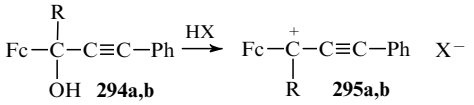
In the presence of H_3PO_4, the alcohol **285** reacts with 2- and 1-naphthols to give products of *O*-alkylation (**287**, **289**), aromatic electrophilic substitution (**290**) and cyclisation (**288**, **291**) (Scheme 2).[151]

When the reaction mixture is kept in the presence of an acid, the compound **287** isomerises to **288**, and the compound **289** isomerises to **291**; apparently, isomerisation involves dissociation of the thermodynamically less favourable naphthol ethers under the action of acids.

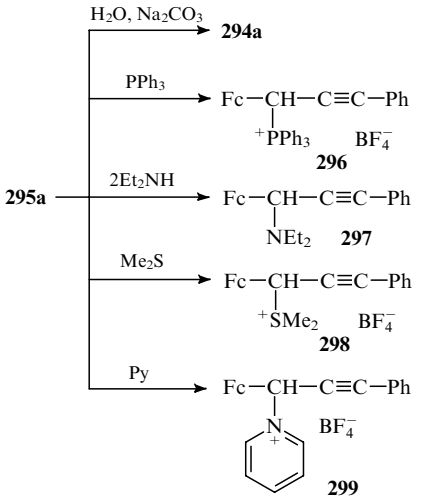
When triarylchloroallenes **292** are irradiated with a mercury lamp at −30 °C in CH_2Cl_2 solutions of alcohols, alkoxycumulenes **293** are formed.[152] This reaction is believed to proceed *via* alkynylcarbenium ions.



A ferrocenyl residue is known to stabilise efficiently a carbenium centre adjacent to it.[153] The treatment of ferrocenyl(phenylethynyl)-methanol **294a** or -ethanol **294b** with acids resulted in the synthesis of stable phenylethynylcarbenium salts **295a**,**b**. They react with nucleophiles at the sp^2-hybridised carbon atom to give charged or neutral ferrocenyl derivatives of the type **296**–**299**.[154] Bis-ferrocenyl cations in which the two ferrocene fragments are linked by one or two acetylene (or butadiyne) bridges have been studied by spectroscopy.[155]



R = H (**a**), Me (**b**); X = BF_4, ClO_4.



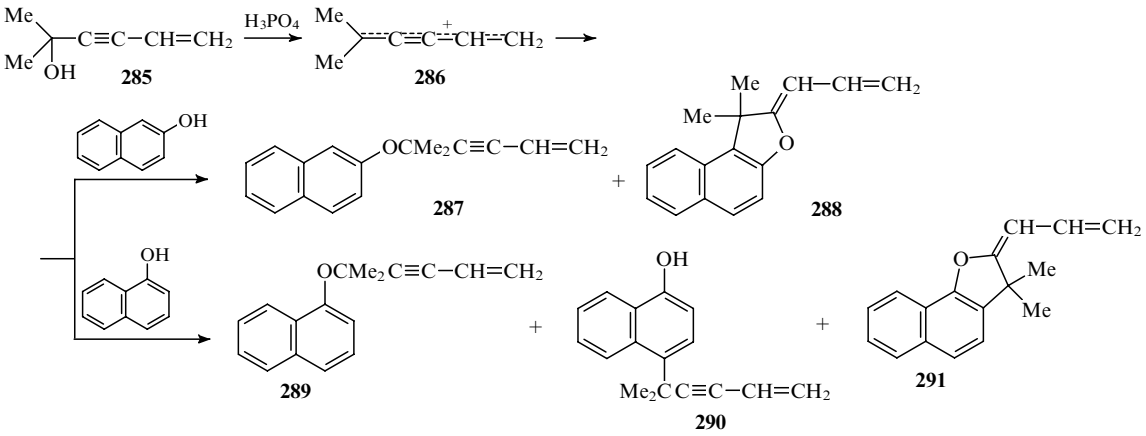
Fc is ferrocenyl, Py is pyridine.

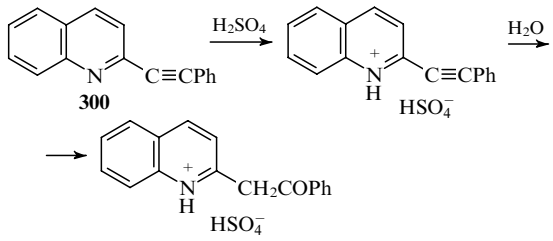
3. Alkynyl-substituted heterocyclic cations

The cationic fragment of the alkynyliminium cations of the type **256** described above can be a part of an aromatic heterocycle. These cations are the most stable due to the charge delocalisation with participation of the aromatic system.

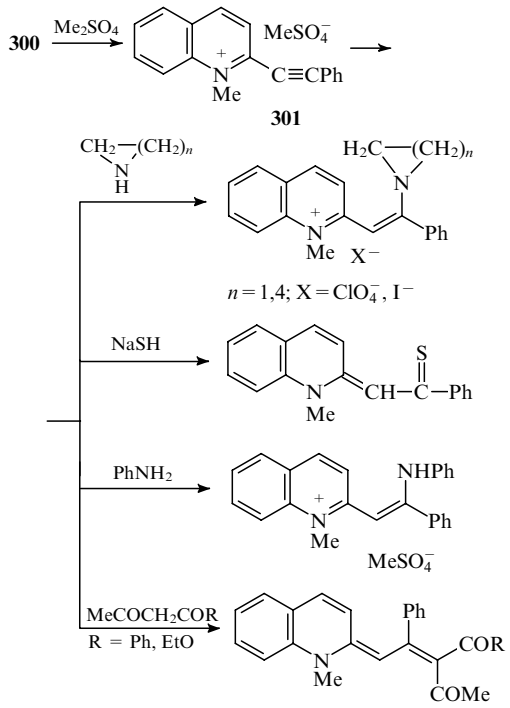
The protonation or alkylation of the nitrogen atom in alkynyl-substituted pyridines and quinolines proved to be an efficient method for activating the acetylene fragment towards reactions with various nucleophiles. Thus 2-phenylethynylquinoline **300** readily adds water in acid media.[156]

Scheme 2

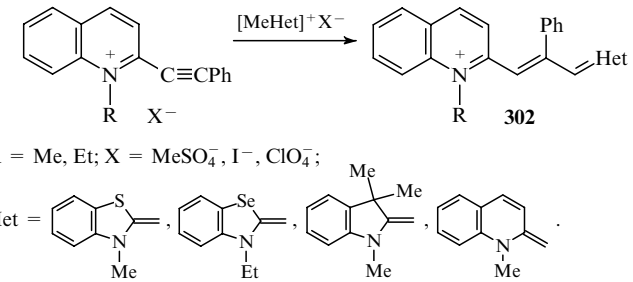




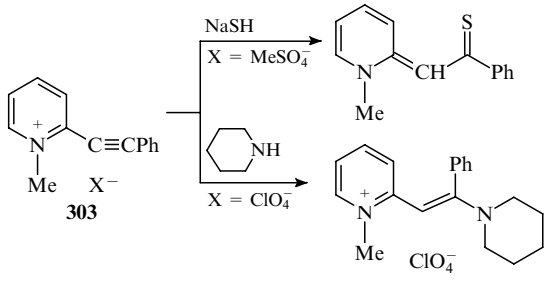
The alkylation of the quinoline **300** with dialkyl sulfates or with esters of toluene-*p*-sulfonic acid yields quaternary salts **301**, which are quite stable in alkaline solutions and are fairly reactive towards S- and N-nucleophiles and CH-acids.[156]

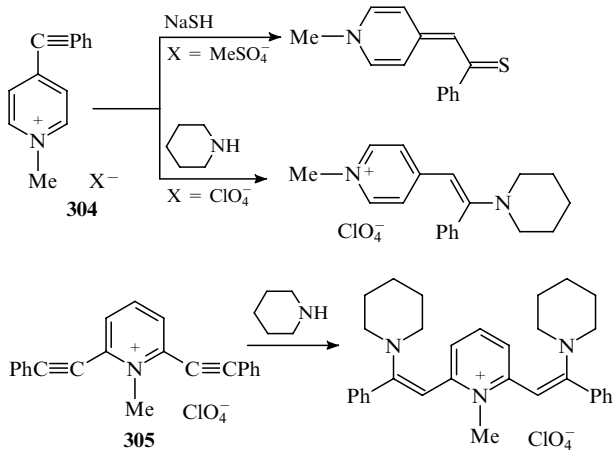


N-Alkylated salts of nitrogen-containing heterocycles readily add to phenylethynylquinolinium salts giving rise to cyanine dyes **302**.[156]

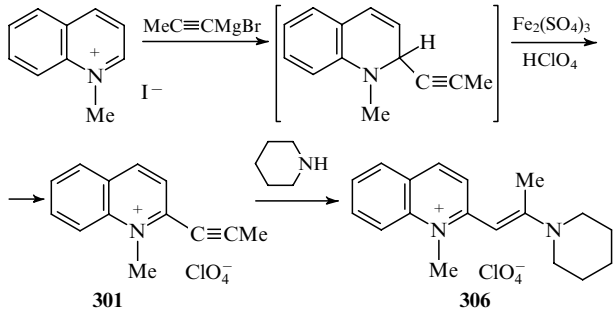


Phenylethynylpyridinium salts **303**–**305**, which add nucleophiles at the C≡C bond, have been obtained by *N*-methylation of the corresponding ethynylpyridines.[157]

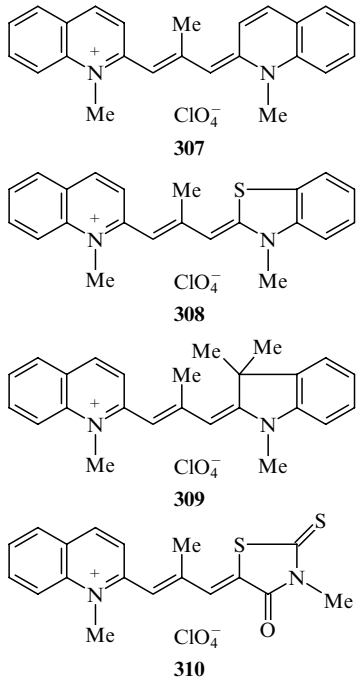




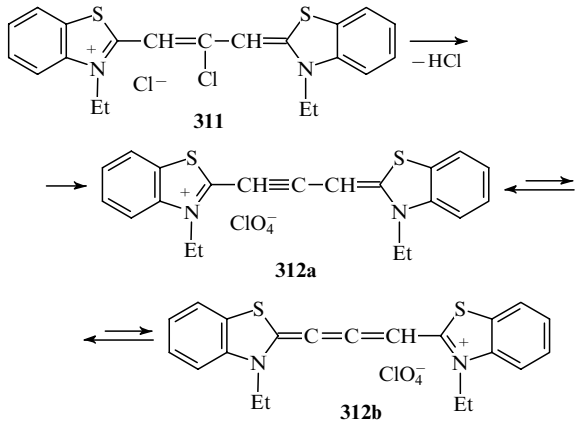
Yet another method for the synthesis of the alkynylquinolinium salt **301** is based on the interaction of *N*-methylquinolinium iodide with propynylmagnesium bromide. The subsequent oxidation in the presence of $HClO_4$ affords the corresponding perchlorate.[158] The IR spectrum of this salt contains an intense absorption band at about 2230 cm^{-1} corresponding to the triple carbon–carbon bond; this confirms the salt structure. As in the case of quinolinium salts with a phenylethynyl substituent, the addition to the propynyl group is also directed at the end of the triple bond that is more distant from the heterocycle. This gives enamine **306**.



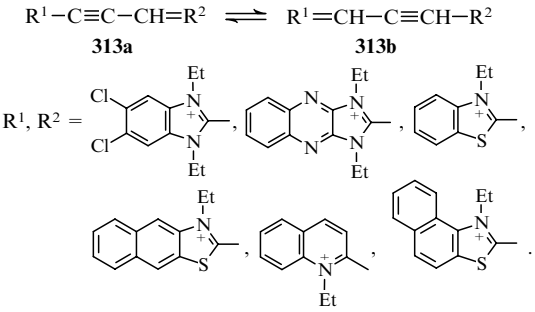
Cyanine dyes containing quinaldine (**307**), 2-methylbenzothiazole (**308**), 2,3,3-trimethylindolenine (**309**) and *N*-methylrhodanine (**310**) residues are synthesised in a similar way.



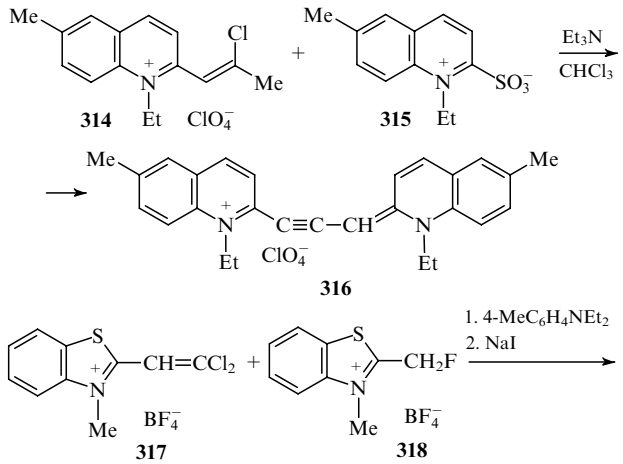
Acetylenic analogues of cyanine dyes containing a carbon–carbon triple bond in the conjugated chain between two heterocycles can be prepared by different methods. Thus perchlorate **312** was synthesised by dehydrochlorination of *meso*-chlorocarbocyanines **311**.[159, 160]

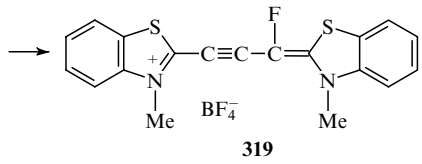


It has been shown by electronic spectroscopy and X-ray diffraction analysis that the alkyne structure **312a** is energetically more favourable than the cumulene structure **312b**. Study of a series of similar conjugated systems containing different heterocycles showed that in this case, an equilibrium of the type **313a** ⇆ **313b** is established; the isomer in which the positive charge is concentrated on the more basic heterocycle (for example, on a benzimidazole rather than benzothiazole ring) predominates in the mixture. The experimental results and spectroscopic data were confirmed by quantum-chemical calculations.[160]

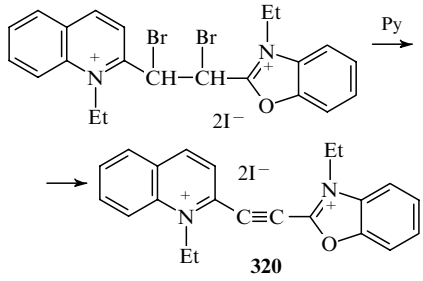


Dyes with similar structures **316** and **319** have been obtained by condensation of the chlorovinylquinolinium salt **314** with betaine **315**[161] or by condensation of benzothiazolium salts **317** and **318** with each other.[162]

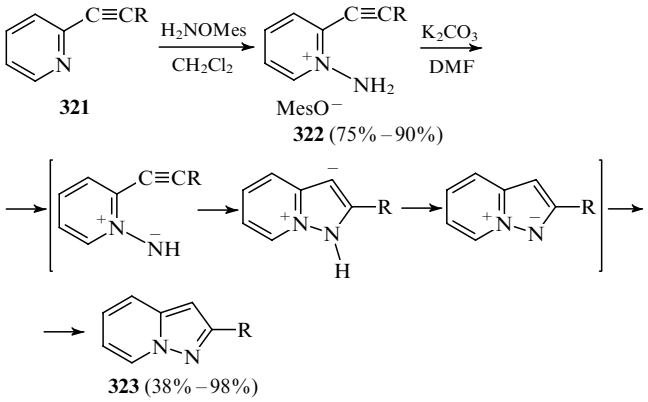




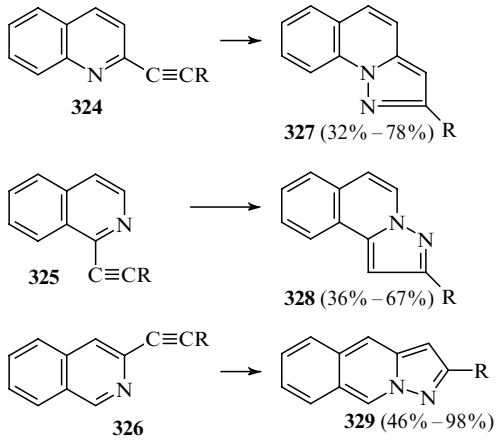
Synthesis, spectral characteristics and chemical properties of dyes including compounds **320** in which an acetylenic fragment connects two heterocyclic cations have been reported.[163]



3-Azaindolizine derivatives **323** are formed upon cyclisation of 2-ethynylpyridine-*N*-imides **322**. The latter, in turn, are obtained by *N*-amination of 2-alkynylpyridines **321** followed by treatment with potassium carbonate in the presence of DMF.[164, 165] Similar cyclisation of 2-alkynylquinoline **324** and alkynylisoquinolines **325**, **326** yields pyrazolo[2,3-*a*]quinolines **327** and pyrazoloisoquinolines **328**, **329**.[165]



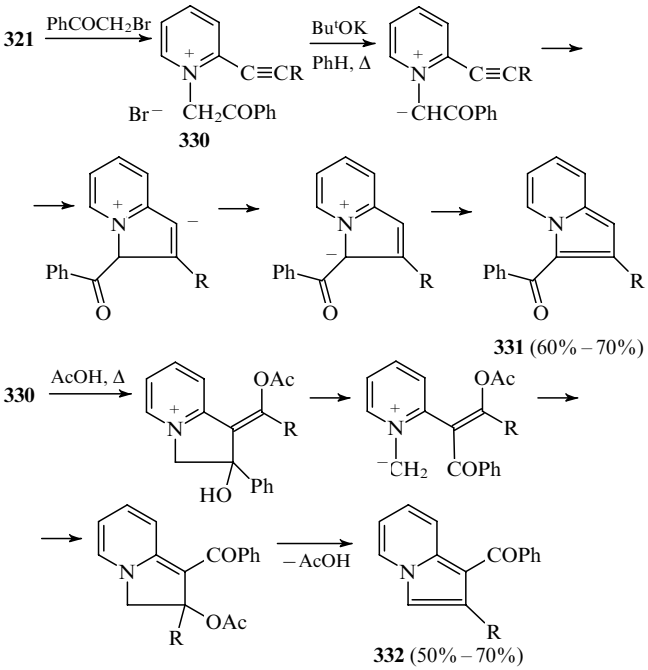
R = H, Me, Bu, CH_2OH, Ph.



R = Bu, CH_2OH, Ph.

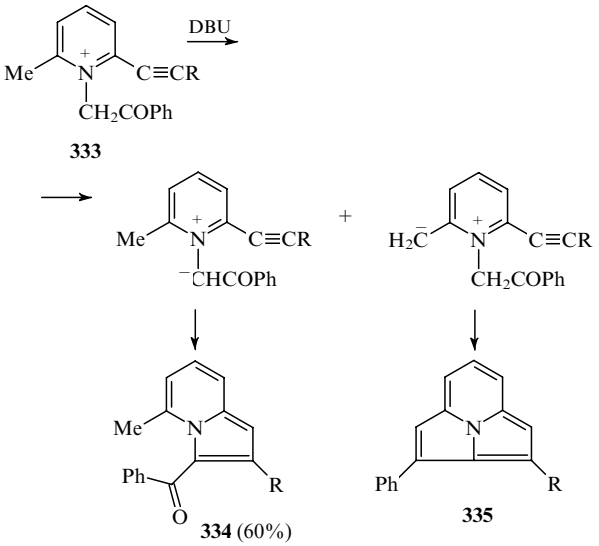
Transformations of 2-alkynyl-*N*-phenacylpyridinium salts **330** follow different pathways depending on their structures and reaction conditions.[166] The monosubstituted 2-alkynylpyridines **321** are converted into the alkynylpyridinium salts **330** on treatment with phenacyl bromide. Refluxing of **330** in benzene in the presence of a base (potassium *tert*-butoxide, 1,5-diazabicy-

clo[5.4.0]undec-5-ene) affords the corresponding ylides, which cyclise to 3-benzoylindolizines **331**; in boiling acetic acid, the salts **330** are converted into 1-benzoylindolizines **332**.



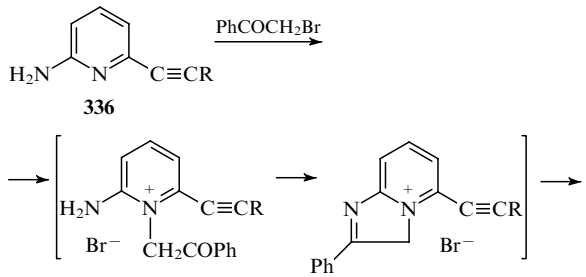
R = Me, Bu, Ph.

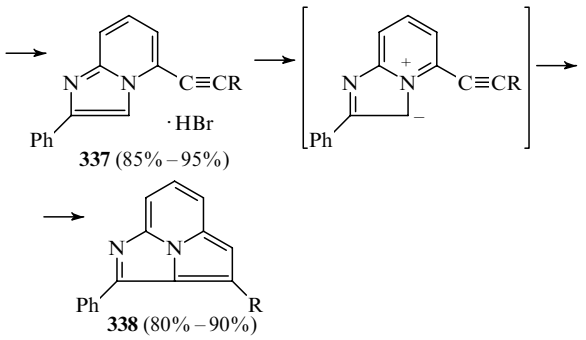
On treatment with bases, 6-methylpyridinium salts **333** give 10% – 15% of 2-phenylcyclazines **335** in addition to 3-benzoylindolizines **334**.[166]



R = Me, Bu, Ph; DBU is diazabicycloundecene.

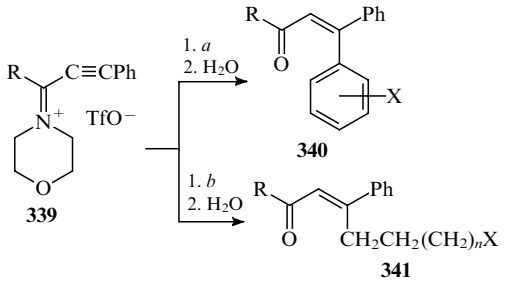
Unlike the examples described above, 6-amino-2-alkynylpyridines **336** are converted into 1-azaindolizinium salts **337** just upon treatment with phenacyl bromide; treatment of the salts **337** with a solution of sodium carbonate yields 1-azacyclazines **338**.[166]





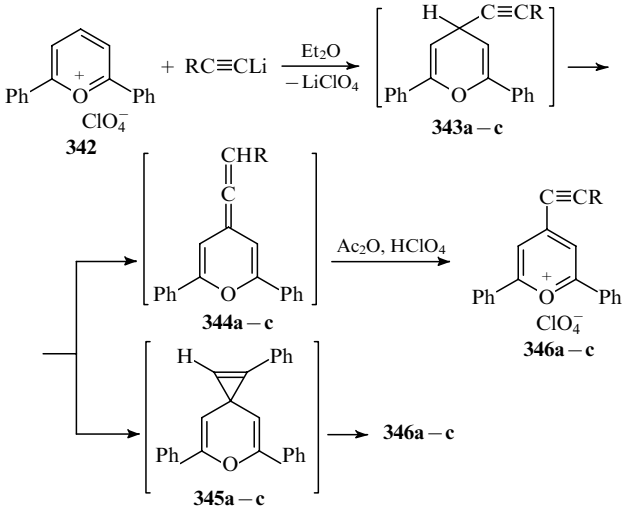
R = Me, Bu, Ph.

Data on these and other related reactions have been surveyed in a review.[167] Synthesis of a reverse transcriptase inhibitor *via* a 2-alkynylpyridinium intermediate has been described in a recent study.[168] An interesting reaction is the conjugated addition of organozinc-copper reagents to (2-propynylidene)morpholinium triflate **339**. Hydrolysis of the addition products gives α,β-unsaturated ketones **340** and **341**, respectively.[169]

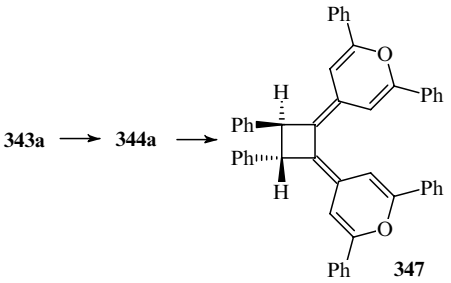


(*a*) IZnCu(CN)C_6H_4X; X = 2-CN, 4-CN, 3-COOEt;
(*b*) IZnCu(CN)$CH_2CH_2(CH_2)_n$X; *n* = 0, 1; X = CN, COOEt.

In recent years, extensive studies on cyclic oxonium ions, pyrylium cations containing alkynyl substituents, have been carried out. The first representative of these stable alkynylcarboxonium ions, namely, 2,6-diphenyl-4-phenylethynylpyrylium perchlorate, was prepared by the reaction of 2,6-diphenylpyrylium perchlorate **342** with lithium phenylacetylenide and subsequent oxidative dehydration of the pyran intermediate.[170] Later, other lithium acetylenide derivatives have also been involved in this reaction.[171] Three possible structures, **343** – **345**, have been proposed for the reaction intermediate;[170] based on the data of IR spectroscopy, the allene species **344** was preferred. The IR spectrum of salts **346** contains an absorption band at 2210 cm^{-1} typical of acetylene derivatives.[170]



R = Ph (**a**), $MeOCH_2$ (**b**), $Me_2(MeO)C$ (**c**).

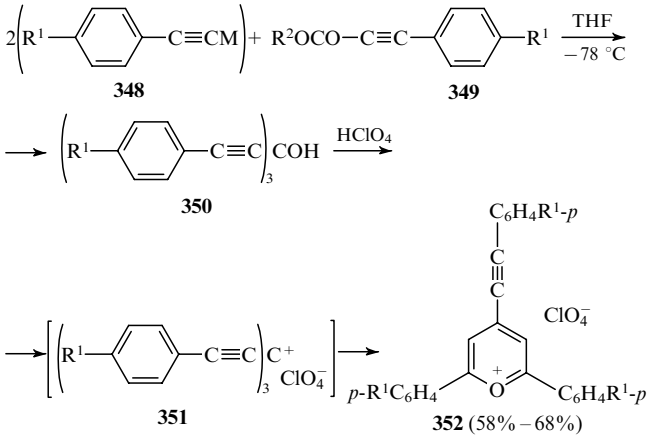


343a → **344a** → **347**

It has been found that the outcome of this reaction depends on the nature of the solvent.[172] When the reaction between the salt **342** and lithium phenylacetylenide was carried out in diethyl ether, only 4-phenylethynylpyran **343a** was formed. The replacement of ether by tetrahydrofuran resulted in the formation of the [2 + 2]-cycloaddition product **347**. The researcher cited believe [172] that it is formed *via* dimerisation of allenylpyran **344a**.

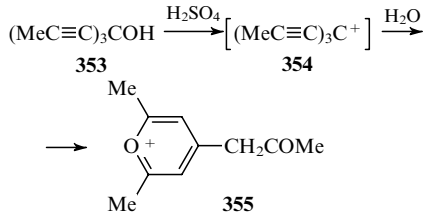
Later, this difference between the routes of nucleophilic addition to the pyrylium salt **342** was explained [173] by different conditions of metallation of phenylacetylene. In fact, Doney *et al.*[172] used an equimolar amount of a standard solution of n-butyllithium, whereas other investigators [170, 171] employed an excess of butyllithium, which then remained in the reaction mixture and acted as a base during the isomerisation of the compound **343a** to **344a**.[173]

Study of dyes containing carbon–carbon triple bonds have led to the synthesis of acetylenic analogues of triarylmethane dyes, which are able to acquire an alleno-quinoid structure and, hence, they exhibit interesting photochemical properties. Alcohols **350** can be synthesised by the reaction of organometallic derivatives of arylacetylenes **348** with the corresponding esters **347**. The compounds **350** were converted into the corresponding 4-arylethynylpyrylium salts **352** by treatment with 70% $HClO_4$ in a 2 : 1 C_6H_6 : EtOH mixture.[174]



348 **349** **350** **351** **352** (58%–68%)

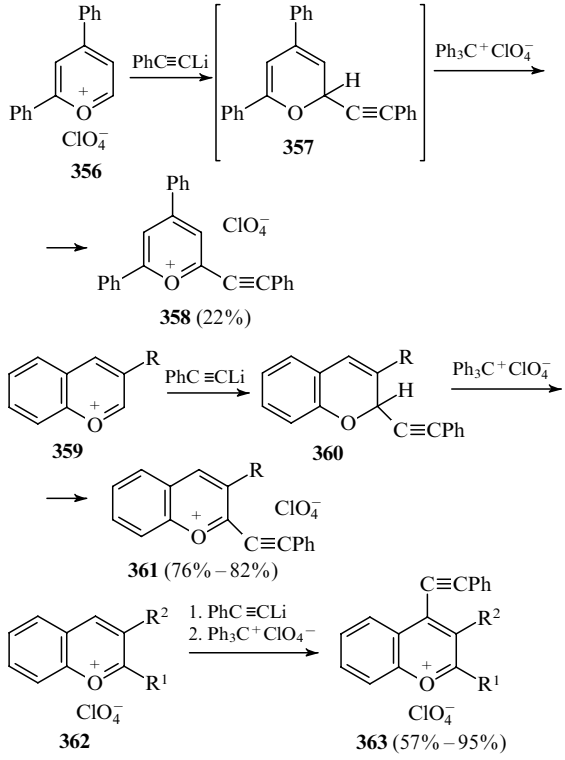
R^1 = H, Me_2N; R^2 = Me, Et; M = Li, MgBr.



353 **354** **355**

The IR spectra of the salts **352** exhibit absorption bands at about 2170 cm^{-1}. It has been assumed that under the reaction conditions, the trialkynylcarbenium ions **351** undergo the Meyer–Schuster rearrangement to give arylethynyl-substituted pentene-1,5-diones, which then form the pyrylium ring.[175, 176] This was confirmed using simpler systems. Thus treatment of alcohol **353** with an acid gives rise to the 4-acetonylpyrylium cation **355** *via* alkynylcarbenium intermediate **354**.[177]

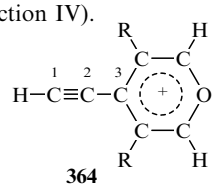
Recently it has been shown that non-symmetrical 2,4-diphenypyrylium perchlorate **356** adds lithium phenylacetylenide at the free α-position yielding unstable 2*H*-pyran intermediate **357**. Oxidative dehydration of the latter affords extremely explosive 2-phenylethynylpyrylium perchlorate **358**.[178] Conversely, 2*H*-pyran intermediates **360**, obtained analogously from 2-unsubstituted 1-benzopyrylium salts **359**, are stable and can be isolated. 4-Phenylethynyl-1-benzopyrylium salts **363** were synthesised in the same way from 1-benzopyrylium salts **362** unsubstituted at the 4-position.[178]



356 **357** **358** (22%) **359** **360** **361** (76%–82%) **362** **363** (57%–95%)

R^1 = Ph, Bu^t; R^2 = H, Me, Et.

The IR spectra of the salts **358**, **361** and **363** exhibit absorption bands in the region of 2180–2200 cm^{-1} typical of C≡C triple bond vibrations. This means that in phenylethynylpyrylium salts, this bond is retained, the positive charge being concentrated in the heteroaromatic ring. This conclusion has been confirmed by MINDO/3 quantum-chemical calculations [178] according to which the C(1)–C(2) bond length in species **364** (0.1209–0.1210 nm) is close to the length of a C≡C triple bond, whereas the C(2)–C(3) bond (0.1429–0.1437 nm) is substantially longer than the corresponding bond in an allenyl cation [109] (see Section IV).

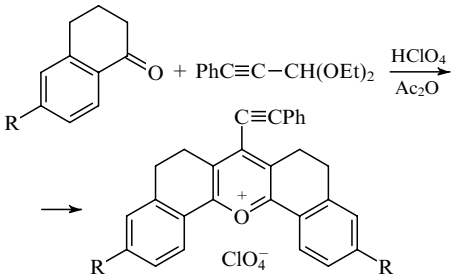


364

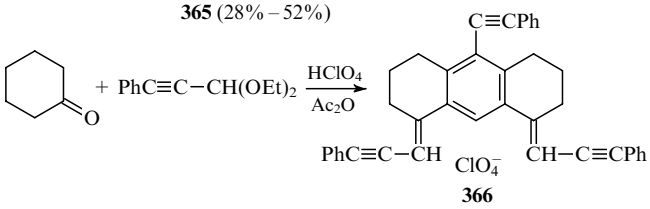
R = H, Me.

The above reactions of the pyrylium salts **342**, **356** and 1-benzopyrylium salts **359**, **362** with lithium phenylacetylenide are, in essence, examples of nucleophilic substitution in the aromatic nucleus, little studied so far. Processes of this type involving heteroaromatic cations as the substrates are known mainly for azinium salts.[179] Study of nucleophilic aromatic substitution with pyrylium salts as substrates is of interest because it does not require substrate activation. In addition, the low nucleofugal activity of hydrogen in the non-charged intermediates (*i.e.*, pyran systems) permits conducting the S_N^H (AE) process [179] in two separate stages.

Besides the nucleophilic substitution of a hydrogen atom in a pyrylium cation by an alkynyl group, alkynylpyrylium salts can also be synthesised by forming a pyrylium ring. Two examples of this type, namely, cyclisation of trialkynyl carbocations **351** and **354**, are shown above.[174,177] However, methods for the synthesis of pyrylium salts involving two or three components [175,176] are not very suitable for the preparation of alkynyl-substituted derivatives, because of the high probability of involvement of the triple bond in condensation. Only few examples of synthesis of 4-phenylethynylpyrylium salts such as **365** and **366** by the reaction of 3-phenylprop-2-ynal diethyl acetal with cyclic ketones like 1-tetralone or cyclohexanone have been reported.[180]

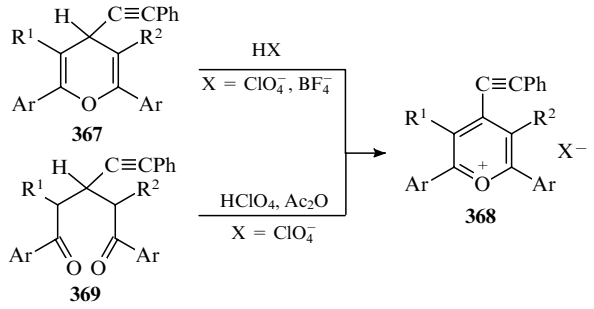


365 (28% – 52%)



366

Alkynylpyrylium salts **368** are obtained by oxidative dehydrogenation of the corresponding 4*H*-pyrans **367** on treatment with triphenylmethyl perchlorate (yields 92% – 95%), an Ac_2O – $HClO_4$ mixture (yields 53% – 71%) or $BF_3 \cdot Et_2O$ (yields 43% – 82%),[181] or by cyclisation of difficultly accessible 3-alkynylpentane-1,5-diones **369** on treatment with $HClO_4$ in acetic anhydride, acting as dehydrating and dehydrogenating agent (yields 78% – 84%).[182]

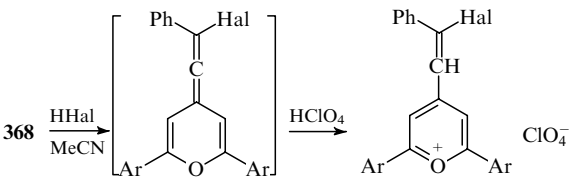


367 **369** **368**

R^1, R^2 = H, Me; Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$.

The combination of the highly stable heteroaromatic cation and the alkynyl fragment in the molecules of **368** makes these compounds fairly useful for organic synthesis. Thus the presence of the cationic pyrylium fragment efficiently activates the C≡C bond towards nucleophilic substitution reactions. Nucleophilic reagents, irrespective of their structure, attack the triple bond in the alkynyl substituent at the end that is remote from the heterocycle. It should be emphasised that the reactivity of the pyrylium fragment in the compounds formed in these reactions remains virtually unchanged. Therefore, after the nucleophilic reaction of the alkynyl group, diverse transformations of the oxygen-containing heterocycle can be performed by treatment with the same or other nucleophilic reagents.

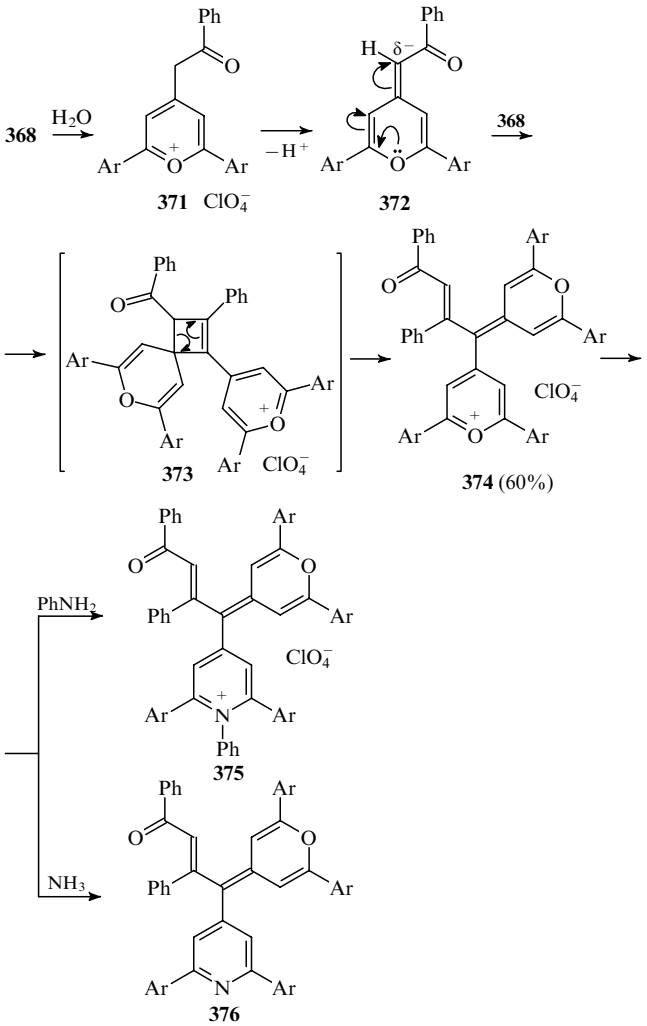
For example, 2,6-diaryl-4-phenylethynylpyrylium perchlorates **368** (R^1 = R^2 = H) easily add hydrogen halides to give halo-derivatives **370**.[181]



370 (76% – 93%)

Ar = Ph, 4-$MeOC_6H_4$; Hal = Cl, Br.

It might be expected that the reactions of **368** with water or alcohols would afford 4-phenacylpyrylium derivatives **371** (or the corresponding alkyl ethers) upon hydration of the triple bond or addition of alcohols. However, refluxing of the salts **368** with water, methanol or ethanol resulted in the isolation of monomethinecyanines **374** the structures of which were confirmed by IR and ^{1}H NMR spectroscopy and by X-ray diffraction analysis of the pyridinium analogue **376** (Ar = Ph) prepared by the reaction with NH_3.[183] The pathway to these monomethinecyanines includes hydration of the triple bond in the initial salts **368** yielding benzoylmethylenepyrans **372**. However, the reaction does not stop at this stage, and the hydration products **372** react with the 4-phenylethynylpyrylium salts **368** as C-nucleophiles according to the [2+2]-cycloaddition pattern. The final products **374** result from electrocyclic ring opening in the cyclobutene intermediates **373**.

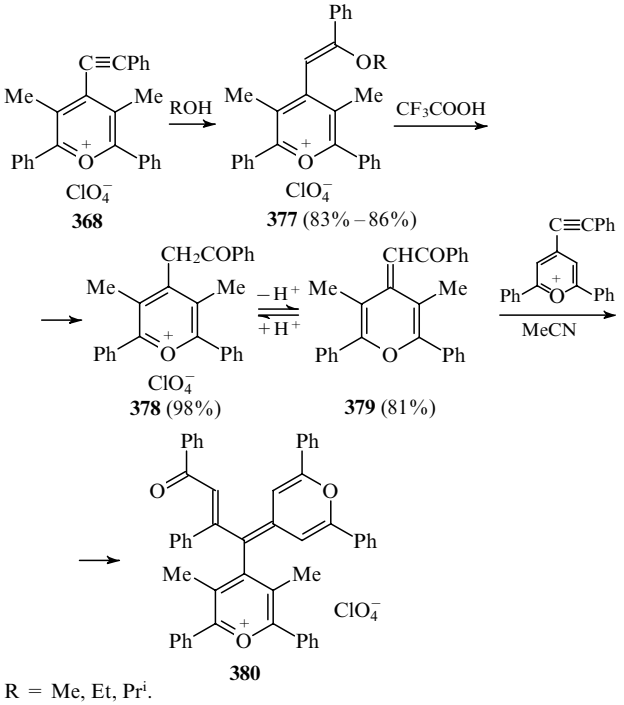


371 **372** **373** **374** (60%) **375** **376**

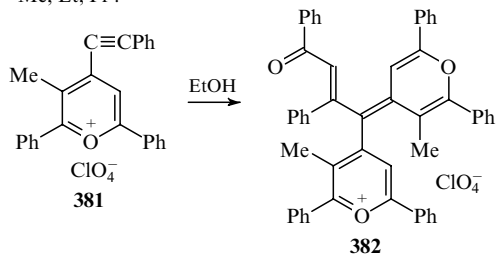
Ar = Ph, 4-$MeOC_6H_4$.

The 4-phenacylpyrylium salt **378** and benzoylmethylenepyran **379** have been obtained only when the 3,5-dimethyl-substituted 4-phenylethynylpyrylium salt **368** (R^1 = R^2 = H, Ar = Ph) was treated with alcohols and the resulting vinyl ethers **377** were dealkylated.[184] Apparently, the methyl groups decrease the elec-

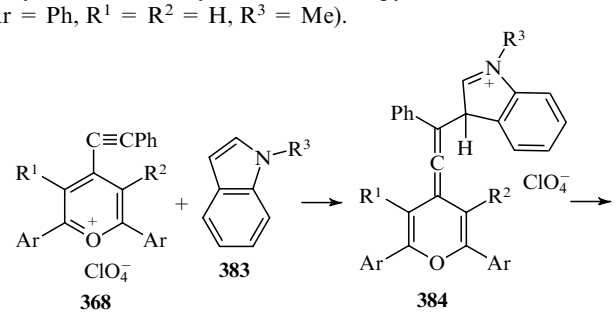
tron-withdrawing influence of the pyrylium ring on the alkynyl fragment and thus hamper [2 + 2]-cycloaddition. However, it was shown that these groups do not create steric hindrance, because refluxing of benzoylmethylenepyran **379** with 2,6-diphenyl-4-phenylethynylpyrylium perchlorate **368** (Ar = Ph) gave monomethinecyanine **380** in 97% yield. This result confirms the validity of the reaction scheme presented above. The pyrylium salt **381**, which contains only one methyl substituent, like the salts **368**, is directly converted into monomethinecyanine **382**.[184]

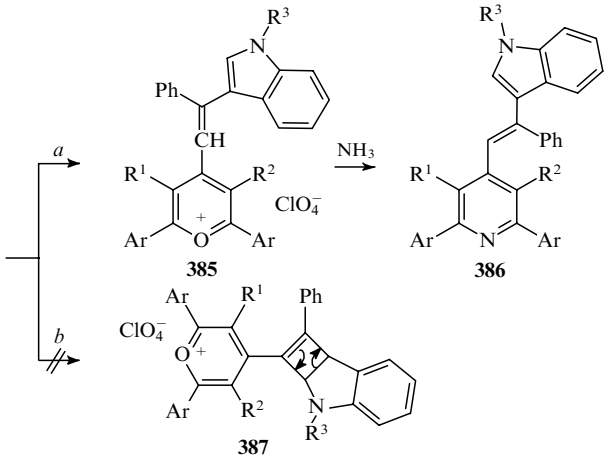


R = Me, Et, Pr^i.



It should be noted that the monomethinecyanine **374** (Ar = Ph) was prepared from tris(phenylethynyl)methanol **353** back in 1957, and its structure was then established by virtue of cumbersome chemical transformations.[177] The suggestion of Koblik *et al.*[183] that this and related compounds are produced *via* a cyclobutene intermediate was based on some analogies found in the literature, for example, on the formation of benzoazepines in reactions of indoles with esters of acetylenedicarboxylic acid.[185] However, the reaction of indoles **383** with 4-phenylethynylpyrylium salts **368** yields indolevinylpyrylium salts **385** rather than benzoazepines.[186] The structure of these products was proved by IR and ^{1}H NMR spectroscopy, and by mass spectrometry and X-ray diffraction analysis of one of the pyridine derivatives **386** (Ar = Ph, R^1 = R^2 = H, R^3 = Me).

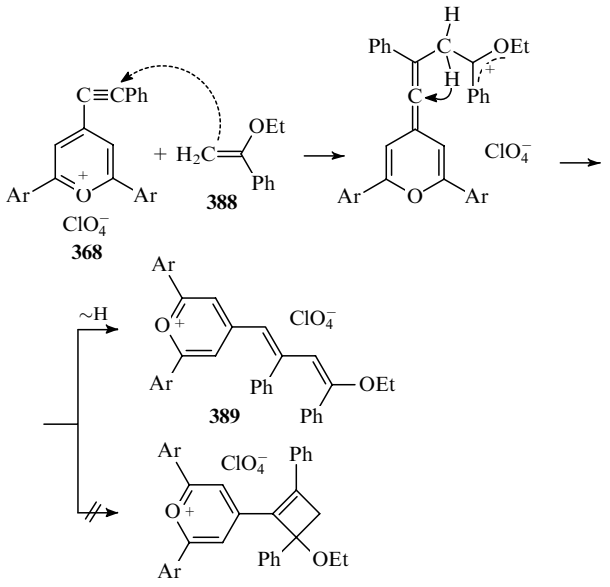




R^1, R^2, R^3 = H, Me; Ar = Ph, 4-MeOC$_6$H$_4$.

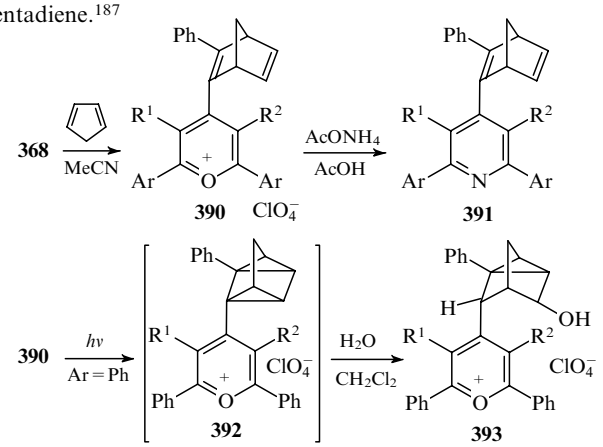
This reaction is believed [186] to occur by a stepwise mechanism. The first stage is addition of the enamine fragment of the indole **383** to the distant end of the triple C≡C bond. The transformations of the resulting allene intermediate **384** can follow two routes: proton transfer from the C(3) atom of the indole residue to the *sp*-hybridised carbon atom (pathway *a*) and the nucleophilic attack by the C(2) atom of the indole fragment on the *sp*-hybridised carbon atom of the allene fragment (pathway *b*). It is obvious that pathway *a* is energetically more favourable, because it is accompanied by aromatisation of two heterocycles, resulting in a conjugated chain with the maximum charge delocalisation possible in this case.

The formation of the cyclobutene intermediate in the reaction of the salts **368** with the benzoylmethylenepyrans **372** is apparently due to the fact that the pyran and pyrylium rings can approach each other as a result of π–π donor-acceptor interaction, and this creates favourable conditions for [2 + 2]-cycloaddition. When the salts **368** react with indoles, the reactants do not come close to each other in this way, and, hence, intramolecular proton transfer occurs. This interpretation is quite consistent with the outcome of the reaction of the pyrylium perchlorate **368** (R^1 = R^2 = H, Ar = 4-MeOC$_6$H$_4$) with vinyl ether **388** involving a similar proton transfer.[186] The structure of the reaction product **389** was confirmed by the ^{1}H NMR spectrum.



The 4-phenylethynylpyrylium salts **368** are also able to enter into [2 + 4]-cycloaddition reactions. Thus norbornadiene derivatives **390** containing a positively charged heteroaromatic ring were

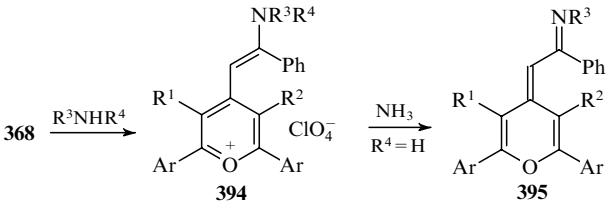
obtained for the first time by the reaction of **368** with cyclopentadiene.[187]



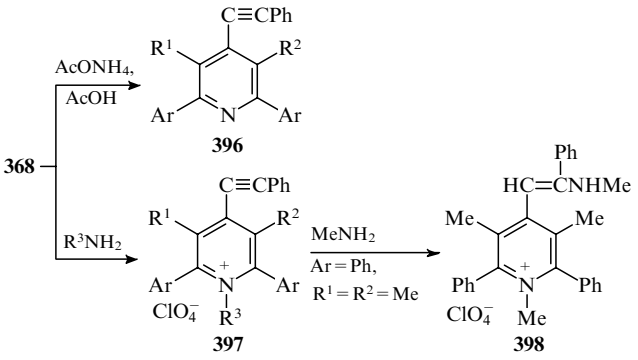
R^1, R^2 = H, Me; Ar = Ph, 4-$MeOC_6H_4$.

When solutions of the norbornadiene derivatives **390** are exposed to the light of a mercury lamp (λ_{max} = 546 nm) or to sunlight, they undergo fast photochemical transformation into quadricyclanes **392**. However, these products are readily hydrated under the reaction conditions, which unfortunately precludes the possibility of thermally induced back reaction.

The pyrylium salts **368** add alcohols and aromatic amines (aniline, *p*-toluidine, *N*-methylaniline) as well as *tert*-butylamine to the *sp*-hybridised carbon atom that is remote from the pyrylium ring; this gives enaminopyrylium salts **394**.[184] It should be emphasised that in the case of pyrylium salts containing no ethynyl substituent, the reactions with ammonia and amines involve the pyrylium fragment and are used typically to prepare pyridines and pyridinium salts.[176] Unlike normal pyrylium salts, the compounds **394** are deprotonated on treatment with ammonia (at R^4 = H) to unsaturated imines **395** rather than exchange the oxygen atom in the ring for nitrogen. However, ammonium acetate and methyl-, butyl- and benzyl-amines attack the pyrylium ring in the salts **368**, which gives rise to alkynyl-substituted pyridine derivatives **396** and **397**.[184]



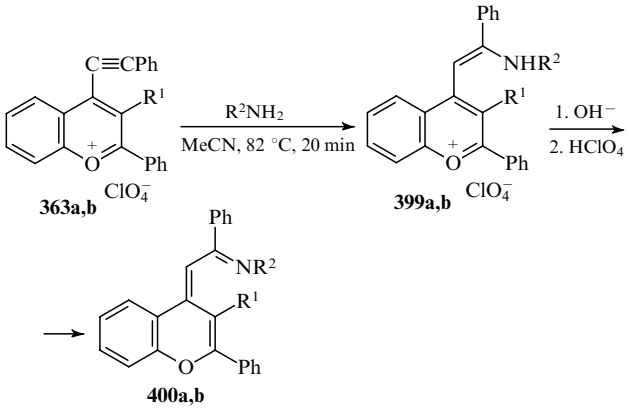
R^1, R^2 = H, Me; Ar = Ph, 4-$MeOC_6H_4$; R^3 = Bu^t, Ph, 4-MeC_6H_4; R^4 = H, Me.



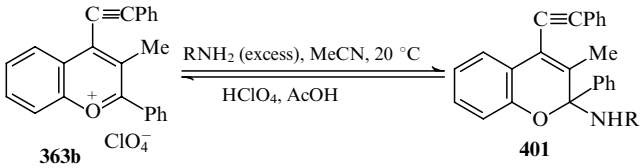
R^1, R^2 = H, Me; Ar = Ph, 4-$MeOC_6H_4$; R^3 = Me, Bu, $PhCH_2$.

The acetylenic fragment in the 4-phenylethynylpyridinium salts **397** is still sufficiently activated to add one more amine molecule; this affords aminovinylpyridinium salts **398**.

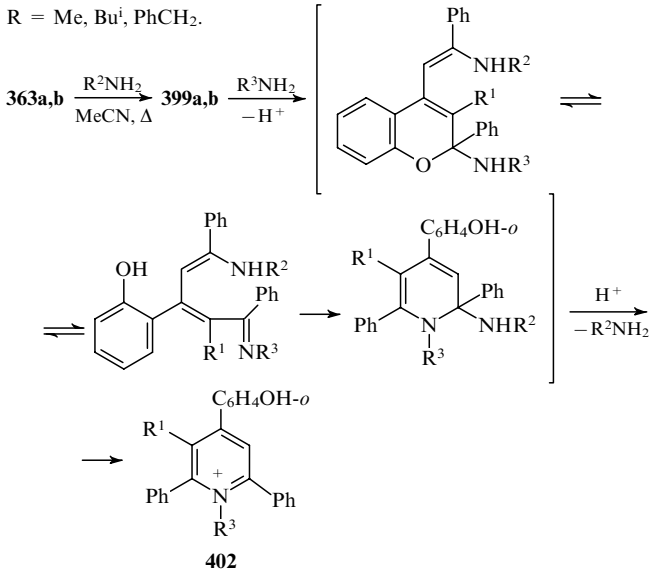
Unlike monocyclic pyrylium salts, 1-benzopyrylium salts do not tend to exchange the ring oxygen atom for nitrogen.[188] Therefore, it comes as no surprise that 4-phenylethynyl-1-benzopyrylium salts **363a**,**b** are converted into aminovinyl derivatives **400a**,**b** on refluxing with an equimolar amount of an aliphatic amine or benzylamine followed by treatment with $HClO_4$.[189] However, when the salt **363b** is mixed with excess amine at room temperature, the products of the amine addition at the 2-position of the ring — 2-alkylaminoflavenes **401** — are rapidly formed. On treatment with $HClO_4$ they easily decompose giving the initial salt **363b**. Thus, this addition is reversible and kinetically controlled. Refluxing of the salts **363a**,**b** with a two- or three-fold excess of an amine in acetonitrile for 1–5 h affords 4-(2-hydroxyphenyl)pyridinium salts **402**. The same products are formed under similar conditions from the aminovinyl salts **399a**,**b**, which are evidently formed as intermediates in the transformation of the 4-phenylethynyl-1-benzopyrylium salts **363**.



R^1 = H (**a**), Me (**b**), R^2 = $PhCH_2$, Bu^t, Bu^i.



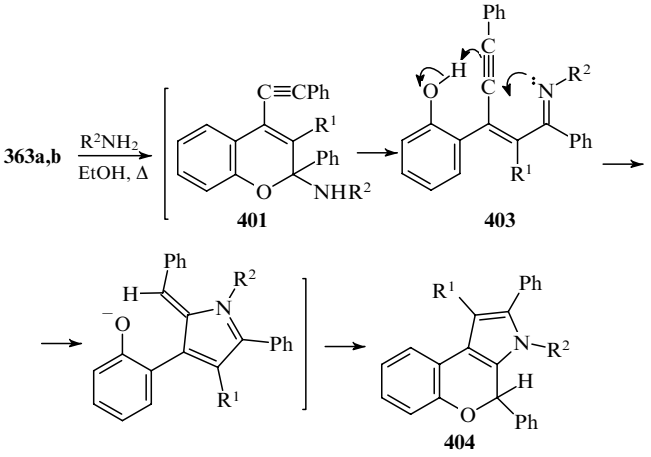
R = Me, Bu^i, $PhCH_2$.



R^1 = H (**a**), Me (**b**); R^2, R^3 = Me, Bu^i, $PhCH_2$.

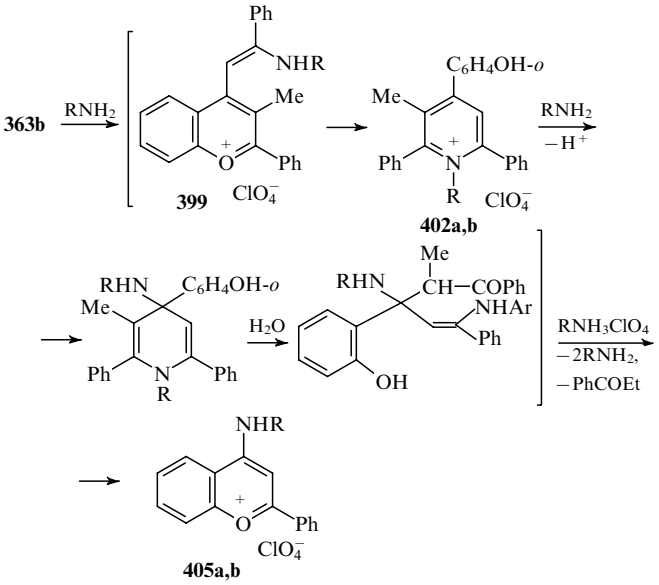
It is obvious that the 2-aminoflavenes **401** are not formed as intermediates in this thermodynamically controlled recyclisation. However, the formation of aminoflavenes proved to be the key stage in the transformation of the 4-phenylethynyl-1-benzopyrylium salts **363a**,**b** into 2*H*-chromeno[3,4-*b*]pyrroles **404**.[189] These products are formed in 36%–75% yields upon refluxing of the

salts with excess primary amines in ethanol. Presumably, ethanol acts as a competing nucleophile and suppresses the formation of the 4-alkylaminostyryl salts **399**. The unstable adducts **401** have enough time to undergo ring cleavage yielding phenol intermediates **403**, which again cyclise to chromenopyrroles **404**. The structure of one of the tricyclic products **404** was established by X-ray diffraction analysis.[189]



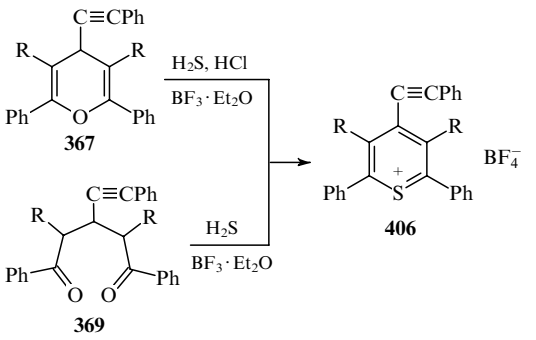
R^1 = H, Me; R^2 = Me, Bu^i, $PhCH_2$.

Recently, unexpected recyclisations of the 3-methyl-2-phenyl-4-phenylethynyl-1-benzopyrylium perchlorate **363b**, which occur on its refluxing with a two- or three-fold excess of aromatic amines, have been reported.[190] Treatment of the salt **363b** with aniline in dichloroethane or acetonitrile gives 4-anilino-2-phenyl-1-benzopyrylium salt **405a**. On treatment with *p*-toluidine under the same conditions, the pyridinium (**402b**) and 4-(*p*-toluidino)-1-benzopyrylium (**405b**) perchlorates are formed. It has been noted above that the compounds **402** result from recyclisation of the 4-aminovinyl-1-benzopyrylium salts **399**. It has been suggested and confirmed experimentally[190] that the compounds **399** can arise as intermediates in the recyclisation of the salts **363b** to the 4-(*R*-amino)-1-benzopyrylium salts **405a**,**b**.

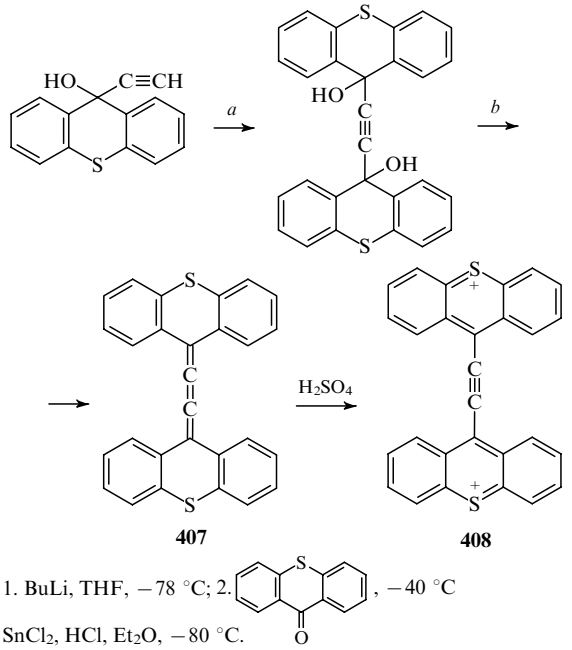


R = Ph (**a**), 4-MeC_6H_4 (**b**).

4-Phenylethynylthiopyrylium salts **406** have been obtained recently from 4-phenylethynyl-4*H*-pyrans **367** (yields 30% – 40%) and from 3-phenylethynylpentane-1,5-diones **369** (yields up to 80%) on treatment with hydrogen sulfide in the presence of boron trifluoride etherate.[191]



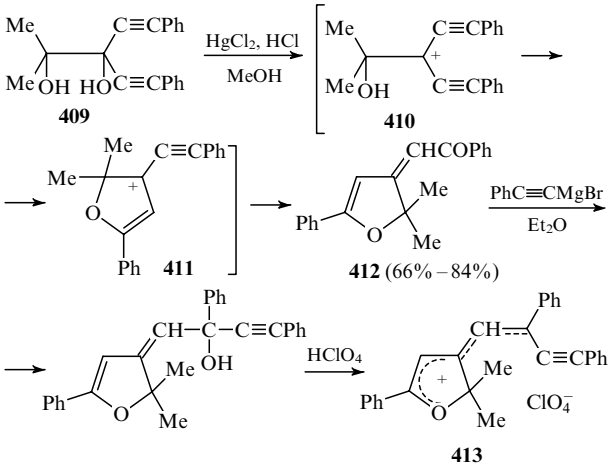
Bis-thioxanthene cumulene **407** has been prepared within the framework of studies aimed at the synthesis of π-electron-donating systems for charge transfer complexes possessing metallic conduction. When this product is treated with concentrated sulfuric acid, it is readily oxidised to acetylenic dication **408**, but does not undergo the expected triple bond protonation.[192]



(*a*) 1. BuLi, THF, −78 °C; 2. , −40 °C

(*b*) $SnCl_2$, HCl, Et_2O, −80 °C.

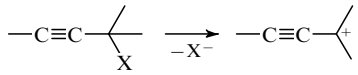
Development of a simple method for the synthesis of 3-acylmethylene-2,3-dihydrofurans from diacetylenic vicinal diols[193,194] has led to the preparation of the dihydrofurylium salt **413** containing a conjugated enyne fragment. Apparently, the transformation of the diol **409** to the furan **412** occurs *via* the intermediate formation of dialkynyl carbocation **410** and cyclic alkynyl carbocation **411**, which then undergoes the Meyer–Schuster rearrangement.



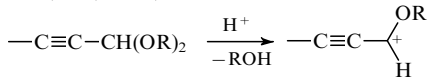
Comparison of the electronic spectra of the cation **413** (λ_{max} = 509 nm) with those of some other 4-styryldihydrofurylium salts containing H, Me, Et or Ar instead of the phenylethynyl group has demonstrated that the bathochromic shift caused by the PhC≡C group is twice as large as that caused by Ph. This is due to the fact that the triple bond efficiently participates in charge delocalisation.[194]

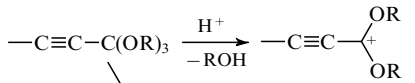
To summarise the foregoing, it can be concluded that all the methods that are, in principle, suitable for generation of carbenium ions have been used to generate alkynyl carbocations.[2]

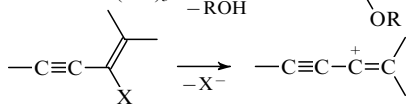
The most widely used procedure is detachment of a nucleofugal species from functional acetylene derivatives of the propargyl type containing one, two or three heteroatomic functions at the sp^3-hybridised carbon atoms [Eqns (1)–(3)].[135,136] Methods based on abstraction of nucleofuges from functionally substituted enynes, allenes and cumulenes [Eqns (4)–(6)] are more difficult for practical implementation and, therefore, are used more rarely.[113–115,128,145,146]. In the two latter cases [Eqns (5), (6)], the appearance of a carbenium centre results as well in the formation of a C≡C triple bond. The oxidative dehydrogenation of ethynylpyran systems[171,181] [Eqn (7)] also belongs to this type of reactions.


(1)

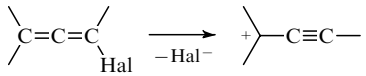
X = Hal, OH, OAlk, OAc.

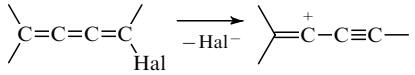

(2)

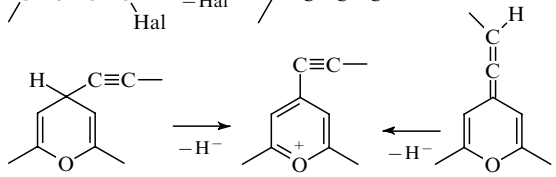

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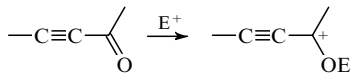

(4)

X = Br, TfO.

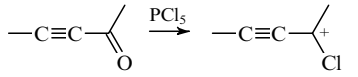

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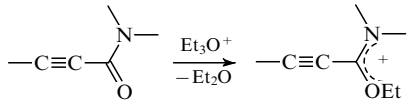

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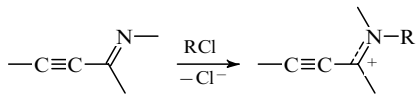

(7)

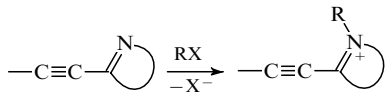

(8)

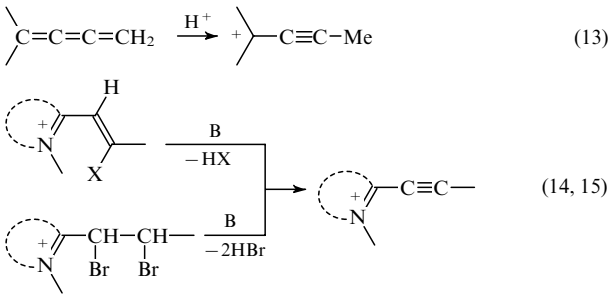
E = H, CF_3SO_2.


(9)


(10)


(11)


(12)


(13)

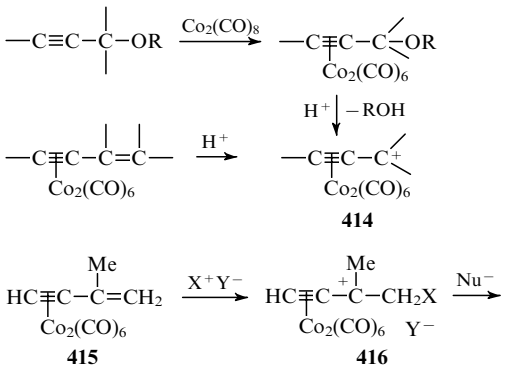
(14, 15)

The general approach to the generation of carbocations consisting in the addition of a cationic electrophile to an unsaturated system has also been used for the preparation of alkynylcarbenium ions. Compounds used most often as the precursors are alkynones[88,129,130,146] [Eqns (8), (9)], amides[34,143] [Eqn (10)], linear imines[8] and nitrogen-containing heterocycles[156–158,165–166] [Eqns (11), (12)]. The protonation of terminal cumulenes [Eqn (13)] is represented by only one example.[127] Electrophilic reactions of enynes deserve a more detailed discussion, which is presented in the last paragraphs of this Section.

One more fundamental approach to the generation of alkynylcarbenium ions is formation of a carbon–carbon triple bond in cationic structures. Known examples are deprotonation of iminium salts and quaternised nitrogen-containing heterocycles followed by elimination of a nucleofuge (Hal^-, $CF_3SO_3^-$)[142,144,159–161] [Eqn (14), (15)].

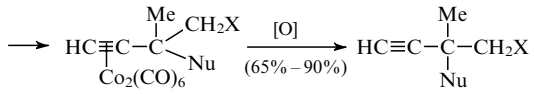
Several studies have been reported in which a carbenium centre near a triple bond was generated *via* 1,2-migration during the pinacolic rearrangement;[79] an example of two-electron oxidation of cumulene to a dication, which is a rarely encountered type of process in the preparative chemistry of carbocations, has also been described.[192]

In the case of conjugated enynes, electrophilic reactions of enynes, which have been mentioned among the methods for generation of alkynyl carbocations, proceed ambigously.[4,195] Therefore, generation of alkynylcarbenium ions from these substrates is problematic. However, it is known that cations of the type **9**, which are not detected even in superacidic media (see Section III), can be readily prepared or even isolated as dicobalthexacarbonyl (DCHC) complexes of the type **414**.[196] The DCHC complexes **415** derived from a number of enynes, namely, isopropenylacetylene, 1-ethynylcyclohexene, 1-ethynylcyclopentene, have been used to conduct a large series of Ad_E reactions according to a two-stage pattern. The natures of the electrophile X^+ and the nucleophile Y^- in these reactions can be varied independently, due to the high stability of the alkynylcarbocationic intermediates **416**.[196–198]



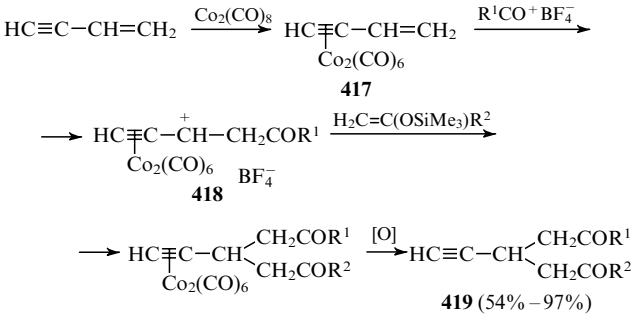
414

415 **416**



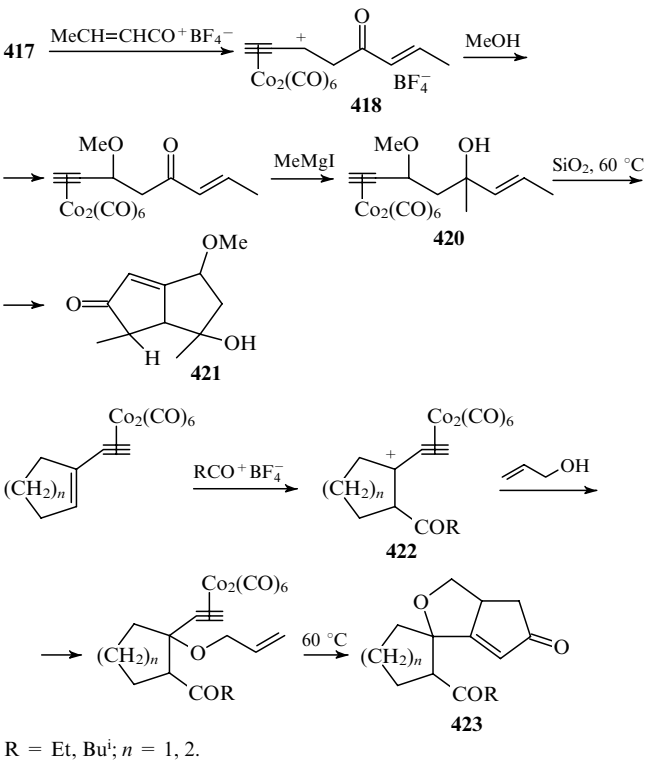
X^+Y^- = $RCOBF_4$ (R = Me, Bu^t, MeCH=CH), RBF_4 (R = Bu^t, 1-adamantyl), $ArSbF_6$ (Ar = 4-ClC_6H_4, 4-MeC_6H_4), NO_2BF_4; Nu = OH, MeO.

The vinylacetylene complex **417** regioselectively adds C-electrophiles and C-nucleophiles to the double bond to give alkyne-1,5-diones **419**, which are difficult to obtain by other methods.[199]



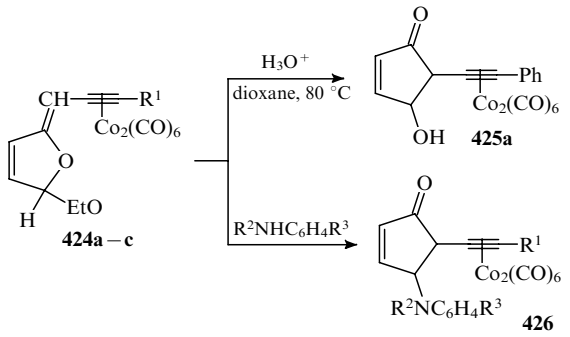
R^1 = Me_2CHCH_2, cyclo-C_4H_7, MeCH=CH, 1-adamantyl;
R^2 = Me, Ph, cyclo-C_3H_5.

The same process involving an α,β-unsaturated acyl cation and methanol as the nucleophile gives rise to the alcohol **420**. Thermal cisilation of **420** yields bicyclic ketone **421** (as a mixture of stereoisomers).[200] The reaction of allyl alcohol acting as a nucleophile with ethynyl cation **422** gives spirotricyclic products **423**.[200]



R = Et, Bu^i; n = 1, 2.

The alkynylcarbenium ions of the type **418**, **422** stabilised by complex formation have been generated and successfully used in a number of syntheses.[71, 72, 201–208] For example, from the DCHC complex of enyne **424**, hydroxycyclopentanone **425a** has been prepared in a quantitative yield [71] and arylaminocyclopentanones **426** have been prepared in yields of up to 93%.[208]

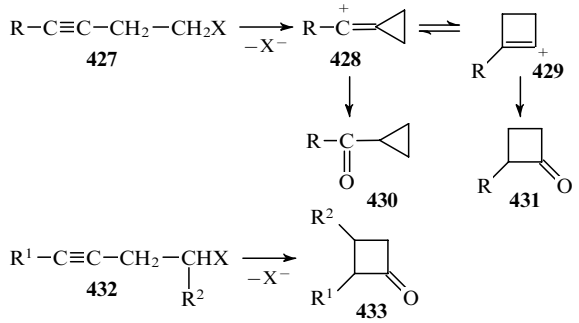


R^1 = Ph (**a**), Pr (**b**), C_6H_{13} (**c**); R^2 = H, Et; R^3 = COOH, NO_2, I.

VI. Alkynyl carbocations with a remote triple bond

Finally, a special place is occupied by the reactions of alkynyl carbocations of the type **9** with alkenes giving new cations with structures **A** and **B** (see Fig. 1). These species are, in principle, alkynylcarbenium ions in which the carbenium centre is separated from the acetylenic fragment by one or more carbon atoms. They are fairly reactive, and their transformations are being vigorously studied.

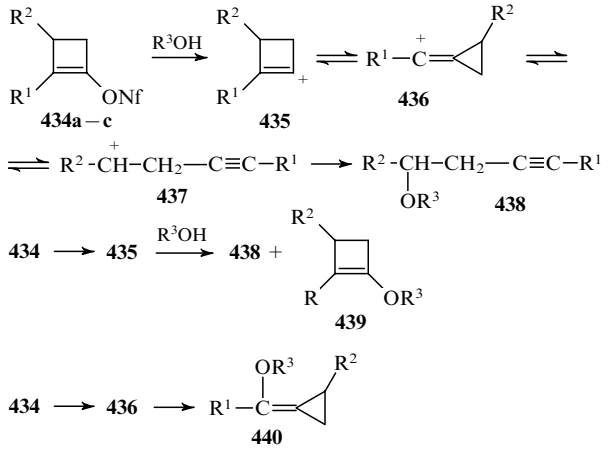
In 1965, Hanack *et al.*[209] discovered that solvolysis of acetylene derivatives **427** yields cyclopropyl ketones **430** and cyclobutanones **431**. Later, it was shown by detailed experiments and quantum-chemical calculations that cyclopropylidenemethyl cations **428** and cyclobut-1-enyl cations **429** are formed as intermediates during this reaction.[22, 23, 26, 27]



This transformation has been called 'homopropargyl rearrangement'. Normally it occurs quantitatively if the solvolysis is carried out in a highly polar and weakly nucleophilic solvent (for example, in HCOOH or CF_3COOH) and the initial compound **427** contains a good leaving group (tosylates, nitrobenzene-*p*-sulfonates, nonaflates and triflates). The ratio of the rearrangement products **430** and **431** depends on the nature of the substituent R. When R = H or Alk, the cyclobutanones **431** are the main reaction products, because in this case, the cations **429** are more stable than **428**. When R = Ar or cyclopropyl, the ketones **430** predominate in the product mixture. Homopropargyl derivatives of type **432** are mostly converted into cyclobutanones **433**.[210]

The mechanism of the homopropargyl rearrangement has been determined based on the investigation of the solvolysis of functionally substituted alkylidenecyclopropanes [22] and cyclobutenes [211] as well as various open-chain and cyclic propargyl derivatives.[212, 213] Studies of isotope effects involved in the solvolysis [121] and stereochemical aspects of the rearrangements of chiral pentynyl triflates [214] have also been invoked. The results of these studies led to the conclusion that the solvolysis directly proceeds to the cations **428** and **429** *via* a transition state typical of S_N2 type reactions.[27, 121, 210] However, it has been shown for the solvolysis of cyclobut-1-enyl nonaflates **434** in trifluoroethanol that the presence of substituents stabilising the cationic centre at the 3-position of the ring is favourable for the formation of

secondary homopropargyl cations **437**. The latter are converted into the corresponding ethers **438**.[27,212,213,215]

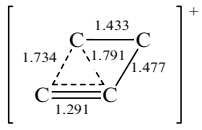


Nf = $C_4F_9SO_2$; R^3 = CF_3CH_2.

Compound	R^1	R^2	Yield (%)	
			438	**439**
434a	Me	H	3	95
434b	H	Me	63	34
434c	$(CH_2)_6$		68	32

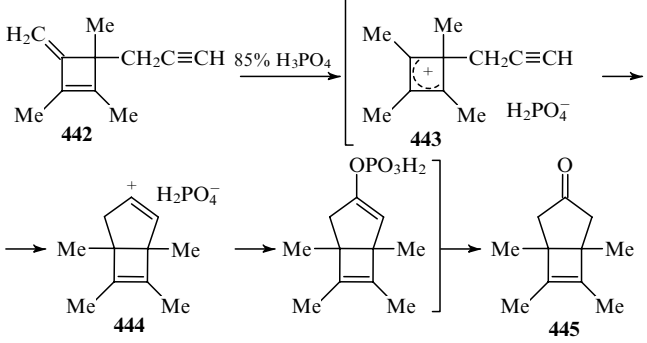
The homopropargyl rearrangement is important from the synthetic viewpoint as a facile and convenient method for the preparation of cyclobutanones containing diverse substituents including those fused with carbocycles.

The processes of cyclisation of alkynyl carbocations **197** (n = 2) with two methylene units between the triple bond and the carbenium centre are described in detail in Section V.1. It is noteworthy that upon the solvolysis of pent-4-ynyl triflates R–C≡C–$(CH_2)_2CH_2$OTf, no cyclic products have been detected.[26] This is due to the extremely high strain in the five-membered cyclic vinylic (*i.e.* cyclopent-1-enyl) cations (see structures **K**, Fig. 1, and **202**). Meanwhile, the cyclobut-1-enyl cations **429** and **435** are quite stable owing to delocalisation of the positive charge over three carbon atoms across the ring.[27,216] Therefore, the cation **441** is, in essence, a bridged non-classical ion in which the C(3) atom is equidistant from the ends of the double bond.

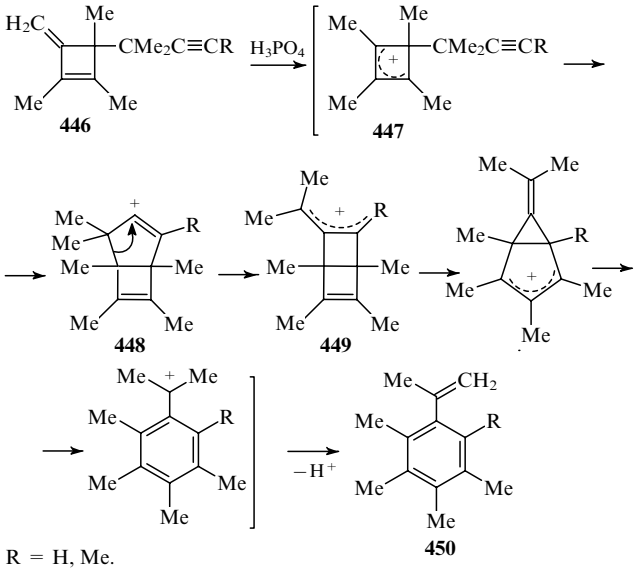


441

The cyclopent-1-enyl cations **202** can arise during this process if the cationic intermediates are sufficiently stabilised by appropriate substituents. Thus protonation of 1,2,4-trimethyl-3-methylene-4-(prop-2-ynyl)cyclobut-1-ene **442** affords bicyclic ketone **445**. The reaction scheme includes the formation of cyclobutenylallyl cation **443**, which cyclises to bicyclic vinylic cation **444**.[217] The structure of the cation **443** was confirmed by its ^{1}H NMR spectrum (in HSO_3F-SO_2FCl, −120 °C).



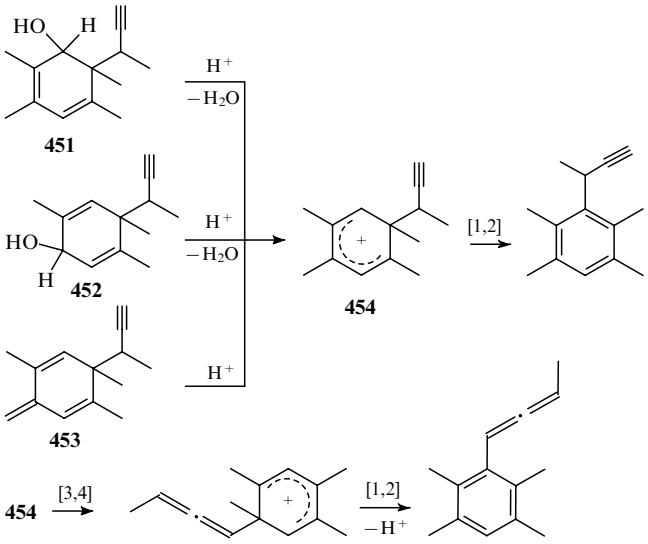
A variation of the degree of substitution in the substrate sharply changes the reaction route. Under the same conditions, cyclobutenes **446** substituted in the side chain afford polymethylated styrenes **450**, presumably according to the following scheme:[218]



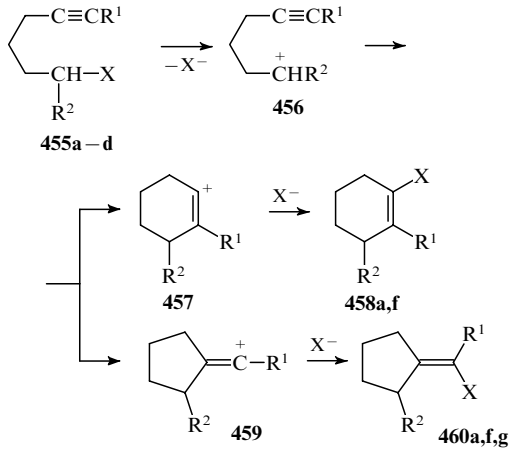
R = H, Me.

The spectral characteristics of the cationic intermediates formed in this process have been described in detail.[219] It is clear that the cations **443** and **447** correspond to structure **B**, the cations **444** and **448**, to structures **L** and **M** and the ion **449**, to allylic cation **Q** (see Fig. 1). Two other theoretically possible cation structures with participation of a C≡C triple bond are also formed during this transformation.

Protonation of propynyl-substituted cyclohexadienols **451** and **452** and methylenecyclohexadienes **453** results in the formation of cations **454**. The subsequent [1,2]-migration or two successive migrations of the propynyl fragment give rise to substituted benzenes.[220] Evidently, these rearrangements are energetically favourable because they lead to ring aromatisation.



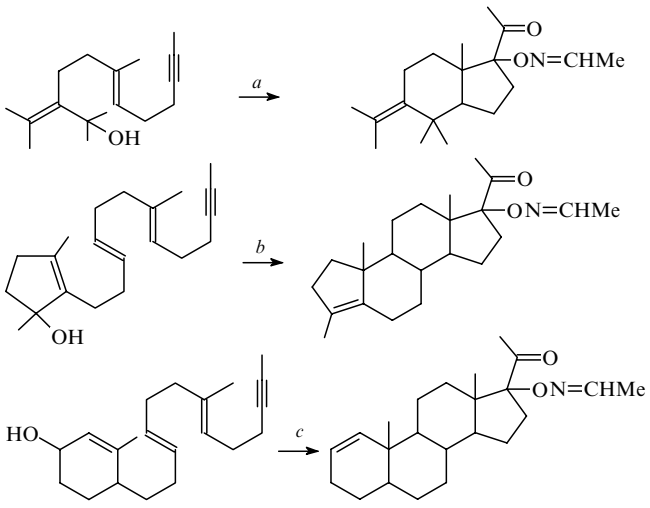
In alkynyl carbocations **456** in which the carbenium centre and the acetylenic fragment are separated by three carbon atoms, due to the close arrangement of groups in space, conditions are created for the formation of cations **457** and **459**. The predominance of one of these ions is determined by their relative stability, which depends on the substituents present in the initial acetylene derivative.



$R^1 = R^2 = H$, X = OTf (**a**); R^1 = Me, R^2 = H, X = OTf (**b**); R^1 = Ph, R^2 = H, X = OTs (**c**); R^1 = H, R^2 = Me, X = OTs (**d**); $R^1 = R^2$ = Me, X = OTs (**e**).

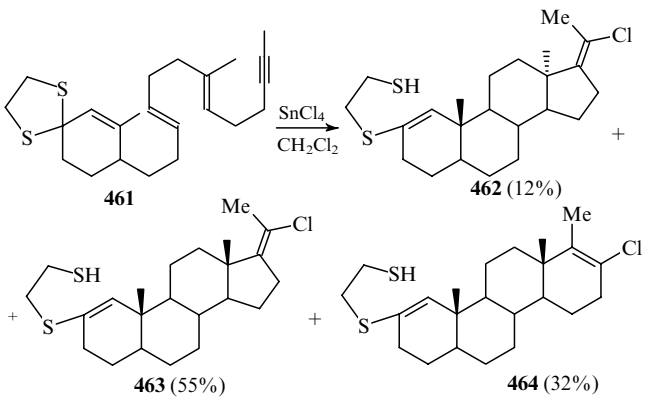
Thus solvolysis of terminal hex-5-ynyl triflate **455a** in trifluoroethanol results in the formation of an open-chain ether (X = OCH_2CF_3, 58%) and cyclohexene derivatives **458a** (12%) and **458f** (X = OCH_2CF_3, 24%).[22] Conversely, the methyl homologue **455b** is converted by approximately 85% into cyclopentane derivatives **460a** (67%) and **460f** (17%). The introduction of a terminal phenyl group (compound **455c**) stabilises the exocyclic vinylic cation **459** to even a greater extent; therefore, the transformation of **455c** gives almost exclusively methylenecyclopentane derivatives **460g** (X = OAc). The secondary tosylates **455d**,**e** behave in a similar way.[22]

The alkynylcarbenium (**456**) and vinylic (**457**, **459**) cations can arise as intermediates in cascade cyclisations used in elegant syntheses of steroids. Within the framework of a general approach to the preparation of testosterone, biomimetic syntheses of some of its precursors have been reported.[221–223]



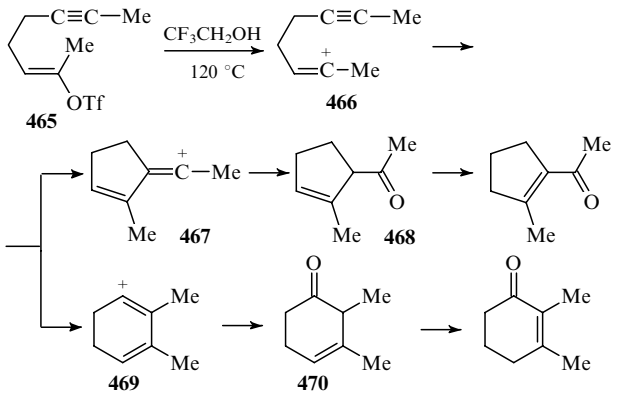
(*a*) CF_3COOH, $EtNO_2$, −78 °C, 80%; (*b*) CF_3COOH, Me_3N, $EtNO_2$, −25 °C, 30%; (*c*) Cl_3CCOOH, Me_2CHNO_2, 0 °C, 45%–65%

The treatment of thioketal **461** with $SnCl_4$ has given a mixture of cyclisation products **462**–**464** in 12%, 55% and 32% yields, respectively.[224]



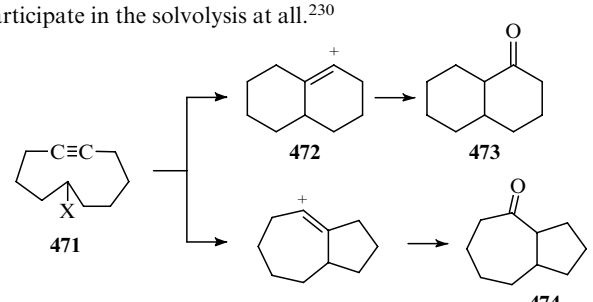
The synthetic potential of an approach to the synthesis of steroids, which, in principle, imitates the transformation of squalene into polycyclic products occurring in living organisms, has been discussed.[221–225] It was noted that the propynyl group plays a special role, since it makes possible the formation of both five- and six-membered rings *via* two vinyl cationic intermediates. Using this scheme, linear compounds can be converted in one stage into tetracyclic systems with seven chiral centres, this reaction being highly stereoselective (see also relevant reviews[226, 227]).

Cyclisations of alkynylvinyl cations **466** formed upon solvolysis of vinyl triflates **465** afford vinylic cations **467** and **469**, which are then converted into cyclopentenyl ketones **468** and cyclohexenones **470**, respectively. These ketones are unstable under the solvolysis conditions and rearrange into the corresponding α,β-unsaturated ketones.[228, 229]

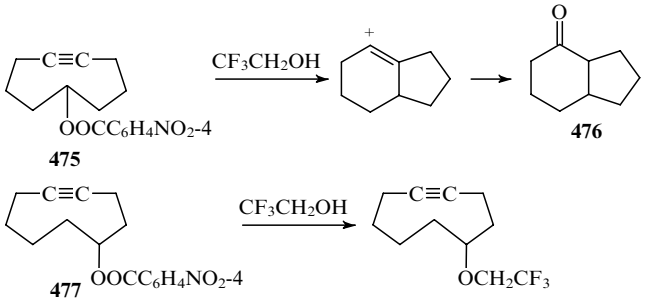


The dependence of the reaction route on the mutual orientation of the carbenium centre and the acetylenic fragment can be clearly followed for the solvolysis of cycloalkynyl esters. Thus cyclodec-5-ynyl derivatives **471** are mostly converted into decalone **473** *via* cation **472**. Only traces of bicyclo[5.3.0]decan-2-one **474** were found in reaction mixtures.[22, 26, 230, 231]

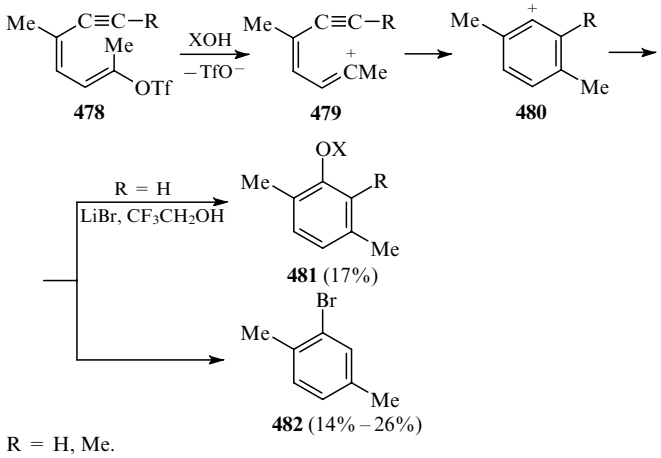
Solvolysis of 4-nitrobenzoate **475** containing a nine-membered ring yields almost quantitatively bicyclic ketone **476**,[22, 230] whereas in the case of isomeric ester **477**, the triple bond does not participate in the solvolysis at all.[230]



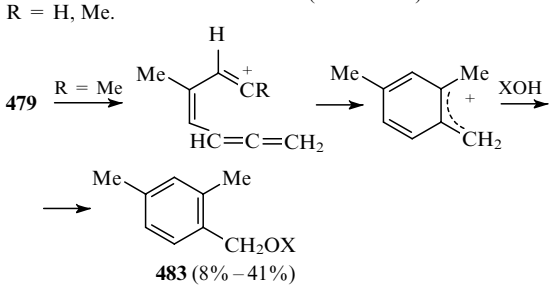
X = OTs, 4-$NO_2C_6H_4COO$.



Further progress of the studies described above resulted in the development of a new approach to the generation of fairly unstable phenyl cations of the type **6**.[27,229,232] Suffice it to say that these cations are 20–25 kcal mol^{-1} less stable than the propen-2-yl cation $H_2C=C^+CH_3$,[29] and it was not until 1985 that they were obtained for the first time by solvolysis.[28] The intermediate formation of the phenyl cations **480** was confirmed by the detection of functional derivatives of benzene **481** and **482** among the products of solvolysis of conjugated dienyne triflates **478**. Benzyl ethers **483** result from transprotonation of the cationic intermediate **479**.

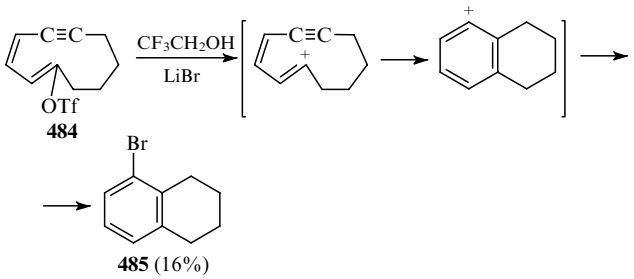


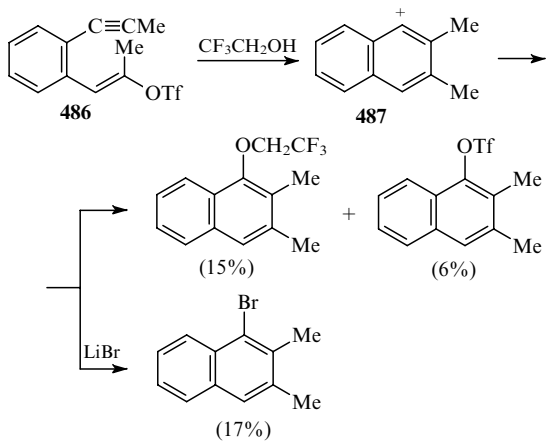
R = H, Me.



X = H, Et, CF_3CH_2.

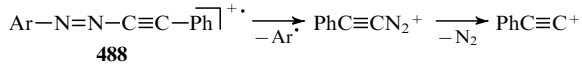
Solvolysis of cyclic dienyne vinyl triflate **484** in the presence of LiBr gives bromo-substituted tetrahydronaphthalene **485**.[233] Naphthyl cations **487** have been generated in the same way from enol triflate **486**.[27,234]



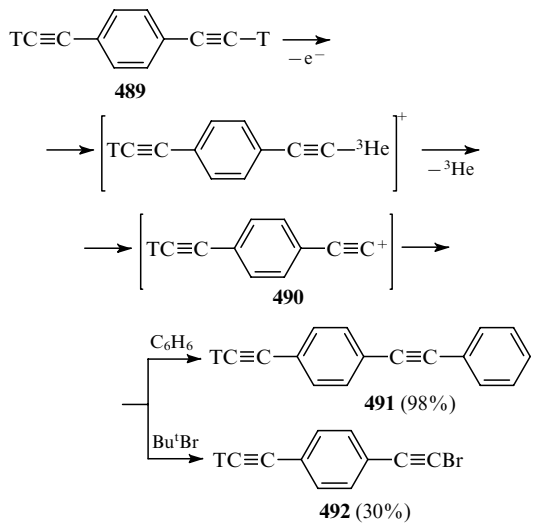


When the carbon–carbon triple bond is further removed from the carbenium centre, the cyclisation becomes virtually impossible.[22,26]

Another, barely studied, type of cations with a triple carbon–carbon bond, namely the alkynyl cations $R-C\equiv C^+$, should also be mentioned. These species are extremely unstable; their energy is 130 kcal mol^{-1} higher than that of primary vinyl cations or phenyl cations described above.[235] Phenylethynyl cations were detected for the first time in the mass spectra of arylazoethynylbenzenes **488**.[236]



Alkynyl cations can be generated in solution only by the nuclear-chemical method [235] (see also Ref. 237). Reactions of 1,4-diethynylbenzene **489** containing tritium atoms with benzene and brominated hydrocarbons were studied. The β-decay of tritium yields a helium atom, which is the best leaving group.

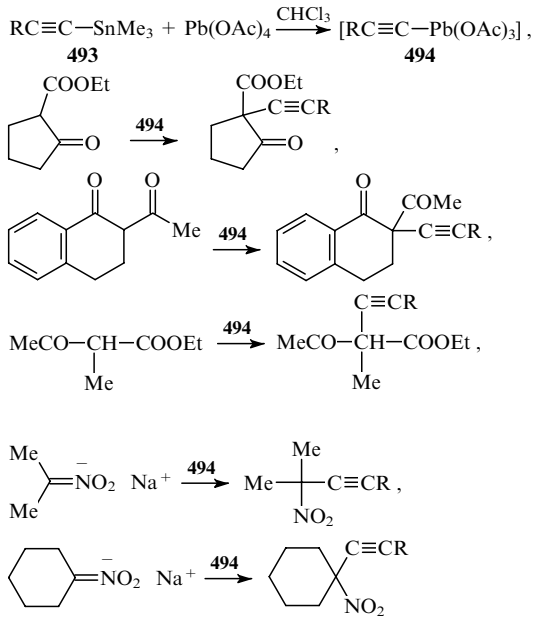


The intermediate formation of alkynyl cation **490** was proved by chromatographic isolation of the products of its reactions **491**, **492**.[235]

Recently, in order to find pathways to ethynyl cations, nitrosation of enamines, bis-silylated at the nitrogen atom, has been studied.[238] In the multicomponent reaction mixtures formed upon these reactions, some products that could have arisen with participation of the ions in question were detected.

It has been proposed to use alkynyllead triacetates **494**, which are formed *in situ* on treatment of alkynyltrimethylstannanes **493** with lead tetraacetate, as synthetic equivalents of alkynyl cations; these compounds permit easy introduction of an alkynyl group

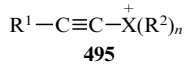
into 1,3-dicarbonyl compounds and nitronates. The reaction products are formed in 47% – 87% yields.[239]



R = H, $Me(CH_2)_5$, Ph, Me_3Si.

VII. Hetero-analogues of alkynyl carbocations

The principle of activation of a carbon – carbon triple bond by means of a positively charged substituent can be realised in compounds containing an acetylene fragment and a heteroatomic cation. Unlike alkynylcarbenium ions, onium cations **495** containing an ethynyl group cannot have allenyl structure like **10**.

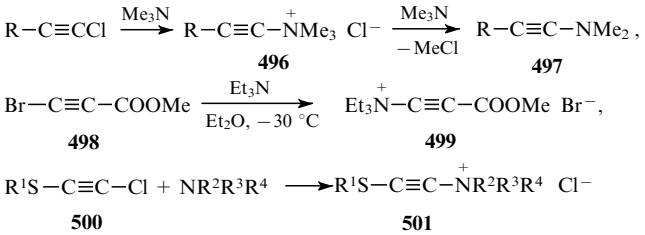


X = N, P, Hal.

An obvious merit of these systems is the possibility of removing the activating heterocationic fragment from the molecule after a transformation of the acetylene group.[35]

1. Alkynylammonium and alkynyldiazonium ions

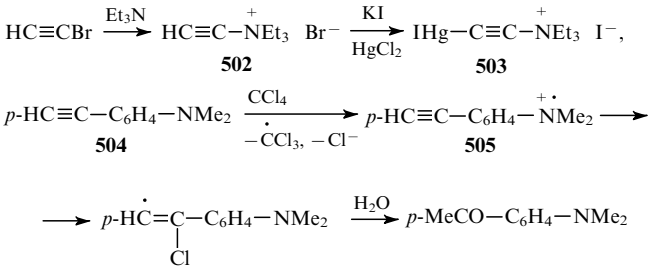
Alkynylammonium ions **496** are usually regarded as intermediates in the formation of ynamines **497** from alkynyl halides.[36] As a rule, these species are unstable, although in some cases, they have been isolated as salts and characterised. Thus the ethynylammonium salt **499** was prepared from methyl bromopropiolate **498**. The IR spectrum of this salt exhibits an absorption band typical of acetylene derivatives at about 2180 cm^{-1}.[240] Organyl chloroethynyl sulfides **500** react with tertiary amines to give quite stable salts **501**, which are soluble in water and alcohols. The acetylene absorption band in the IR spectra of these salts (2205 cm^{-1}) is shifted to shorter wavelengths with respect to this band in the spectra of the initial sulfides (2170 cm^{-1}).[241]



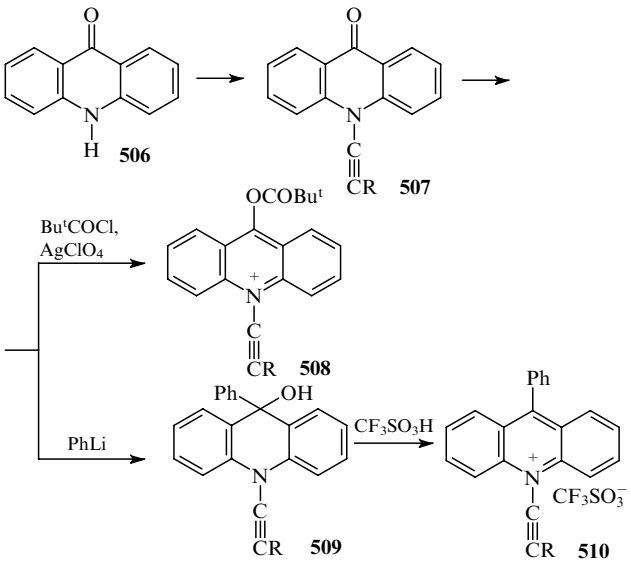
R^1 = Et, Bu; R^2, R^3, R^4 = Et, $(CH_2)_5$.

During studies on nucleophilic substitution at an acetylenic carbon atom, fairly unstable ethynyltriethylammonium bromide **502** has been isolated. Upon mixing with an alkaline solution of KI and $HgCl_2$, this salt was converted into stable mercurioethynylammonium iodide **503**.[242, 243]

An unusual type of hydration of a C≡C triple bond without a catalyst has been performed [244] by irradiation of 4-ethynyl-*N*,*N*-dimethylaniline **504**. This reaction was assumed [244] to occur *via* the formation of radical cation **505**.



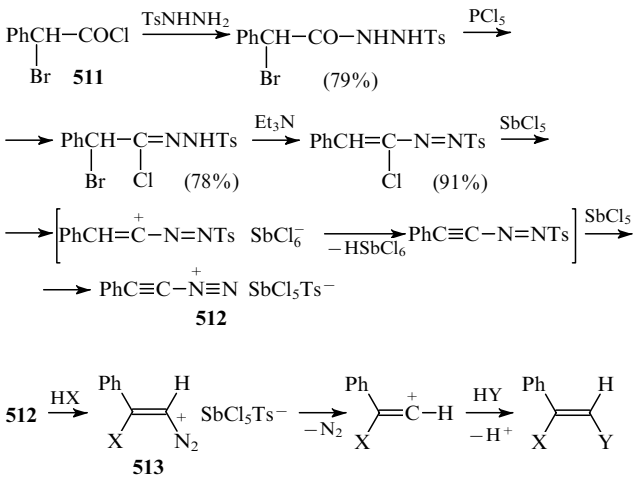
Published data on alkynylammonium cations are scarce. A comprehensive review of the available information can be found in a paper by Katrizky [245] devoted to the synthesis and spectroscopic characteristics of heterocyclic ynammonium salts. Since these salts cannot be prepared from highly nucleophilic 4-dimethylaminopyridine, acridone **506** was used as the heterocyclic substrate. This permitted the N-alkylation and quaternisation stages to be conducted separately. *N*-Alkynylacridinium salts **508**, **510** were prepared *via* two routes, namely, by *O*-acylation of *N*-alkynylacridones **507** and by dehydroxylation of pseudo-bases **509** with trifluoromethanesulfonic acid.[245]



R = Me, Ph, 2,4,6-$Me_3C_6H_2$.

In the ^{13}C NMR spectra of the salts **510**, the signal of the triple-bond carbon atom, more distant from the heterocycle, is shifted downfield (on the average, by 12 – 14 ppm) in relation to its position in the spectra of the precursors **507**, **509**. On treatment with nucleophiles, the salts **510** are converted into stable ynamines of the type **509**, the attack of the nucleophile being directed at the 9-position of the acridinium ring.[245]

After several unsuccessful attempts to prepare alkynyldiazonium salts, Hanack *et al.* [246] described the synthesis of phenylethynyldiazonium salt **512** from α-bromo-1-phenylacetyl chloride **511**. The salt **512** obtained at −30 °C was made to react with nucleophiles without isolation. It was found that nucleophiles first add to the C≡C triple bond. The alkenyldiazonium salts **513** thus formed eliminate a nitrogen molecule. The initial salt **512** itself cannot abstract a nitrogen molecule, because the energy of the alkynyl cation that would result from this process is extremely high (see Section VI).

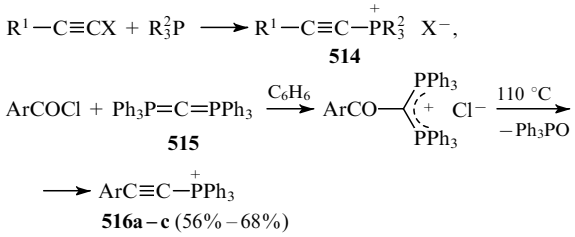


X, Y = OH, OMe, Cl.

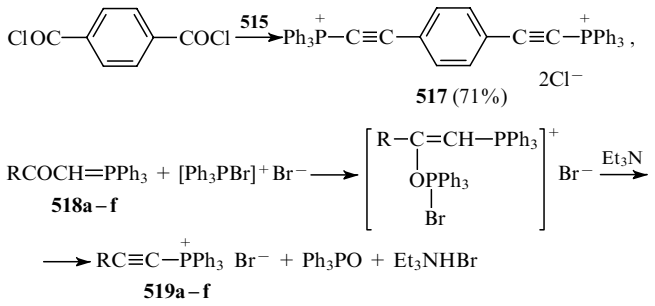
The IR spectrum of a solution of the diazonium salt **512** (CH_2Cl_2, −20 °C) contains absorption bands due to the triple bond (2150 and 2255 cm^{-1}) and the diazo group (2295 cm^{-1}). The researchers were unable to isolate this salt in the solid state.

2. Alkynylphosphonium cations

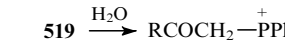
Unlike ynammonium salts, alkynylphosphonium salts of the type **514** are fairly stable, and by now, they have become significant from the synthetic viewpoint. These compounds were discovered in 1962 by Viehe *et al.*,[247] who studied reactions of alkynyl halides with nucleophiles. An important method for the synthesis of the salt **514** consists in treatment of alkynyl halides with triphenylphosphine (more rarely, with trialkylphosphines) in aprotic solvents (for example, in ether).[248–250] Arylethynylphosphonium salts **516** and **517** are prepared by acylation of hexaphenylcarbodiphosphorane **515**.[251]



Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), α-$C_{10}H_7$ (**c**).



R = EtO (**a**), PhO (**b**), Et_2N (**c**), Ph_2N (**d**), Pr^i_2N (**e**), PhMeN (**f**).

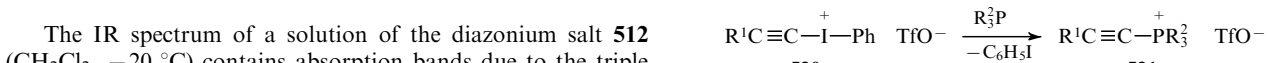


R = Ar, Alk_3N.

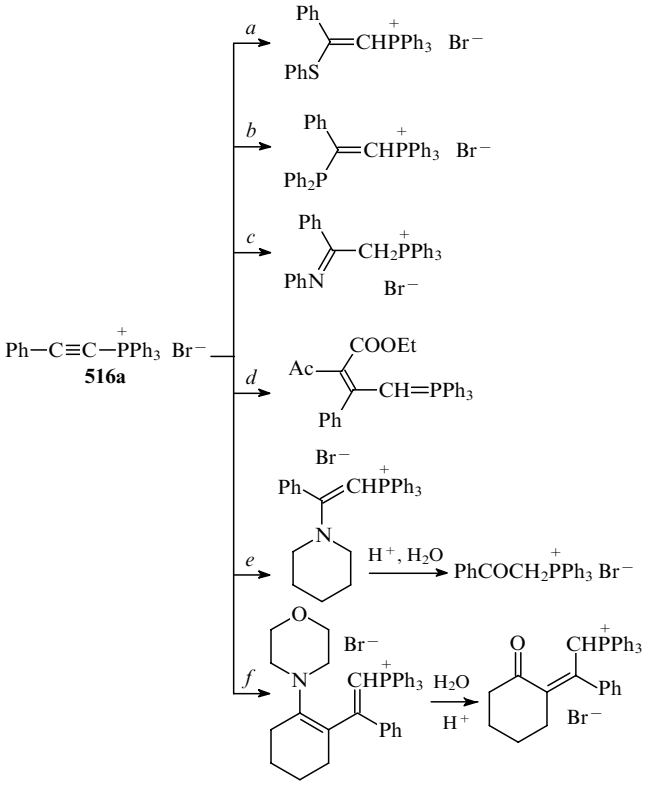
Yet another approach to the alkynylphosphonium salts of the type **514** is based on interaction of aroylmethylenetriphenylphosphoranes **518** with triphenylphosphine dibromide.[252] The attempts to prepare salts **519** with aliphatic substituents R by this method failed. However, ethoxycarbonyl- (**518a**) and phenoxycarbonyl-methylenetriphenylphosphoranes (**518b**) were converted into the alkoxyethynylphosphonium salts **519a**,**b**, and *N*,*N*-dialkylcarbamoylmethylenephosphoranes **518c**–**f** were converted into the aminoethynylphosphonium salts **519c**–**f**, which represent a new type of push–pull acetylenes.

The alkynylphosphonium salts **519** with alkylamino or aryl groups as the substituents R are quite stable on heating and do not tend to be oxidised by atmospheric oxygen. As a rule, alkynylphosphonium bromides are solids, whereas the corresponding chlorides are normally oils. The IR spectra of these salts exhibit absorption bands of moderate intensity at about 2150–2200 cm^{-1}. In aqueous solutions, anion exchange is possible, for example, bromide can be replaced by iodide,[253] and chloride can be replaced by chloroplatinate.[249] On heating with water or acetic acid, the acetylene fragment in the salts **519** is hydrated giving a carbonyl group at the carbon atom furthest from phosphorus.[252, 253]

Recently, preparation of alkynylphosphonium salts **521** by treatment of alkynyliodonium salts **520** with polycyclic trialkylphosphines has been described [524] (see Section VII.3).

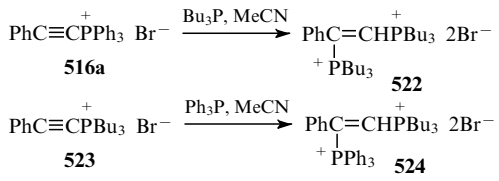


The addition of nucleophilic reagents to alkynylphosphonium salts is directed at the triple-bond carbon atom that is furthest from the phosphonium group.[249, 253] Some of these reactions are presented below

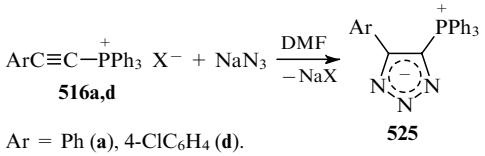


(*a*) PhSH; (*b*) Ph_2PH (72%); (*c*) $PhNH_2$ (80%); (*d*) $AcCH_2COOEt$, Et_3N (72%); (*e*) HN⟨⟩ (95%); (*f*) ⟨⟩N—O.

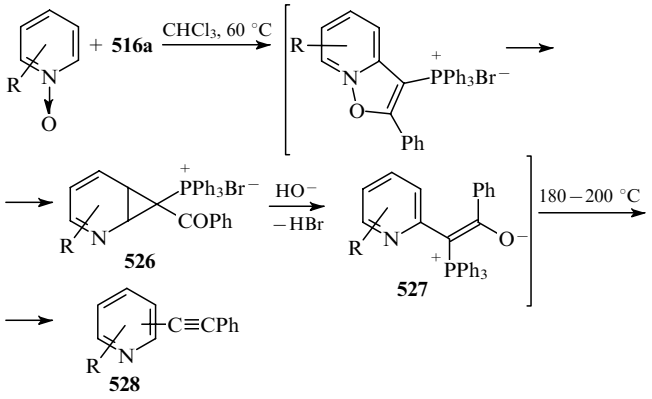
The addition of tributylphosphine is accompanied by displacement of the triphenylphosphine residue, because tributylphosphine is a stronger nucleophile, and affords bis-tributylphosphonium styrene derivative **522**. Triphenylphosphine adds to the compound **523** to yield mixed bis-phosphonium salt **524**.



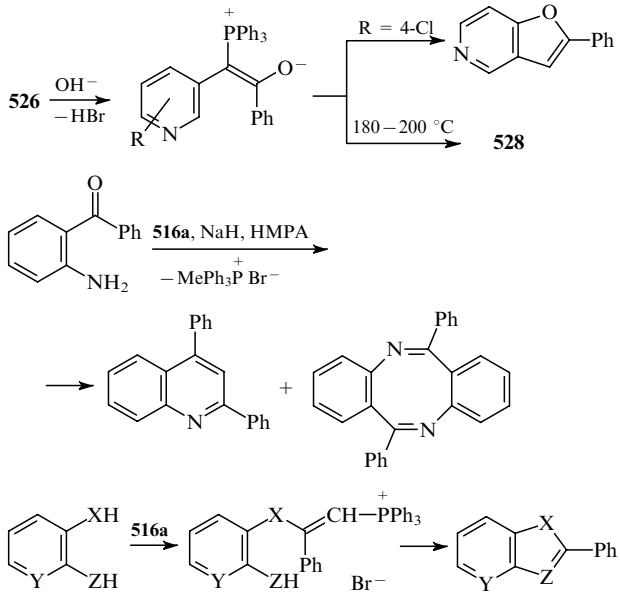
A method for the synthesis of a new family of heterocyclic ylides **525** based on reactions of alkynylphosphonium salts with sodium azide has been developed.[250] Phenylethynylpyridines **528** have been obtained by the reaction of the salt **516a** with pyridine *N*-oxides.[255]



Ar = Ph (**a**), 4-ClC_6H_4 (**d**).



The use of alkynylphosphonium salts in the synthesis of heterocycles comprising the addition of nucleophiles to a triple C≡C bond and subsequent cyclisation with the removal of the activating triphenylphosphine fragment has been demonstrated [35] in relation to reactions of the salt **516a**.

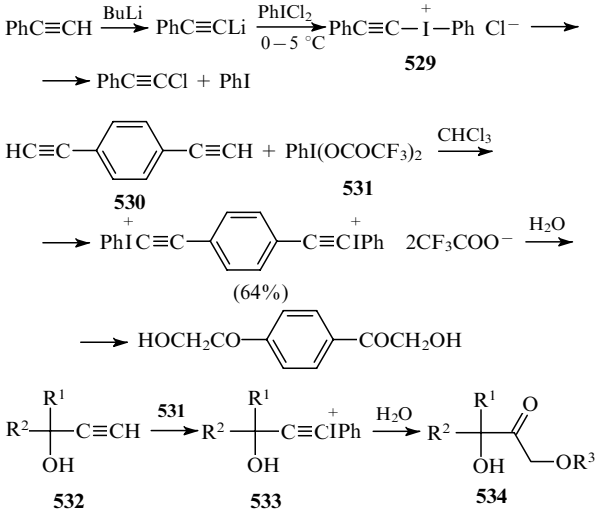


X = NH, S; Y = CH, N; Z = O, NH.

Numerous syntheses based on propynylphosphonium salts have been described in a number of studies [256–258] and have been surveyed in a review.[259]

3. Alkynyliodonium ions

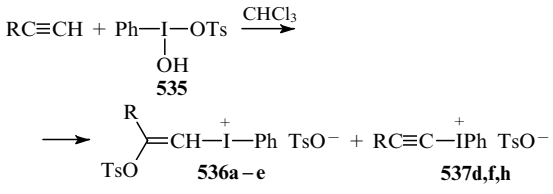
Alkynyl derivatives of tricoordinated iodine have been known since 1965. The interest in the chemistry of tricoordinated iodine, which has sharply increased in recent years,[260] has stimulated studies of its ethynyl derivatives. Phenyl(phenylethynyl)iodonium chloride **529** was synthesised in a yield of up to 20% by the reaction of lithium phenylacetylenide with λ³-iodanylbenzene dichloride. The IR spectrum of this salt [261] contains a characteristic absorption band in the region of 2170 cm^{-1}. On storage for several hours at room temperature, the salt **529** spontaneously decomposes to give iodobenzene and chloro(phenyl)acetylene. Phenyliodanyl bis(trifluoroacetate) **531**, capable of oxidising terminal triple bonds in compounds **530**, proved to be a more efficient reagent.[262]



R^3 = H, CF_3CO.

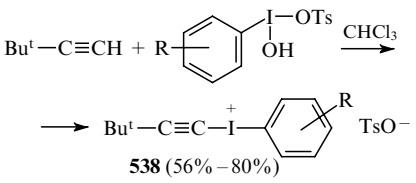
The reagent **531** was used for efficient transformation of alkynols and arylalkynols **532** into 1,3-dihydroxy 2-carbonyl derivatives **534** *via* alkynyliodonium intermediates **533**.[263]

The first method, really suitable for the preparative-scale synthesis of alkynyliodonium salts, is based on the reaction of alkynes with hydroxy(tosyloxy)iodanylbenzene **535**. Short-term refluxing of the reagents in $CHCl_3$ gave alkenyl (**536a–e**) and alkynyl (**537d,f–h**) iodonium salts.[264, 265]



R	Yield (%)		R	Yield (%)	
	536	**537**		**536**	**537**
Pr (**a**)	58		Bu^i (**e**)	29	33
Bu (**b**)	52		Bu^s (**f**)		50
n-C_5H_{11} (**c**)	26		Bu^t (**g**)		74
Pr^i (**d**)	11	15	Ph (**h**)		61

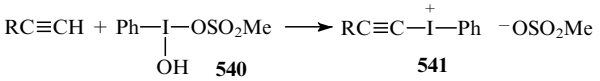
Alkylethynyliodonium salts **538** can be prepared only in those cases where the alkyl group in the alkyne (Pr^i, Bu^t) creates steric hindrance hampering nucleophilic attack on the triple bond.[266] This strategy was also employed to synthesise 4-alkoxyphenylethynyliodonium salts **539** containing long alkyl chains.[267]



R = H, 2-Me, 3-Me, 4-Me, 2-F, 3-F, 4-F, 3-Cl, 4-Cl.

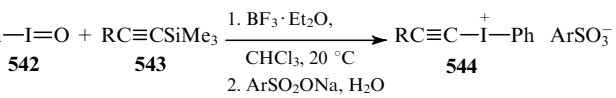


R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$.

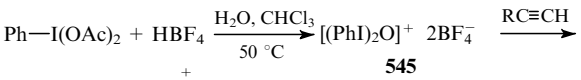


R = Me, Bu, Bu^t.

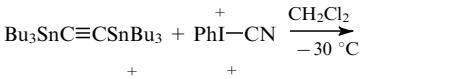
The use of hydroxy(mesyloxy)-λ^3-iodanylbenzene **540** made it possible to produce alkynyliodonium mesylates **541**.[268] However, this synthetic approach has a substantial limitation: due to the high nucleophilicity of the counter-ion, the reaction affords alkenyliodonium salts of the type **536** as side products. This decreases the yield and purity of the target products. Therefore, a new approach has been developed; it includes interaction of readily accessible iodosylbenzene **542** with silylated alkynes **543** in the presence of an equimolar amount of $BF_3 \cdot Et_2O$ and subsequent treatment of the reaction mixture with an aqueous solution of sodium arenesulfonate.[269] In addition, two methods for the synthesis of alkynyliodonium salts **546** and **547** have been described; one of them is based on the use of iodonium salt **545**,[270] and the other involves the use of alkynylstannanes.[271–273]



R = Me, Et, Pr, Bu, Me_3Si; Ar = 4-MeC_6H_4, 4-$NO_2C_6H_4$.



R = Pr, Ph.

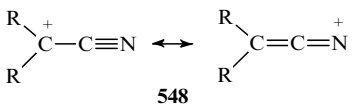


R = CF_3, C_4F_9.

The IR spectra of the alkynyliodonium salts **546** and **547** contain absorption bands at 2155–2190 cm^{-1} due to the acetylenic fragment. X-Ray diffraction analysis of phenyl(phenylethynyl)iodonium tosylate **537h** have demonstrated that the cation has an angular structure[268] and that Ph–C≡ and C≡C bond lengths are close to the typical values for the corresponding single and triple bonds. At the same time, the acetylenic fragment is substantially activated towards efficient interaction with diverse nucleophiles. In recent years, alkynyliodonium salts have acquired large synthetic significance; numerous examples of the preparation and synthetic application of these compounds have been described in detail in recent reviews.[274–278]

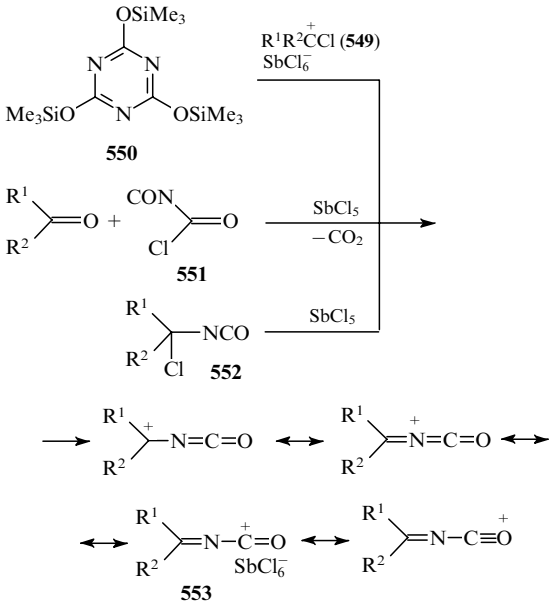
In conclusion, we would like to mention heteroanalogues of alkynylcarbenium ions containing heteroatoms in the unsaturated fragment.

Cyanocarbenium ions of type **548** have scarcely been studied. The results of quantum-chemical calculations for these systems and study of solvolysis of a number of tertiary α-cyanoalkyl tosylates and related compounds have been surveyed in a review.[17]

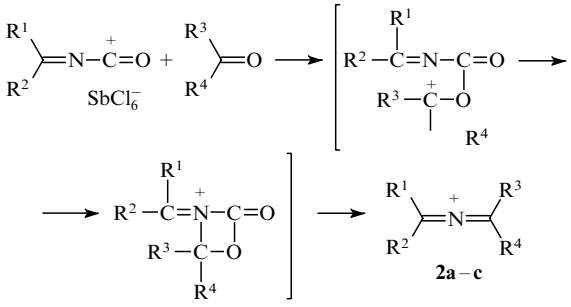


548

Finally, 1-oxa-3-azabutatrienium cations **553** present considerable interest from the synthetic viewpoint. The chemistry of these species is being vigorously studied by Jochims *et al.*[11,279–283] These cations are prepared by ionisation of α-chloroalkyl isocyanates **552**, by treatment of silylated cyanuric acid **550** with chlorocarbenium ions[280,281] or by the reaction of ketones with chlorocarbonyl isocyanate **551**.[12]



Similarly to alkynylcarbenium ions, these cations add nucleophiles at the carbonyl carbon atom and the nitrogen atom, for example, in reactions with ketones.[11]



The salts **553** and their thio-analogues have been used to develop a number of procedures for the synthesis of various nitrogen- and oxygen-containing heterocyclic and polyfunctional compounds; these methods deserve generalisation in a separate review.

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