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Electrophilic activation of acetylene compounds in Brønsted superacids. Reactions of vinyl type cations

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Abstract. Published data on the reactions of vinyl type cations generated upon protonation of the carbon – carbon triple bond of acetylene compounds in proton-donor Brønsted superacids and conjugate Brønsted – Lewis systems: HSO_3F, CF_3SO_3H, $HSO_3F – SbF_5$, $CF_3SO_3H – SbF_5$, $HF – SbF_5$, $HBr – AlBr_3$, *etc*., are summarized. Charasteristics of vinyl type cations by physicochemical methods (NMR spectroscopy, X-ray diffraction analysis, IR spectroscopy) are given. The bibliography includes 88 references.

I. Introduction

Alkynes are widely used to obtain compounds of practical value: monomers for polymerization, nonlinear optical materials and liquid crystals, organic semiconductors and sensors, pharmaceuticals, *etc*.[1,2] The solution of theoretical and applied problems associated with synthetic methods and properties of alkynes, is of great importance for the development of organic chemistry.

One way to activate acetylene derivatives is to generate positively charged intermediates through the interaction of electrophilic species with a carbon – carbon triple bond. Such activation, facilitating the reactions with nucleophiles, can be performed by protonation of the alkyne triple bond or by its coordination to Lewis acids or transition metal complexes. Historically, the first example of an electrophilic metal-catalyzed reaction of alkynes was hydration of the C≡C bond under the action of mercury(II) compounds discovered by Kucherov in 1881 in Saint-Petersburg at the Imperial Forest Institute (today Saint-Petersburg State Forest Technical University).[3,4]

The generation of cationic intermediates from organic molecules under the action of superacid reagents followed by reactions of the cations with superacids, which are accompanied by an increase in the electrophilicity of these species, was given the name 'superelectrophilic activation'.[5] Unique properties of liquid and solid Brønsted and Lewis superacids[6] such as a high protonating (ionizing) ability and extremely low nucleophilicity make it possible to obtain not only mono-charged cations but also more reactive species having the charge $\geqslant 2$ from organic compounds.[5,6] Various methods of formation of superelectrophilic cations and their reactions are presented in several reviews.[7–15] The general philisophy of superelectrophilic activation is outlined in the monograph,[5] which covers, like the review article,[15] only some aspects of the chemistry of alkynes in superacidic media.

During the last 10 – 15 years, the number of investigations concerned with the application of Brønsted superacids in organic synthesis has increased.[5,6] This is due both to various promising applications of superelectrophilic activation of organic compounds and to the wide application of easy-to-handle superacidic reagents such as, *e.g*., trifluoromethanesulfonic acid and its imide in laboratory practice. In the 2000s, publications on the chemistry of alkynes in superacids started to appear, and the present work reflects this relatively new trend.

The present review deals with reactions of vinyl type cations $RHC{=}C^+R'$ generated upon protonation of a carbon–carbon triple bond of acetylene compounds in proton-donating Brønsted superacids and conjugate Brønsted – Lewis systems: HSO_3F, CF_3SO_3H, $HSO_3F – SbF_5$, $CF_3SO_3H – SbF_5$, $HF – SbF_5$, $HBr – AlBr_3$, *etc*. Studies of vinyl type cations by means of NMR spectroscopy, X-ray diffraction analysis and IR spectroscopy and their characteristics obtained using quantum chemical calculations, are summarized.

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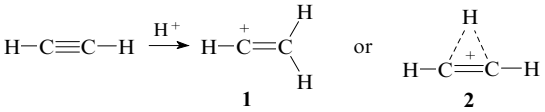
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II. Study of vinyl type cations by physicochemical methods and results of quantum chemical calculations

Up to the mid-20th century, intermediate formation of vinyl type cations has been postulated for many reactions involving alkynes.[16–18] Hovewer due to the instability and high reactivity, the parent cation of this series — vinyl cation $C_2H_3^+$ (**1**) forming upon protonation of acetylene — was not hitherto detected and identified spectrally in condensed media.

The generation of the vinyl cation $C_2H_3^+$ by plasma methods using $C_2H_2-H_2-He$ and CH_4-H_2-He mixtures allowed recording its spectrum in the gas phase (Scheme 1).[19]

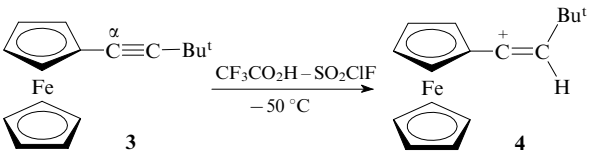
Scheme 1



According to the data obtained, the band at 3142.2 cm^{-1} corresponds to the asymmetric C–H bond vibrations of the nonclassical bridged structure **2**, which is more benefitial in energy than the classical open form **1**. Modern theoretical investigations also confirm higher stability of cation **2** in the gas phase compared to vinyl cation **1**.[20] However, according to quantum chemical calculations,[21,22] the classical structure $R^1C^+=CR^2R^3$ is more stable for substituted vinyl type cations.

The priority in detection of extremely unstable and elusive vinyl type cations belongs to Siehl *et al.*, who were the first to detect cation **4** upon protonation of alkyne **3** in $CF_3CO_2H-SO_2ClF$ system at −50 °C using NMR spectroscopy (Scheme 2).[23,24] On the one hand, species **4** is stablized by the π-donor ferrocenyl moiety and, on the other hand, it is sterically hindered by the *tert*-butyl substitutent. In the ^{13}C NMR spectrum of this cation, the signal (δ_C) of the positively charged α-carbon atom appears at 177.14 ppm, which exceeds the δ_C value of this atom in the parent compound **3** by ~100 ppm (76.37 ppm).

Scheme 2

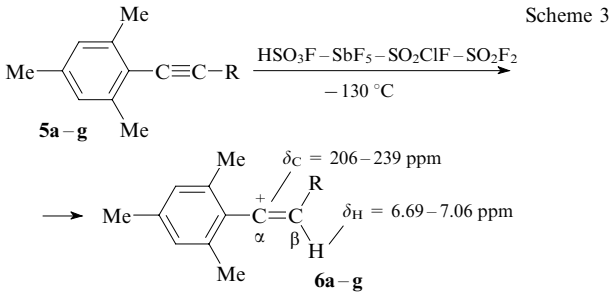


The same research group has obtained and characterized a series of vinyl type cations in superacids at low temperatures.[25–27] In the system $HSO_3F-SbF_5-SO_2ClF-SO_2F_2$ at temperatures between −130 and −100 °C, cations **6a–g** are generated upon protonation of arylacetylene derivatives **5a–g** at the C≡C bond (Scheme 3).[25] 2,4,6-Trimethylphenyl (mesityl) group stabilizes cations **6a–g** due to delocalization of the positive charge by the aromatic π-system and steric hindrance of the cationic centre by *ortho*-methyl substituents.†

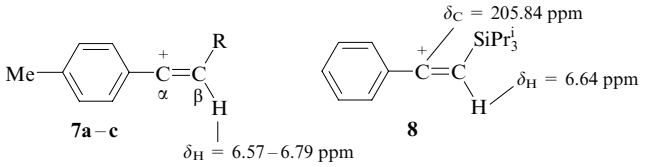
In a similar way, the protonation of the corresponding arylacetylenes in the system $HSO_3F-SbF_5-SO_2ClF-SO_2F_2$ at −125 °C furnished a series of *p*-tolyl-substituted cations **7a–c** and phenyl-substituted cation **8**.[23] The positions of peaks in the ^1H and ^{13}C NMR spectra of these compounds are given below.

† Hereinafter the characteristic signals of atoms in the NMR spectra providing evidence for the structure are shown in schemes for clarity.

Scheme 3



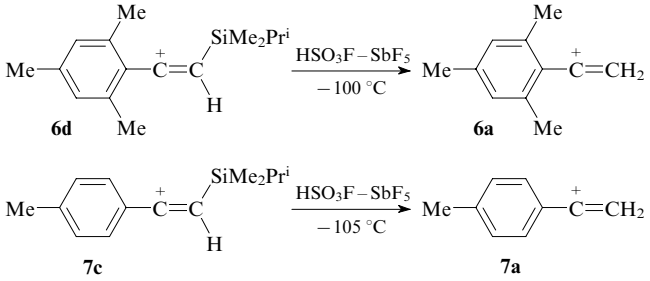
R = H (**a**), Bu^t (**b**), 1-Ad (**c**), $SiMe_2Pr^i$ (**d**), $SiMe_2Bu^t$ (**e**), $SiMe_2CMeEt_2$ (**f**), $SiPr^i_3$ (**g**); Ad is adamantyl



R = H (**a**) ($\delta_{C(\alpha)}$ = 250.94 ppm), $SiPr^i_3$ (**b**) ($\delta_{C(\alpha)}$ = 205.84 ppm), $SiMe_2Pr^i$ (**c**)

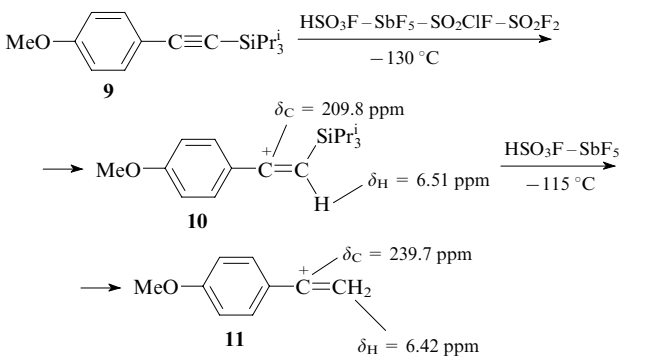
Direct protonation of mesitylacetylene **5a** and *p*-tolylacetylene under the action of HSO_3F-SbF_5 mixture yields cations **6a** and **7a**, respectively, mixed with by-products. To obtain these ions, substitution of the $Pr^iMe_2Si^+$ group in cations **6d** and **7c** pre-generated at −130 °C by a proton was performed under the action of HSO_3F-SbF_5 at −105 to −100 °C (Scheme 4).[23]

Scheme 4



The protonation of 4-methoxyphenylacetylene **9** at −130 °C affords first cation **10**, and as the temperature increases up to −115 °C, ion **11** is formed (Scheme 5).[26]

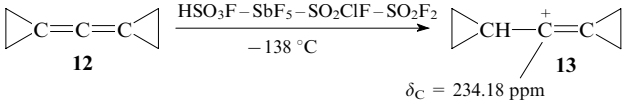
Scheme 5



Trialkylsilyl groups SiR_3 that contain branched alkyl substitutents (R = Pr^i, Bu^t, *tert*-C_6H_{13}) in the β-position of arylacetylenes stabilize cations **6a–g**, **7b**,**c**, **8**, **10** due to steric and electronic (hyperconjugation) factors. Attempts to obtain similar cations bearing trimethylsilyl group were unsuccessful.[23]

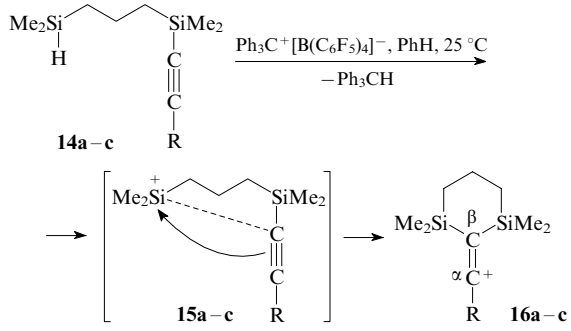
The protonation of bis(cyclopropylidene)methane (**12**) in the system $HSO_3F-SbF_5-SO_2ClF-SO_2F_2$ at −138 °C affords cation **13** stabilized by the α-cyclopropyl group (Scheme 6). [27]

Scheme 6



Organosilicon derivatives **14a–c** react with triphenylmethylium tetrakis(pentafluorophenyl)borate in benzene at room temperature through the intermadiate formation of silyl cations **15a–c**.[28,29] Subsequent rearrangement furnishes cations **16a–c** bearing two silyl substituents in the β-position; these cations are highly stable and do not react with benzene at room temperature (Scheme 7).

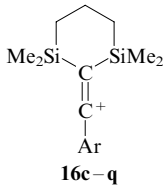
Scheme 7



R = H (**a**) [$\delta_{C(\alpha)}$ = 184 ppm], Bu^t (**b**) [$\delta_{C(\alpha)}$ = 202.4 ppm], Ph (**c**) [$\delta_{C(\alpha)}$ = 185.8 ppm]

The structure of the salt formed by the α-*tert*-butyl-substituted cation **16b** and the $[CB_{11}H_6Br_6]^-$ counter-ion has been confirmed by the X-ray diffraction data,[29] according to which the cationic carbon atom in the α-position has sp hybridization. The C(α)=C(β) double bond is unusually short, 1.221 Å, being close to the C≡C bond length in alkynes. The fact that the $^+$C(α)=C(β) bond order in cation **16b** exceeds 2 was also established on evidence derived from the IR spectroscopy data: the stretching band of this bond appears at 1987 cm^{-1}, being close to the C≡C bond vibrations.[29] Moreover, according to X-ray diffraction data, the C(β)–Si bond in cation **16b** is 0.1 Å longer than the similar bonds in structurally related uncharged silicon-containing molecules. The authors of Ref. 29 interpreted this fact as evidence of β-silyl group participation in stabilization of the cationic centre by hyperconjugation mechanism, which is also confirmed by quantum chemical calculations for similar vinyl type cations.[26–31]

A series of stable α-aryl-β,β-disilyl-substituted cations **16c–q** have been obtained using the above approach and characterized by NMR spectroscopy.[31] The signal of the α-carbon atom in the ^{13}C NMR spectra of these cations appears in the range of 178–194 ppm.



16c–q

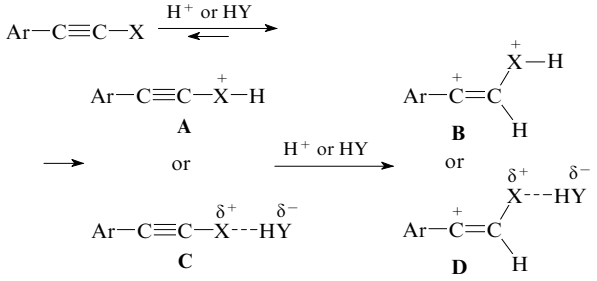
Ar = $C_6H_{5-n}R_n$ [R_n = H (**c**), 4-Me (**d**), 4-Et (**e**), 2,4-Me_2 (**f**), 2,5-Me_2 (**g**), 3,4-Me_2 (**h**), 4-Ph (**i**), 2-F (**j**), 3-F (**k**), 4-F (**l**), 4-Cl (**m**), 3-CF_3 (**n**), 4-CF_3 (**o**), 1-Naph (**p**), Fc (**q**)];
Naph is naphthyl, Fc is ferrocenyl

III. Protonation of acetylene compounds bearing electron-withdrawing substitutents in superacids

The following are the data obtained in studies of the alkyne protonation by NMR spectroscopy and quantum chemical calculations.

The basicity of heteroatom functionalities[32] and the values of their proton affinities exceed the corresponding characterictics for the C≡C triple bond. Therefore, the protonation of acetylene compounds ArC≡CX bearing electron-withdrawing groups X [X = C(O)R, CO_2R, $P(O)(OR)_2$, $C(O)CF_3$, $C(O)CO_2R$, CN, SO_2R (R = Alk, Ar), *etc.*] in superacids proceeds first at the heteroatom contained in group X, yielding monocations **A** and subsequently at the carbon atom of the triple bond yielding dications **B** (Scheme 8). Depending on the basicity of the group X, this gives either completely protonated mono- and dications (**A** and **B**), or, generally, species **C** and **D** protosolvated with molecules. Cations **B** and **D** are considered as superelectrophilic species because of an increase in their electrophilic properties (positive charge and orbital interactions) on the vinyl cationic carbon due to the vicinity of the substituent X, which is solvated or completely protonated in the superacid.

Scheme 8



X = C(O)R, CO_2R, $P(O)(OR)_2$, $C(O)CF_3$, $C(O)CO_2R$, CN, SO_2R, *etc.*; HY = HSO_3F, CF_3SO_3H, HF–SbF_5, HSO_3F–SbF_5, CF_3SO_3H–SbF_5

The first step of protonation (protosolvation) of the compounds ArC≡CX at the group X resulting in **A** or **C** is kinetically reversible. The subsequent protonation at the triple bond is irreversible, since the vinyl cations **B** and **D** formed are very reactive intermediates (see Sections IV–VI), which cannot be detected by low-temperature NMR spectroscopy.

To evaluate the reactivity of different protonated alkyne ArC≡CX forms, quantum chemical calculations were performed by the density functional theory (DFT) B3LYP/6-31G(2d2p) method.[33] The molecule of 1,3-diphenylpropynone (**17a**) and its forms protonated at the carbonyl oxygen atom (**18a**), at the O and C atoms (**19**), and at only the

carbon atom of the triple bond (**20**) have been chosen as examples.

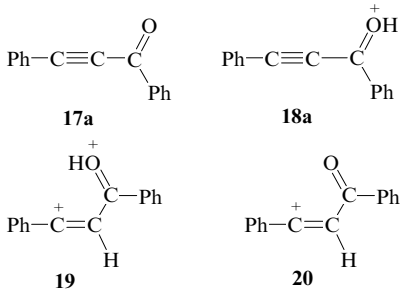


Table 1 summarizes the energies (ε) of the lowest unoccupied molecular orbitals (LUMO), the charges on the carbon atoms in the 2-position of the C(2)≡C(1)—C=O moiety (q_1) and carbonyl group (q_2), and the contributions of these atoms (m_1 and m_2) to the common LUMO of the molecule for the neutral structure of 1,3-diphenylpropynone (**17a**) and cations **18a**, **19** and **20** calculated by the DFT/B3LYP/6-31G(2d2p) method.

Table 1. Results of quantum chemical calculations of structures **17**–**20**.[33]

Parameter	Structure			
	17a	**18a**	**19**	**20**
ε (LUMO) /eV	−2.343	−7.287	−11.785	−7.932
q_1 /NBO [a]	0.056	0.227	0.388	0.422
m_1 (%)	11.4	16.4	37.0	36.3
q_2 /NBO [a]	0.487	0.496	0.563	0.582
m_2 (%)	15.3	29.8	3.1	4.7

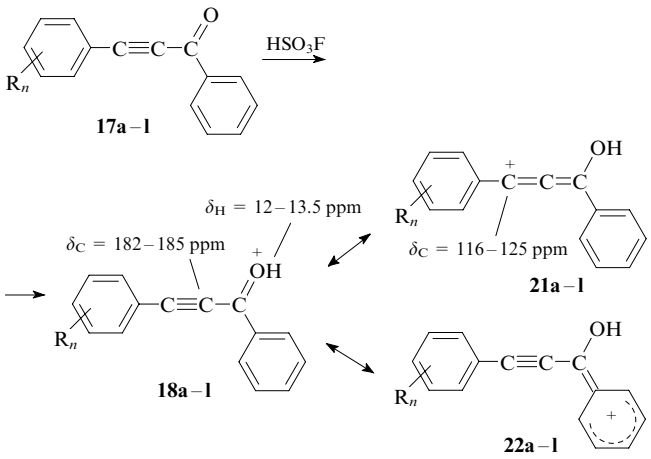
[a] NBO (Natural Bond Orbital) are units of charge on the atoms.

The calculation data indicate that the lowest energy of the LUMO belongs to dication **19**, which falls into the class of superelectrophiles.[5] The LUMO energy of the dication is lower than the calculated energy of the highest occupied molecular orbital (HOMO) of benzene (ε = −9.3 eV; the ionization potential of benzene determined experimentally is 9.24 eV).[34] This attests to energetically beneficial interaction between diprotonated forms and aromatic substrates.

Attention is drawn by the considerable positive charge on the carbonyl carbon atom in ions **18**–**20**, exceeding the charge on the carbon atom C(2). Hovewer, for acetylene compounds comprising propynone moiety C(2)≡C(1)—C=O, only the carbon atom in 2-position rather than the carbonyl carbon atom acts the reaction centre in Brønsted superacids (see Sections IV–VI). The contribution of C(2) atom to the common LUMO is the highest for ion **20**, indicating the significant orbital control in reaction of such type cations.

A ^{1}H and ^{13}C NMR study of protonation of 1,3-diarylpropynones **17a**–**l** has revealed that these compounds exist in HSO_3F as O-protonated species **18a**–**l** (Scheme 9).[35,36] A comparison of the ^{13}C NMR spectra of the parent ketones and their protonated forms (HSO_3F, −80 or 0 °C) indicates that the positive charge of the protonated carbonyl group of ions **18a**–**l** is delocalized both on the arylacetylenic part of the molecule (resonance structures **21a**–**l**) and on the phenyl ring conjugated with the carbonyl substituent (structures **22a**–**l**).[35]

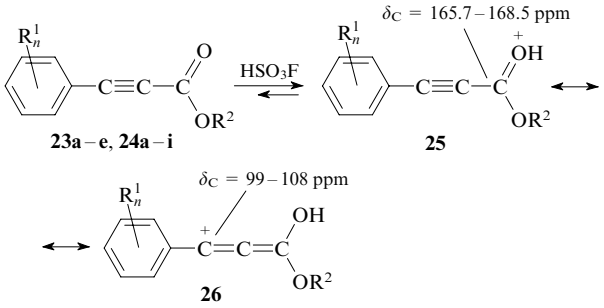
Scheme 9



R_n = H (**a**), 4-Me (**b**), 2,4,6-Me_3 (**c**), 4-OMe (**d**), 3-NO_2 (**e**), 4-NO_2 (**f**), 4-CN (**g**), 4-OMe-3-NO_2 (**h**), 2,4,6-Me_3-3-NO_2 (**i**), 2,3,5,6-Me_4-4-NO_2 (**j**), 4-Ac (**k**), 4-CO_2Me (**l**)

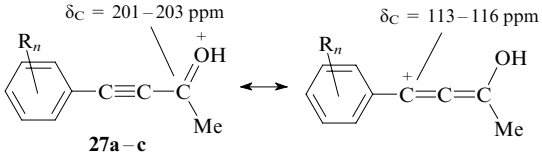
According to the ^{1}H and ^{13}C NMR spectroscopy data, in HSO_3F at −80 °C, 3-arylpropynoic acids **23a**–**e** and their alkyl esters **24a**–**i** form stable cations **25** O-protonated at the ketone group where allenyl resonance structures **26** contribute to the charge distribution (Scheme 10).[37]

Scheme 10



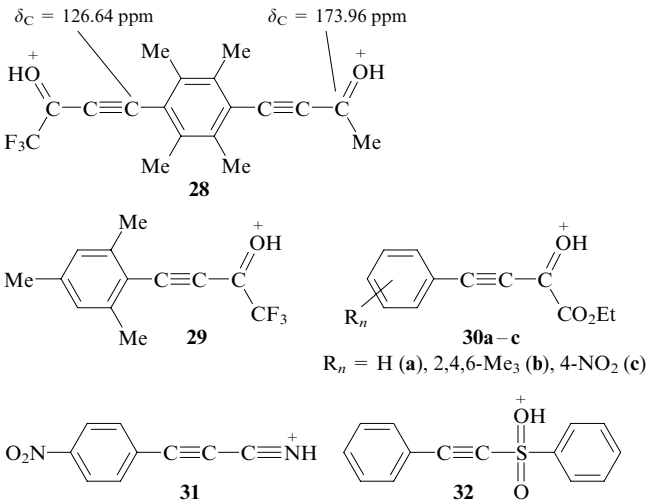
23: R^2 = H: R^1 = 3-NO_2 (**a**), 4-NO_2 (**b**), 4-CN (**c**), 4-F (**d**), 4-OMe-3-NO_2 (**e**); **24**: R^2 = Me, R^1 = H (**a**); R^2 = Et: R^1 = 3-NO_2 (**b**), 4-NO_2 (**c**), 4-CN (**d**), 4-Ac (**e**), 4-CO_2Me (**f**), 3,4-$(NO_2)_2$ (**g**), 2,5-Me_2-4-NO_2 (**h**), 4-OMe-3-NO_2 (**i**)

Similarly, the protonated forms of 4-arylbutynones (structures **27a**–**c**),[38,39]



R_n = H (**a**), 4-Me (**b**), 2,4,6-Me_3 (**c**)

trifluoromethylcarbonyl-substituted arylacetylenes (**28**, **29**), keto-ester derivatives (**30a**–**c**), cyanoacetylenes (**31**) and acetylenic sulfone (**32**)[38] were obtained and characterized by ^{1}H and ^{13}C NMR spectroscopy. Cations **26**, **28**–**32** are stable: they are non-reactive under 'long life' conditions in HSO_3F at −80 °C.

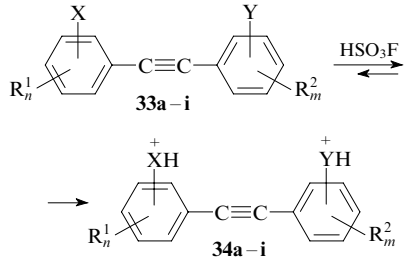


On the basis of ^{1}H and ^{13}C NMR spectroscopy data on the protonation in HSO_3F of various electron-withdrawing groups (X) present in acetylene derivatives ArC≡CX, it is possible to perform an approximate qualitative estimate of the basic properties of groups X and propose the following order of their basicity in HSO_3F: Bz > Ac > CO_2Et > CO_2H > C(O)CO_2Et ≈ C(O)CF_3 ≈ C≡N ≈ SO_2Ph.

More basic groups Bz and CO_2Et clearly show the signal of the attached (strongly bonded) proton in the ^{1}H NMR spectra of the protonated forms $ArC{\equiv}CX^+H$ (**A**). For easily protonated acceptors X containing a carbonyl group, the ^{13}C NMR chemical shifts of the carbonyl carbon atoms of the protonated and parent neutral forms are significantly different. Moreover, proton addition to the group X induces a considerable positive charge on the C(2) atom of the triple bond in the $ArC{\equiv}CX^+H$ ions, determining also the difference between the ^{13}C NMR signals of this atom in protonated and neutral forms.[35–39]

The protonation of diarylacetylenes **33a–i** bearing electron-withdrawing groups X,Y in each of the aromatic rings has been investigated using ^{1}H and ^{13}C NMR spectroscopy.[40] Such substrates are protonated in HSO_3F at −80 °C at the acceptor groups yielding ions **34a–i** (Scheme 11).

Scheme 11



Compounds **33**, **34**	R^1_n	R^2_m	X	Y
a	H	H	4-NO_2	4-NO_2
b	H	H	3-NO_2	3-NO_2
c	H	H	4-Ac	4-Ac
d	H	H	4-CN	4-CN
e	H	H	4-CO_2Me	4-CO_2Me
f	2,5-Me_2	2,5-Me_2	4-NO_2	4-NO_2
g	2,4,6-Me_3	2,4,6-Me_3	3-NO_2	3-NO_2
h	2,3,5,6-Me_4	2,3,5,6-Me_4	4-NO_2	4-NO_2
i	4,5-OCH_2O	H	2-Ac	4-NO_2

Thus, ^{1}H and ^{13}C NMR studies[35–40] have demonstrated that ions $ArC{\equiv}CX^+H$ protonated in the superacid HSO_3F at the electron-withdrawing group X or ions **34a–i** protonated at substituents in the aromatic rings of diarylacetylenes are stable and non-reactive species. They do not react with the superacid molecules to give vinyl fluorosulfonates or vinyl triflates (see Section IV). Such protonated forms do not react with external π-nucleophiles, aromatic compounds, added to the reaction medium (see Section V).

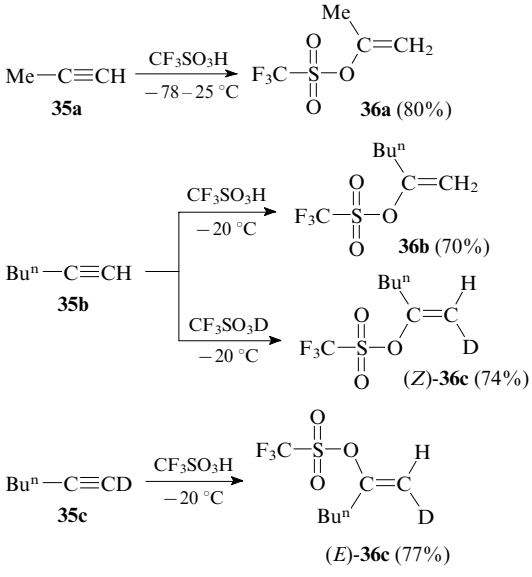
An increase in the temperature of the superacidic medium or an increase in the acidity by using the systems $HSO_3F–SbF_5$, $CF_3SO_3H–SbF_5$, $HF–SbF_5$, as well as the presence of electron-donating substituents in alkynes results in the protonation of the C≡C bond and generation of vinyl type cations, the latter being extremely unstable and highly reactive intermediates.

IV. Addition of superacids to alkynes. Nitration of arylacetylene derivatives in superacids

One transformation roule of vinyl type cations generated in the superacids HSO_3F or CF_3SO_3H is the formation of vinyl fluorosulfonates or vinyl triflates. These vinyl derivatives are valuable synthons for various transformations: metal-catalyzed cross-coupling reactions, reactions with organometallic compounds, nucleophilic substitution at a multiple bond, *etc.*[41,42]

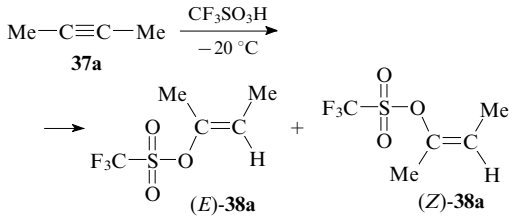
Stang and Summerville[43–45] were the first to add CF_3SO_3H to alkynes. In the case of terminal alkylacetylenes **35a**,**b**, vinyl triflates were obtained in high yields (Scheme 12).[44,45] Using the reaction of hex-1-yne (**35b**) with deuterated trifluorosulfonic acid or the reaction of 1-deuterohex-1-yne (**35c**) with CF_3SO_3H, it was shown that both fragments (hydrogen or deuterium and triflate moiety) of the reagent add from the same side of the terminal bond C≡CH (*syn*-addition) affording *Z*- or *E*-isomer of the compound **36**, respectively.[45]

Scheme 12



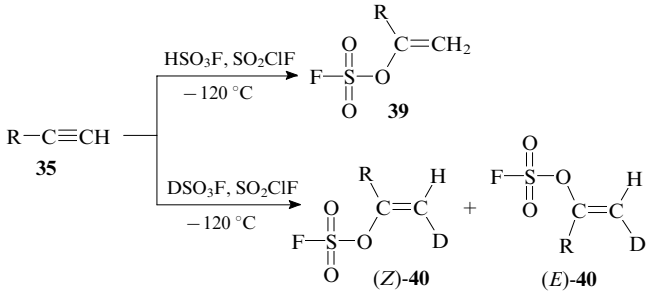
The same reaction with but-2-yne (**37a**) resulted in the isomeric *syn*- [(*E*)-**38a**] and *anti*-addition [(*Z*)-**38a**] products, the latter being predominant (ratio 35 : 65, the total yield 68%, Scheme 13).

Scheme 13

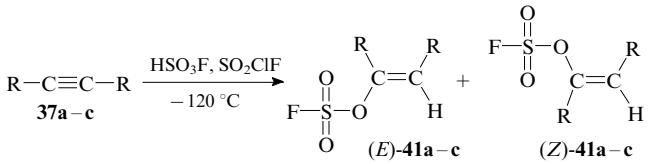


Olah and Spear[46] have studied a similar interaction of HSO_3F with alkynes by NMR spectroscopy. In relation to a series of acetylenes having a terminal (**35**) or internal (**37a–c**) triple bond, the reaction was shown to give vinyl fluorosulfonates **39–41** in all cases (Scheme 14). The reaction of the deuterated acid (DSO_3F) with alkynes **35** attests to the predominant *syn*-addition of the superacid to the terminal C≡CH bonds (*Z* : *E* isomer ratio is ~4 : 1). To the contrary, for internal alkynes **37a–c**, *anti*-addition predominates: the amount of the major products (*Z*)-**41a–c** may be 7 times higher than the amount of *E*-isomers.

Scheme 14



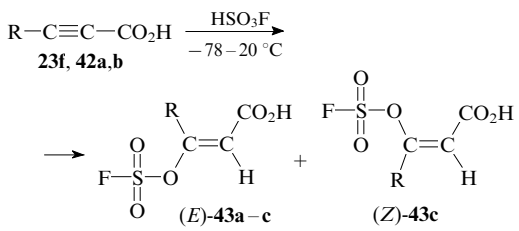
R = H, Alk, OAlk, CF_3, CH=CH_2



R = Me (**a**), Et (**b**), CH_2Cl (**c**)

The addition of HSO_3F to acetylenecarboxylic acids has been investigated. For phenylpropiolic (**23f**) and propargylic (**42a**) acids, *syn*-adducts (*E*)-**43a,b** are formed exclusively, while the use of the tetrolic acid (**42b**) results in a mixture of *syn*-[(*E*)-**43c**] and *anti*-addition [(*Z*)-**43c**] products in a ratio of 5.5 : 1 (Scheme 15).[46]

Scheme 15

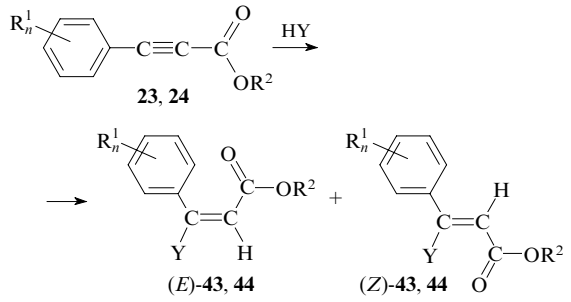


R = Ph (**23f**, **43a**), H (**42a**, **43b**), Me (**42b**, **43c**)

Note that the formation of compounds **39**, **40**, **41a–c** and **43a–c** was detected only by means of the ^1H and ^{19}F NMR spectroscopy without preparative isolation the individual compounds.[46]

These reactions can be easily monitored *in situ* directly in NMR tubes. Table 2 gives examples of preparation of vinyl fluorosulfonates **43** and vinyl triflates **44** from arylacetylene carboxylic acids **23** and esters **24** detected by ^1H NMR spectroscopy (Scheme 16).[37, 47]

Scheme 16



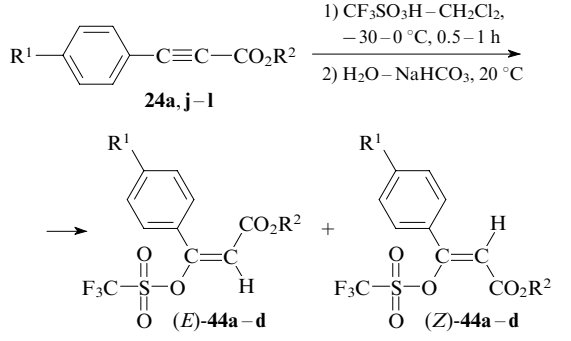
R^2 = H (**23**), Alk (**24**); Y = OSO_2F (**43**), OSO_2CF_3 (**44**)

The geometric isomer ratio was determined from the vinyl proton signals in the ^1H NMR spectra: the signal of this proton occurs in a higher field for *E*-isomers (see Table 2). For the most part, arylacetylenecarboxylic acids **23** (see Table 2, runs 1–7) and their esters **24** (runs 8–16) yield mixtures of the corresponding *E*- and *Z*-isomeric products with the significant predominance of the *E*-form resulting from *syn*-addition of the superacid molecules to the triple bond.

As it is evident from Table 2, *E*- and *Z*-isomer ratio is temperature dependent: a rise in temperature from −40 to 0 °C initiates the isomerization of the *E*-form (an increase in the proportion of *Z*-isomers in runs 1 and 2, 4 and 5, 10 and 11 in Table 2). In the case of fluorosulfonates obtained in HSO_3F at 0 °C (runs 7 and 16,), the exclusive or predominant formation of *Z*-isomers is accounted for by the presence of the electron-donating methoxy group in the aromatic moiety in *para*-position of the benzene ring, facilitating the isomerization.

In the preparation of vinyl triflates **44a–d** from esters **24a,j–l**, the triflate moiety proved to be stable under the conditions of hydrolytic treatement with aqueous sodium bicarbonate (Scheme 17).[37, 47]

Scheme 17



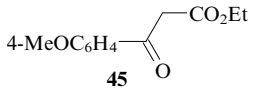
Compounds	R^1	R^2	Yield of **44** (%)	*E* : *Z*
24a, **44a**	H	Me	90	95 : 5
24j, **44b**	H	Et	94	96 : 4
24k, **44c**	Me	Me	91	96 : 4
24l, **44d**	F	Et	90	91 : 9

Table 2. Study of *in situ* formation of vinyl fluorosulfonates **43** and vinyl triflates **44** by Scheme 16 in NMR tubes.[37,47]

Run	Parent alkyne		Conditions of spectra recording	Reaction products		δ/ppm	
	R^1	R^2		Y	$E:Z$	E	Z
1	H	H	HSO_3F, −40 °C, 0.5 h	OSO_2F	90 : 10	6.65	6.72
2	H	H	HSO_3F, 0 °C, 1 h	OSO_2F	76 : 24	6.62	6.71
3	H	H	CF_3SO_3H, −30 °C, 0.5 h	OSO_2CF_3	93 : 7	6.61	6.70
4	4-F	H	HSO_3F, −40 °C, 0.5 h	OSO_2F	87 : 13	6.58	6.65
5	4-F	H	HSO_3F, 0 °C, 1 h	OSO_2F	65 : 35	6.57	6.61
6	4-F	H	CF_3SO_3H, −30 °C, 0.5 h	OSO_2CF_3	85 : 15	6.52	6.60
7	3-NO_2, 4-OMe	H	HSO_3F, 0 °C, 1 h	OSO_2F	0 : 100	–	6.85
8	H	Me	HSO_3F, 0 °C, 0.5 h	OSO_2F	78 : 22	6.64	6.71
9	H	Me	CF_3SO_3H, 0 °C, 0.5 h	OSO_2CF_3	95 : 5	6.62	6.73
10	4-Me	Me	CF_3SO_3H, −30 °C, 0.5 h	OSO_2CF_3	85 : 15	6.49	6.68
11	4-Me	Me	CF_3SO_3H, 0 °C, 1 h	OSO_2CF_3	77 : 23	6.50	6.67
12	4-F	Me	HSO_3F, −30 °C, 1 h	OSO_2F	89 : 11	6.60	6.70
13	4-F	Et	HSO_3F, −30 °C, 0.5 h	OSO_2F	85 : 15	6.60	6.70
14	4-F	Et	CF_3SO_3H, −30 °C, 0.5 h	OSO_2CF_3	75 : 25	6.58	6.70
15	4-F	Et	CF_3SO_3H, 0 °C, 0.5 h	OSO_2CF_3	75 : 25	6.59	6.69
16	3-NO_2, 4-OMe	Et	HSO_3F, 0 °C, 0.5 h	OSO_2F	20 : 80	6.78	6.87

Mixtures of triflates **44a**,**c** comprising initially 85% – 96% of the *syn*-addition product were found to be converted to mixtures with up to 91% of *Z*-isomers (products of *anti*-addition) when kept without a solvent (25 °C, 90 days) or in CF_3SO_3H (−20 °C, 7 days).[37,47]

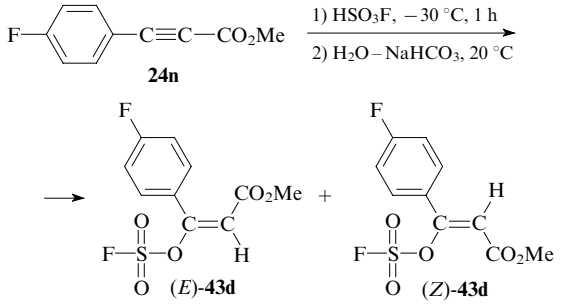
Note that under these conditions, ester **24m** (R^1 = 4-OMe, R^2 = Et) gives ketone **45** — the product of partial hydrolysis of the triflate group (by the Kucherov reaction) in 42% yield — along with triflates **44e** (R^1 = 4-OMe, R^2 = Et)[47] The yield of triflates is 39%, and the isomer ratio is $E:Z$ = 93 : 7.



45

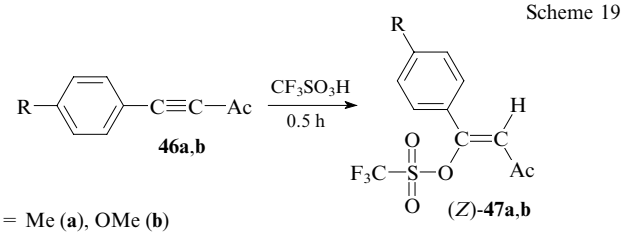
Stability against hydrolysis under basic conditions was also found for the fluorosulfonate group of compound **24n** (R^1 = 4-F, R^2 = Me): after treatment with aqueous sodium bicarbonate, vinyl fluorosulfonate **43d** was isolated from the reaction mixture in 70% yield in *E*- to *Z*-form ratio of 86 : 14 (Scheme 18).[48]

Scheme 18



An NMR study of the reaction of 4-arylbut-3-yn-2-ones **46a**,**b** showed that they react with trifluorosulfonic acid by *anti*-addition mechanism only, contrary to arylacetylenecarboxylic acids and their esters.[37,47] These reactions were found to give triflates **47a**,**b** having *Z*-configuration of the substituent at the C=C double bond, as confirmed by the signals of vinyl protons in the ^{1}H NMR spectra (δ = 7.28 and 7.19 ppm, respectively) (Scheme 19). The reaction temperature for the methyl derivative **46a** is 0 °C, while for the methoxy derivative **46b** it should be lowered down to −30 °C.

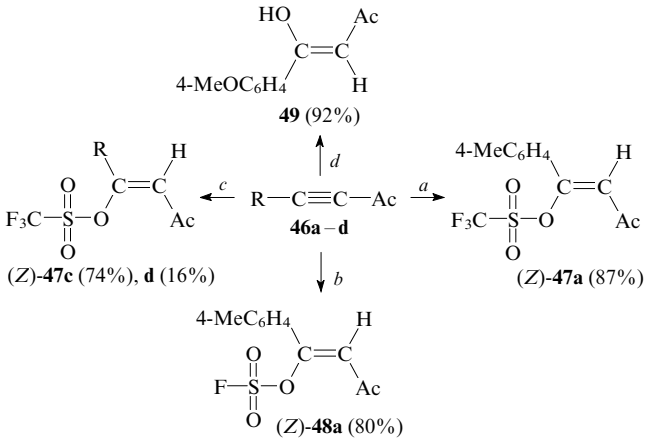
Scheme 19



R = Me (**a**), OMe (**b**)

In preparative reactions, acetylene ketones **46a** – **d** also stereoselectively form triflates **47a**,**c**,**d** and fluorosulfonate **48a** (see Ref. 39) having only *Z*-configuration (Scheme 20).[47]

Scheme 20

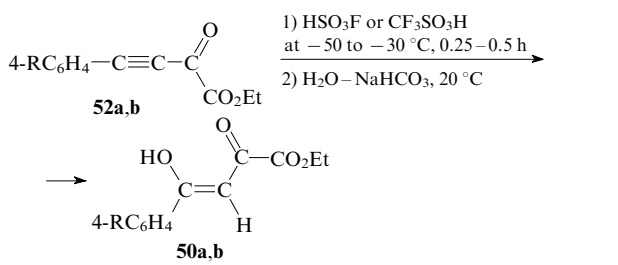


R = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), Ph (**c**), Et (**d**);
(*a*) 1) CF_3SO_3H – CH_2Cl_2, 25 °C, 15 min; 2) H_2O – $NaHCO_3$, 20 °C;
(*b*) 1) HSO_3F, −30 °C, 1 h; 2) H_2O – $NaHCO_3$, 20 °C;
(*c*) 1) CF_3SO_3H – SbF_5, 0 – 25 °C, 0.5 h; 2) H_2O – $NaHCO_3$, 20 °C;
(*d*) 1) HSO_3F, −30 °C, 1 h; 2) H_2O – $NaHCO_3$, 20 °C

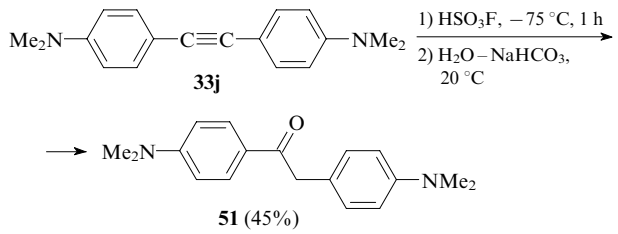
Thus, the addition of HSO_3F or CF_3SO_3H to the acetylene derivatives results in kinetically more rapid formation of *E*-isomers of vinyl fluorosulfonates or vinyl triflates (products of *syn*-addition), which are then converted to thermodynamically more stable *Z*-adducts (*anti*-addition). In the case of fluorosulfonates and triflates obtained from acetylene ketones, such isomerization is seemed to proceed very rapidly.

In reaction with CF_3SO_3H, 4-methoxyphenylbutynone **46b** gives after workup the product of vinyl triflate hydrolysis — enol form **49** (see Scheme 20).[47] The similar products of triple bond hydration **50a**,**b** and **51** were isolated from the reactions of ketoesters **52a**,**b** [38, 39] and diarylacetylene **33j**[40] with HSO_3F or CF_3SO_3H (Scheme 21).

Scheme 21

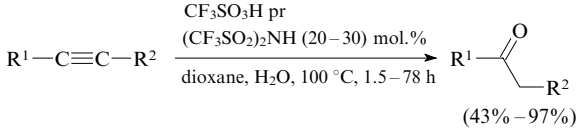


R = Me (**a**, 85%), OMe (**b**, 20%)

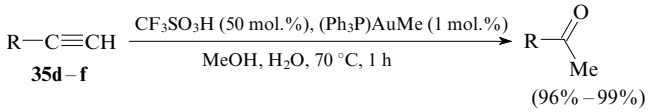


In hydration reactions of alkynes to ketones, trifluoromethansulfonic acid or trifluoromethanesulfone imide may be used as a catalytic additive.[49, 50] Examples of such transformations are shown in Scheme 22.

Scheme 22



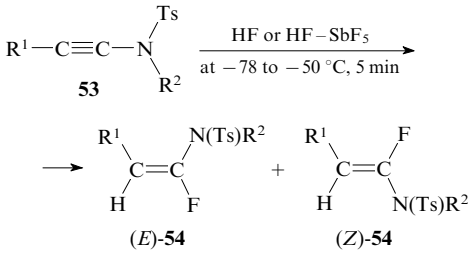
R^1 = Ph, Ar, Alk, Alkenyl; R^2 = H, Alk, Ph, Bz, $C(O)Bu^n$



R = n-C_6H_{13} (**d**), Ph (**e**), 4-MeC_6H_4 (**f**)

It was demonstrated[51] that the addition of HF to aminoalkynes **53** to a triple bond gives predominantly *syn*-addition products, *E*-vinyl fluorides **54**. The overall yields of isomers **54** range from 42% to 97%, and the ratio of *E*- and *Z*-forms is from 93 : 7 to 99 : 1 (Scheme 23).

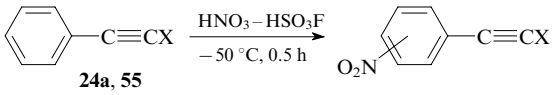
Scheme 23



R^1 = Ar, 2-Naph, Alk, Alkenyl; R^2 = Bn, All, Pr^n, cyclo-C_3H_5

Arylacetylene derivatives can participate in reactions in superacids not affecting the C≡C bond. Thus, methyl 3-phenylpropynoate (**24a**) in HSO_3F at −50 °C is not protonated at the triple bond (see Table 2, run 8, preparation of vinyl fluorophosfonate at 0 °C), and in the system HNO_3–HSO_3F it is nitrated into the phenyl ring affording the corresponding isomeric nitro compounds in 33% yield (the isomer ratio *ortho*:*meta*:*para* = ~1 : 3 : 2).[48] In a similar reaction with 3-phenylpropynonitrile (**55**), the proportion of *p*-nitrophenyl derivative increases, the total yield of the nitration products is 30%, and the isomer ratio *ortho* : *meta* : *para* = ~1 : 3 : 6 (Scheme 24).[48]

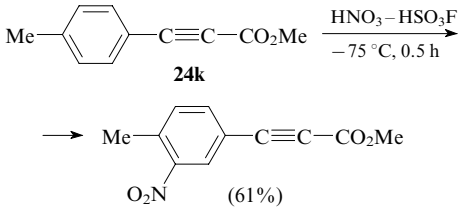
Scheme 24



X = CO_2Me (**24a**), CN (**55**)

Methyl 4-methylphenylpropynoate (**24k**) is nitrated with the system HNO_3–HSO_3F at −75 °C (Scheme 25),[48] while at a higher temperature (−30 °C) in CF_3SO_3H, protonation of the triple bond yielding vinyl triflate occurs (see Table 2, run 10 and Scheme 17).

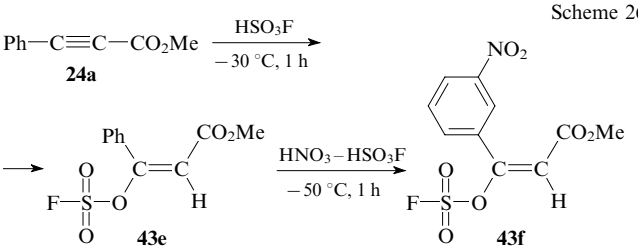
Scheme 25



Therefore, on nitrating the compounds **24a**,**k** and **55**, nitronium cation attacks only the aromatic ring rather than the triple C≡C bond.

Since arylalkyne protonation is temperature-dependent, for the substrate **24a** it is possible to perform first the addition of HSO_3F at −30 °C affording fluorosulfonate **43e**. The latter is nitrated at −50 °C withous isolation from the reaction mixture giving *m*-nitrophenyl derivative **43f**

Scheme 26



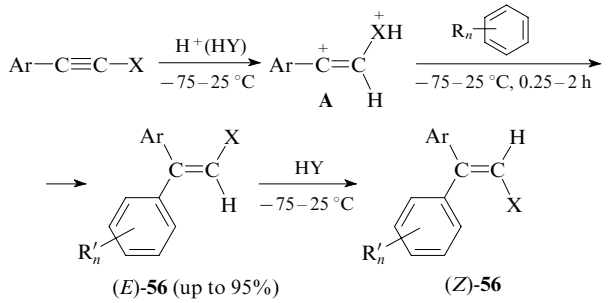
(Scheme 26) (*cf.* Scheme 24 where a mixture of the nitration products is formed).[48]

V. Intermolecular hydroarylation of alkynes in superacids

Vinyl type cations **A** generated upon the protonation of the acetylene derivatives Ar–C≡C–X in superacids (see Scheme 8) react with arene molecules introduced into the reaction medium by the aromatic electrophilic substitution mechanism, furnishing the products of arene alkenylation (Scheme 27).[39, 52–57] The reaction may be considered as hydroarylation of the parent alkynes at the triple bond. A proton and aryl group may add to the C≡C bond from the same or from different sides yielding the products of *syn*- and *anti*-addition, respectively, *E*- and *Z*-isomers **56**.

Tables 3–7 summarize the reaction conditions and product yields for C≡C bond hydroarylation in various acetylenic compounds.

Scheme 27



(*E*)-**56** (up to 95%) (*Z*)-**56**

X = CO_2H, CO_2Alk, CN, Ac, Bz, $C(O)CO_2Et$, $C(O)CF_3$, $P(O)(OEt)_2$; HY = HSO_3F, CF_3SO_3H, $HF–SbF_5$, $HSO_3F–SbF_5$, $CF_3SO_3H–SbF_5$, $HBr–AlBr_3$

The substrates ArC≡CX bearing electron-withdrawing goups X = CO_2Alk (compounds **24**, see Tables 3–5),[52–56] Ac (**44**, see Table 6),[39, 55–57] CO_2H (**23**),[54] CN (**55**),[54] $C(O)CO_2Et$ (**52**),[39] $PO(OEt)_2$ (**57**, see Tables 7),[39, 54] having different substituents in the aromatic ring take part in this reaction. By varying the substituents in the parent compounds, one can change the triple bond basicity and the reactivity of the corresponding cations **A**.

Hydroarylation may be performed in various superacidic systems (HSO_3F, CF_3SO_3H, $HF–SbF_5$, $HSO_3F–SbF_5$, $CF_3SO_3H–SbF_5$, $HBr–AlBr_3$) in the temperature range from −75 to 25 °C during 0.25–2 h. The total yields of the reaction products reach 70%–98%.

Various aromatic compounds: benzene, alkylbenzenes (from mono- to tetrasubstituted ones), hydroxy, mono- and dimethoxybenzenes, halogenated arenes, arylammonium ions, *N*-arylacetamides and arenes bearing electron-withdrawing groups (such as 1-acetyl-2,3,5,6-tetramethylbenzene, 2,3,5,6-tetramethyl-1-fluorosulfonylbenzene, 2,3,5,6-tetramethyl-1-cyanobenzene, *etc.*) along with variuos alkyl substituents can be alkenylated with vinyl type cations **A**. In these reactions, the alkenylation route corresponds to the orientation rules of the aromatic electrophilic substitution, the positions of substituents in the products is shown in Tables 3–7.

Studying the scope of application of this reaction has shown that cations **A** do not interact with the aromatic compounds bearing strong electron-withdrawing substituents. Thus, 1,3,5-trimethyl-2-nitrobenzene (see Table 4,

Table 3. Yields of *E*- and *Z*-isomers **56** (Ar = Ph, X = CO_2Me) resulting from hydroarylation of methyl 3-phenylpropynoate (**24a**) in HSO_3F at −30 °C for 0.5 h (see Scheme 27).[54–56]

Run	R_n	R'_n	Yield (%)	
			E	*Z*
1	H	H	82	–
2	Bu^t	4-Bu^t	–	80
3	1,2-Me_2	3,4-Me_2	17	17
		2,3-Me_2	–	41
4	1,3-Me_2	2,4-Me_2	–	76
5	1,4-Me_2	2,5-Me_2	–	95
6	1,2,4-Me_3	2,3,5-Me_3	–	22
		2,4,5-Me_3	–	22
7	1-OMe-4-F	2-OMe-5-F	13	15
8	1-NH_2-4-Me	2-Me-5-NH_2	12	2
9	1-NH_2-2,4-Me_2	2,4-Me_2-5-NH_2	14	–
10	1-NH_2-2,4,6-Me_3	2,4,6-Me_3-3-NH_2	20	–
11	1-NH_2-2,6-Me_2-4-Bu^t	2,4-Me_2-3-NH_2-6-Bu^t	16	–
12	1-NH_2-2,4,5-Me_3	2,5,6-Me_3-3-NH_2	30	–
		2-NH_2-3,5,6-Me_3	18	–
13	1-NH_2-2,3,5,6-Me_4	2,3,5,6-Me_4-4-NH_2	15	–
14	NHAc	4-NHAc	4	–

Table 4. Yields of *E*- and *Z*-isomers **56** (Ar = 4-MeC_6H_4, X = CO_2Me) resulting from hydroarylation of methyl 3-(4-methylphenyl)propynoate (**24k**) in HSO_3F at −75 °C for 0.25–1 h (see Scheme 27).[53–56]

Run	R_n	R'_n	Yield (%)	
			E	*Z*
1	1-CH_2CN-2,3,5,6-Me_4	2,3,5,6-Me_4-4-CH_2CN	75	–
2	1-CN-2,3,5,6-Me_4	2,3,5,6-Me_4-4-CN	26	–
3	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	33	–
4	1-SO_2F-2,3,5,6-Me_4	2,3,5,6-Me_4-4-SO_2F	38	–
5	1-NO_2-2,4,6-Me_3	2,4,6-Me_3-3-NO_2	9	–
6	1-OMe-2-F	3-F-4-OMe	35	17
7	1-OEt-4-Br	2-OEt-5-Br	45	–
8	1,2-$(OMe)_2$	3,4-$(OMe)_2$	17	–
9	1-OMe-4-F	2-OMe-5-F	18	10
10	1-NH_2-2-Me	3-NH_2-4-Me	17	–
11	1-NH_2-2,4-Me_2	2,4-Me_2-5-NH_2	24	13
12	1-NH_2-3,4-Me_2	2-NH_2-4,5-Me_2	34	–
		2,3-Me_2-5-NH_2	7	–
13	1-NH_2-2,4,6-Me_3	2,4,6-Me_3-3-NH_2	38	–
14	1-NH_2-2,6-Me_2-4-Bu^t	2,4-Me_2-3-NH_2-6-Bu^t	34	–
15	1-NH_2-2,4,5-Me_3	2,5,6-Me_3-3-NH_2	11	–
		2-NH_2-3,5,6-Me_3	19	–
16	1-NH_2-2,3,5,6-Me_4	2,3,5,6-Me_4-4-NH_2	25	–
17	1-NH_2-2-OMe	3-NH_2-4-OMe	45	–
		2-OMe-3-NH_2	17	–
18	NHAc	4-NHAc	18	–
19	1-NHAc-4-Me	2-Me-5-NHAc	29	–
20	1-NHAc-2,4-Me_2	2,4-Me_2-5-NHAc	13	13
21	1-NHAc-2,4,6-Me_3	2,4,6-Me_3-3-NHAc	51	–
22	1-NH_2-2,6-Me_2-4-Bu^t	2,4-Me_2-3-NH_2-6-Bu^t	67	–
23	1-NHAc-2,4,5-Me_3	2,4,6-Me_3-3-NHAc	20	–
		2-NHAc-3,5,6-Me_3	16	–
24	1-NHAc-2,3,5,6-Me_4	2,3,5,6-Me_4-4-NHAc	32	–

Table 5. Yields of *E*- and *Z*-isomers **56** (X = CO_2Alk) resulting from hydroarylation of alkyl 3-arylpropynoates **24** in HSO_3F at −75 to −20 °C for 1 h (see Scheme 27).[54–56]

Run	Ar	Alk	R_n	R'_n	Yield (%)	
					E	*Z*
1	4-FC_6H_4	Me	1-SO_2F-2,3,5,6-Me_4	2,3,5,6-Me_4-4-SO_2F	68	–
2	4-FC_6H_4	Me	1,2-Cl_2	3,4-Cl_2	19	17
3	4-FC_6H_4	Me	1,4-$(OMe)_2$	2,5-$(OMe)_2$	–	47
4	4-IC_6H_4	Et	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	12	–
5	4-$OMeC_6H_4$	Me	OMe	4-OMe	54	–
6	4-$OMeC_6H_4$	Me	1-NHAc-2,4,5-Me_3	2,4,6-Me_3-3-NHAc	17	–
				2-NHAc-3,5,6-Me_3	–	9
7	4-$OMeC_6H_4$	Me	1-NHAc-2,4,6-Me_3	2,4,6-Me_3-3-NHAc	–	52
8	4-OMe-3-NO_2-C_6H_4	Et	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	29	15

Table 6. Yields of *E*- and *Z*-isomers **56** (X = Ac) resulting from hydroarylation of 4-arylbut-3-yn-2-one **46** in HSO_3F or CF_3SO_3H at −75 to −30 °C for 0.3–2 h (see Scheme 27).[39,55–57]

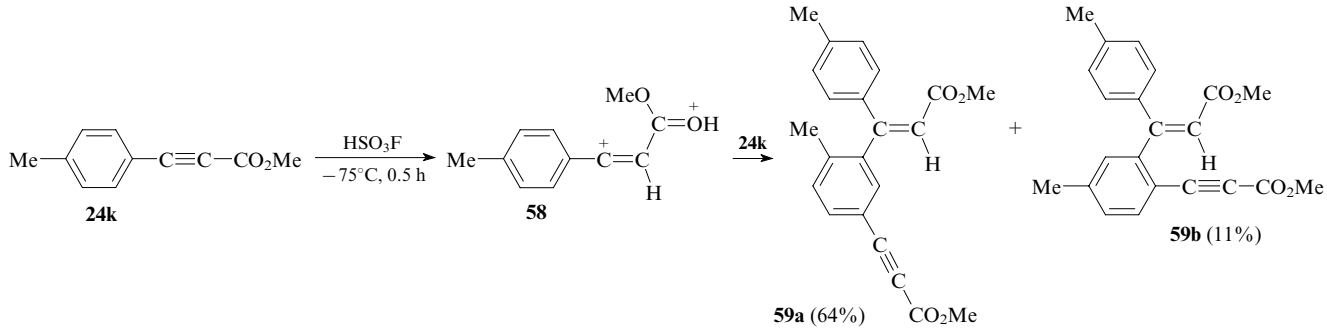
Run	Ar	R_n	R'_n	Yield (%)	
				E	*Z*
1	Ph [a]	H	H	24	–
2	4-MeC_6H_4	H	H	42	42
3	4-MeC_6H_4	OMe	4-OMe	42	42
4	4-MeC_6H_4	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	–	47
5	4-MeC_6H_4	1,2-Cl_2	3,4-Cl_2	30	30
6	4-MeC_6H_4	1-NH_2-4-Me	2-Me-5-NH_2	–	10
7	4-MeC_6H_4	1-NH_2-2,4-Me_2	2,4-Me_2-5-NH_2	–	56
8	4-MeC_6H_4	1-NH_2-2,4,6-Me_3	2,4,6-Me_3-3-NH_2	–	44
9	4-MeC_6H_4	1-NH_2-2,6-Me_2-4-Bu^t	2,4-Me_2-3-NH_2-6-Bu^t	2	15
10	4-MeC_6H_4	1-NH_2-2,4,5-Me_3	2,5,6-Me_3-3-NH_2	–	16
11	4-MeC_6H_4	1-NH_2-2,3,5,6-Me_4	2,3,5,6-Me_4-4-NH_2	–	31
12	4-MeC_6H_4	1-NH_2-2-OMe	3-NH_2-4-OMe	4	20
13	4-MeC_6H_4	NHAc	4-NHAc	3	3
14	4-MeC_6H_4	1-NHAc-4-Me	2-Me-5-NHAc	–	17
15	4-MeC_6H_4	1-NHAc-2,4,6-Me_3	2,4,6-Me_3-3-NHAc	–	29
16	2,4-$Me_2C_6H_3$	1-OMe-4-F	2-MeO-5-F	17	34
17	2,4-$Me_2C_6H_3$	1,2-$(OMe)_2$	3,4-$(OMe)_2$	51	25
18	2,4,6-$Me_3C_6H_2$	OMe	4-OMe	53	–
19	2,3,5,6-Me_4C_6H	MeO	4-OMe	9	–
20	Me_5C_6	H	H	68	–
21	Me_5C_6	OMe	4-OMe	40	–
22	4-$OMeC_6H_4$	H	H	33	65
23	4-$OMeC_6H_4$	OMe	4-OMe	70	–
24	4-$OMeC_6H_4$	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	–	10
25	4-$OMeC_6H_4$	1-SO_2F-2,3,5,6-Me_4	2,3,5,6-Me_4-4-SO_2F	–	45

[a] Reaction proceeds in CF_3SO_3H–SbF_5 at 20 °C for 20 min.

Table 7. Yields of *E*- and *Z*-isomers **56** [X = CO_2H, $C(O)CO_2Et$, CN, $P(O)(OEt)_2$] resulting from hydroarylation of compounds **23**, **52**, **55** and **57** in HSO_3F at −75 to −30 °C for 0.25–1 h (see Scheme 27).[39,54]

Run	Ar	X	R_n	R'_n	Yield (%)	
					E	*Z*
1	Ph	CO_2H	1,2,4,5-Me_4	2,3,5,6-Me_4	19	49
2	Ph	CO_2H	1-Ac-2,3,5,6-Me_4	2,3,5,6-Me_4-4-Ac	27	–
3	Ph	CN	1-SO_2F-2,3,5,6-Me_4	2,3,5,6-Me_4-4-SO_2F	22	–
4	Ph	$P(O)(OEt)_2$	1,2-$(OMe)_2$	3,4-$(OMe)_2$	28	19
5	Ph	$P(O)(OEt)_2$	1-SO_2F-2,3,5,6-Me_4	2,3,5,6-Me_4-4-SO_2F	6	52
6	4-$OMeC_6H_4$	$P(O)(OEt)_2$	OMe	4-OMe	20	–
7	2,4,6-$Me_3C_6H_2$	$P(O)(OEt)_2$	OMe	4-OMe	28	–
8	4-MeC_6H_4	$C(O)CO_2Et$	OMe	4-OMe	18	18
9	2,4,6-$Me_3C_6H_2$	$C(O)CO_2Et$	OMe	4-OMe	19	–
10	4-$OMeC_6H_4$	$C(O)CO_2Et$	OMe	4-OMe	27	–

Scheme 28



run 5) and 1,2-dichlorobenzene (see Table 5, run 2 and Table. 6, run 5) still react with cations **A** under these conditions, while less nucleophilic molecules, methyl 4-methoxybenzoate and 4-methylnitrobenzene, do not react.[39, 54]

The electron-withdrawing NH_3^+ group also deactivates the π-system of phenylammonium ion to electrophilic substitution. N-Protonated forms of aniline and *N*,*N*-dimethylaniline do not react with vinyl type cations in HSO_3F at −30 °C.[55, 56] The presence of a methyl group in the aromatic ring in 2- or 4-positions of methylanilines enables the arylammonium ions to react with vinyl cations (see Table 3, run 8; Table 4, run 10 and Table 6, run 6).[55, 56]

Furthermore, vinyl type cations generated in HSO_3F do not react with pentamethylbenzene existing in HSO_3F as an arenonium ion.[58]

Similarly to the above-described of addition of superacids HSO_3F and CF_3SO_3H to acetylene derivatives (see Section III), hydroarylation also proceeds at −75 °C as *syn*-addition of proton and aryl residue to the C≡C bond. At a higher temperature (−50 °C and higher), *syn*-adducts are converted to the products of *anti*-addition.[39, 54, 55]

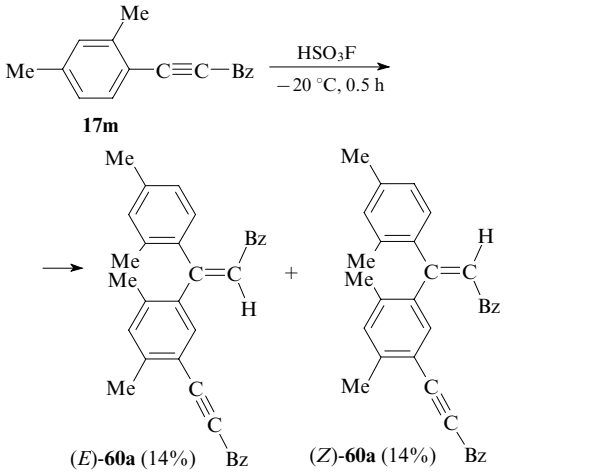
Carrying out the reactions at elevated temperatures in HSO_3F (−30 to −20 °C) or in CF_3SO_3H (−30 to 20 °C) results generally in a mixture of *E*- and *Z*-isomers and only *anti*-adducts are formed selectively.[54] However, the presence of three and more methyl groups (with two of them occupying the *ortho*-positions) in one of the aromatic rings of the hydroarylation products **56** may hamper the isomerization of the initially formed *syn*-adducts to their *anti*-forms even at elevated temperatures (−30 to 20 °C). On the other hand, the presence of methoxy-substituted aromatic rings in compounds **56** facilitates *E*–*Z*-isomerisation.[39, 54, 55]

Similarly to the synthesis of vinyl fluorosulfonates and vinyl triflates (see Section III), hydroarylation of the C≡C bond in acetylene ketones gives predominantly the products of *anti*-addition (see Table 6).[39]

Arylacetylene derivatives ArC≡CX with aromatic ring comprising at least one methyl group are rather reactive π-nucleophiles *per se*. Thus, the dication **58** generated in HSO_3F at −75 °C from ester **24k** attacks the aromatic system of the parent compound in the absence of external π-nucleophiles (*i.e.*, arenes added to the reaction medium). The *syn*-addition results in the formation of regioisomers (*E*)-**59a**,**b** (Scheme 28).[52, 54]

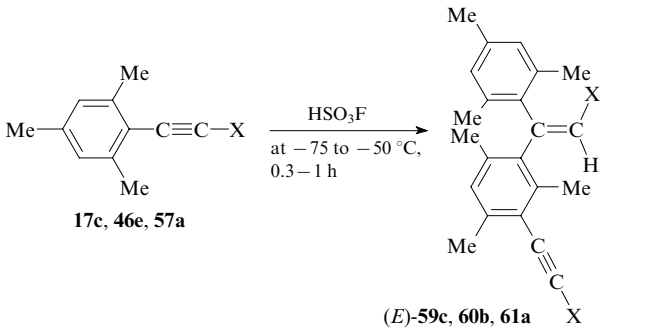
Keeping the solution of disubstituted ketone **17m** in HSO_3F at −20 °C for 0.5 h gives an equimolar mixture of dimers (*E*)- and (*Z*)-**60a** (Scheme 29).[39]

Scheme 29



Despite the steric hindrance, vinyl cations generated in HSO_3F at −75 to −50 °C from trimethyl-substituted derivatives **17c**, **46e** and **57a** attack the aromatic rings of the parent substrates affording dimers **60b**, **59c** and **61a** in 60%, 53% and 10% yields, respectively. The dimers are the products of *syn*-addition of the hydrogen atom and the aryl residue to the C=C bond and have *E*-configuration of the double bond (Scheme 30).[39]

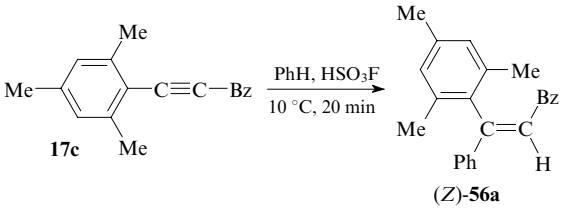
Scheme 30



X = Bz (**17c**, **60b**), Ac (**46e**, **59c**), $P(O)(OEt)_2$ (**57a**, **61a**)

The π-system of a benzene molecule possesses higher nucleophilicity compared to the tetrasubstituted aromatic ring of compound **17c**. Therefore, the latter is alkenylated by benzene by a mechanism of *syn*-addition yielding (*Z*)-**56a**[39] rather than the corresponding dimer (*E*)-**60b** (Scheme 31).

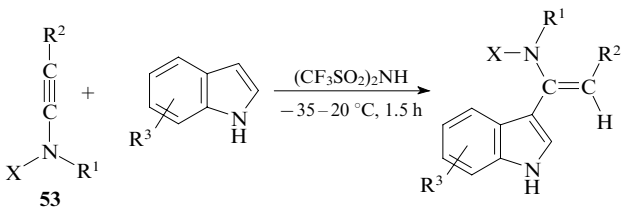
Scheme 31



The vinyl cations generated from arylalkynes **17c**,**m**, **24k**, **46e** and **57a** do not form the corresponding vinylfluorosulfonates in HSO_3F (see Table 2 in Section), indicating more pronounced nucleophilic character of methyl-substituted aromatic rings of these compounds compared to the HSO_3F molecule. Meanwhile, 4-(4-methylphenyl)-but-3-yn-2-one (**46a**) in HSO_3F at -30 °C affords the product of the superacid addition to a triple bond, namely, vinyl fluorosulfonate (*Z*)-**48a** (see Section III) rather than a dimer similar to the structures **60**. The reason is that *p*-tolyl system in ketone **46a** has lower nucleophilicity compared to ester **24k** under the conditions of a specific solvation in HSO_3F.

A general method for the introduction of aminoalkenyl groups in heteroaromatic systems of indole, pyrrole and furan based on reactions of these heterocycles with aminoalkynes **53** under the action of trifluorosulfone imide was presented.[59] In this case, stereoselective *syn*-hydroarylation of the C≡C bond of substrates **53** takes place. 3-Substituted derivatives **62** with *Z*-configuration of the C=C double bond are the only products regioselectively formed from indoles (Scheme 32).

Scheme 32



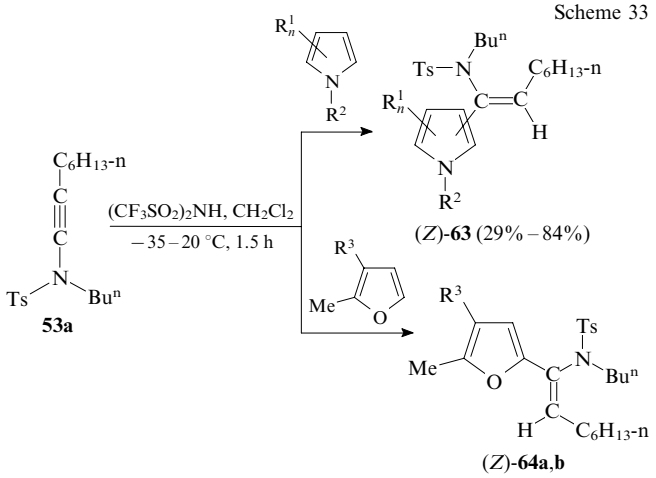
X = Ms, Ts, CO_2Me, N(Alk)C(O)Alk′;
R^1 = Alk; R^2 = Alk, $SiPr^i_3$; R^3 = H, Alk, OMe, Hal;
Ms is methylsulfonyl

Upon reactions with *N*-n-butyl-*N*-oct-1-ynyl-*p*-toluenesulfone amide (**53a**) under similar conditions, pyrroles yield mixtures of isomers **63** bearing an alkenyl group in 2- or 3-position, while 2-methyl- and 2,3-dimethylfurans are alkenylated into the vacant 5-position affording compounds **64a**,**b** in high yields (Scheme 33).

When alkynes are sufficiently basic and are readily protonated in superacids, hydroarylation of the triple bond is not necessarily terminated after the addition of one molecule of the aromatic compound. The alkene formed from alkyne upon monohydroarylation may also undergo protonation at the C=C bond yielding the corresponding alkyl cation, which reacts with arene.

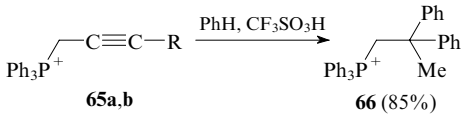
Thus, propargyl derivatives **65a**,**b** yield the product of dihydrophenylation **66** when react with benzene in CF_3SO_3H.[60] In the case of compound **65b**, hydrogen is substituted for the Me_3Si group (Scheme 34).

Scheme 33



R^1_n = H, 2,5-Me_2, 2,4-Me_2, 2,3-$(CH_2)_4$; R^2 = H, Me;
R^3 = H (**a**, 84%), Me (**b**, 79%)

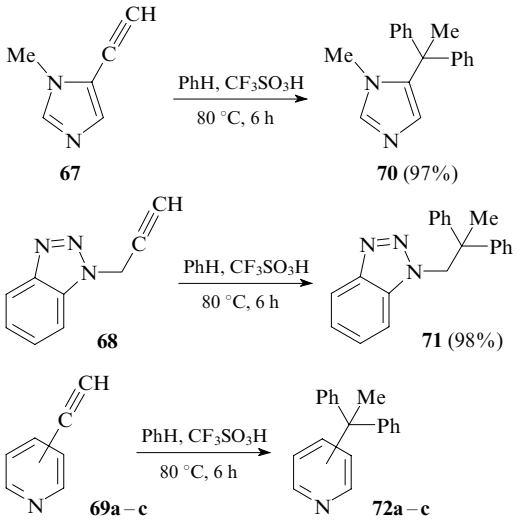
Scheme 34



R = H (**a**), $SiMe_3$ (**b**)

Ethynyl- and propargyl-substituted nitrogen-containing heterocyclic compounds **67**–**69** add two benzene molecules to the C≡C bond in CF_3SO_3H affording products **70**–**72**, respectively (Scheme 35).[61]

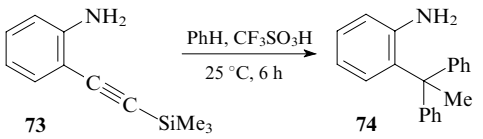
Scheme 35



Isomers: *ortho* (**a**, 5%), *meta* (**b**, 94%), *para* (**c**, 75%)

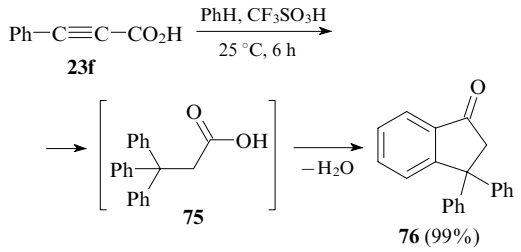
2-(Trimethylsilylethynyl)aniline (**73**) reacts with benzene in trifluoromethanesulfonic acid even at room temperature, the compound **74** being formed in a quantitative yield (Scheme 36).[61]

Scheme 36



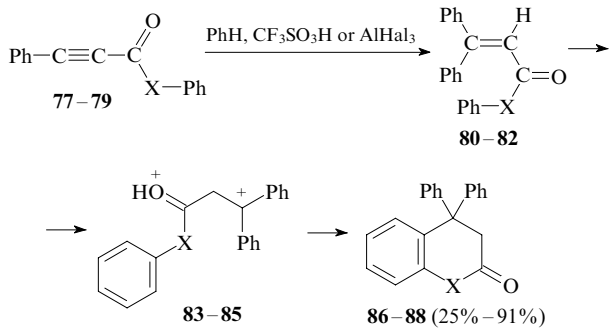
In a similar reaction, 3-phenylpropynoic acid (**23f**) first yields intermediate structure **75**, the intramolecular acylation of which affords 3,3-diphenylindanone (**76**).[62] The same transformation of 3-phenylpropynoic acid takes place in the system benzene–$AlBr_3$ (Scheme 37).[63]

Scheme 37



The reaction of benzene with *N*-phenylamide (**77**), phenyl ester (**78**) and thioester (**79**) of 3-phenylpropynoic acid under the action of CF_3SO_3H or aluminium trihalides results initially in the products of benzene alkenylation, compounds **80**–**82**. Under these conditions, these products form dications **83**–**85**, which undergo subsequently intramolecular cyclization to give 4,4-diphenyl-3,4-dihydro derivatives of dihydroquinolinone (**86**), coumarin (**87**) and thiocoumarin (**88**) (Scheme 38).[64]

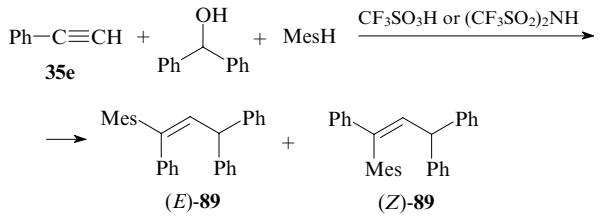
Scheme 38



X = NH (**77**, **80**, **83**, **86**), O (**78**, **81**, **84**, **87**), S (**79**, **82**, **85**, **88**);
Hal = Cl, Br

In a three-component mixture consisting of phenylacetylene (**35e**), diphenylmethanol and mesitylene with a catalyst, trifluoromethanesulfonic acid or its imide, a mixture of *E*- and *Z*-isomers **89** (96 : 4 ratio) is formed in 52% yield. The latter represent products of the mesitylene ring alkenylation (Scheme 39).[65]

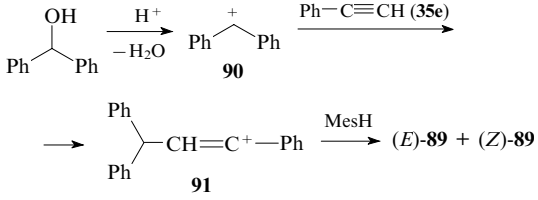
Scheme 39



Mes = 2,4,6-$Me_3C_6H_2$

In this case, cation **90** generated from diphenylmethanol acts as an electrophile. Its attack on the phenylacetylene molecule affords vinyl cation **91**, participating in the alkenylation of mesitylene (Scheme 40).

Scheme 40

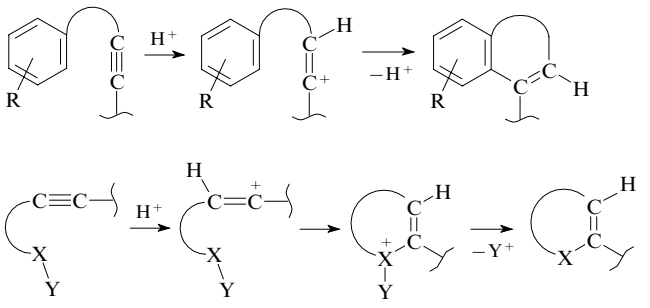


However, the best results in this reaction (higher product yields, greater variability in the reacting substrates) have been reached when using a mixture $(CF_3SO_2)_2O$–$FeCl_3$–$AgNO_3$ as the catalyst.[65]

VI. Intramolecular reactions of vinyl type cations in superacids

Vinyl cations comprising aromatic π-systems and multiple carbon–carbon bonds or heteroaromatic functionalities, generated from acetylene compounds, may attack intramolecularly these nucleophilic centres, yielding neutral or ionic reaction products (Scheme 41).

Scheme 41

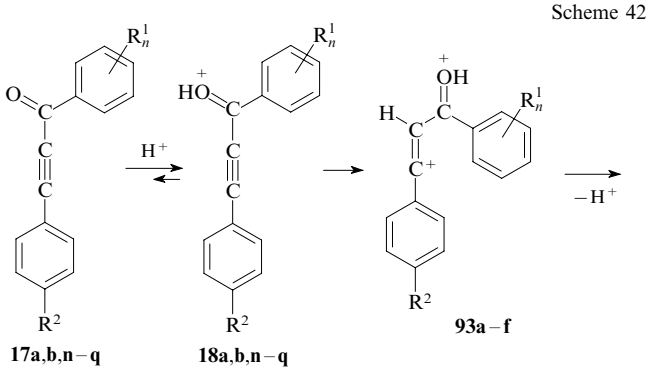


X = S, O

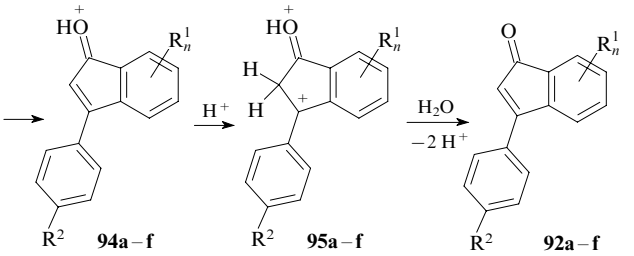
The transformation of 1,3-diarylpropynones **17a**,**b**,**n**–**q** to 3-arylindenones **92a**–**f** in various superacidic media (CF_3SO_3H, HSO_3F, CF_3SO_3H–SbF_5, HF–SbF_5) in a temperature range from −75 to 20 °C during 0.25–2 h has been reported[35,36,66] (Scheme 42). O-Protonated ions **18a**,**b**,**n**–**q** formed initially are stable, non-reactive species (see Section III). The subsequent C-protonation affords superelectrophilic vinyl type dications **93a**–**f**, which cyclize to give cations **94a**–**f**. Under the reaction conditions, the latter are protonated at the C=C bond and exist as stable dications **95a**–**f**, which were characterized by NMR spectroscopy.[35,67] Hydrolytic decomposition of superacidic reaction solutions affords reaction products **92a**–**f**.

3-Arylindenones **92b**,**c** photodimerize surprisingly readily under exposure to daylight at the C=C double bond of the indene moiety affording [2+2]-*syn*–*trans*-adducts **96a**,**b** (Scheme 43).[67,68]

Scheme 42



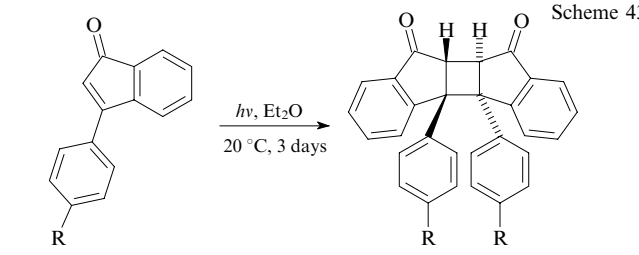
17a,**b**,**n**–**q** **18a**,**b**,**n**–**q** **93a**–**f**



94a–**f** **95a**–**f** **92a**–**f**

Compounds **17**, **18**	Compounds **92**–**95**	R^1_n	R^2
a	**a**	H	H
b	**b**	H	Me
n	**c**	H	OMe
o	**d**	3-OMe	H
p	**e**	3-OMe	OMe
q	**f**	3,4-Me_2	OMe

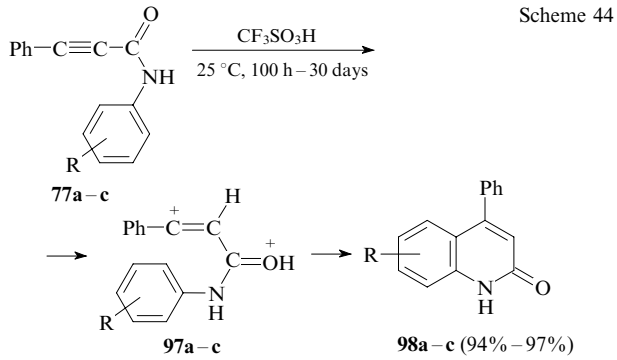
Scheme 43



92b,**c** **96a**,**b**

R = Me (**92b**, **96a**, 67%), OMe (**92c**, **96b**, 72%)

Scheme 44



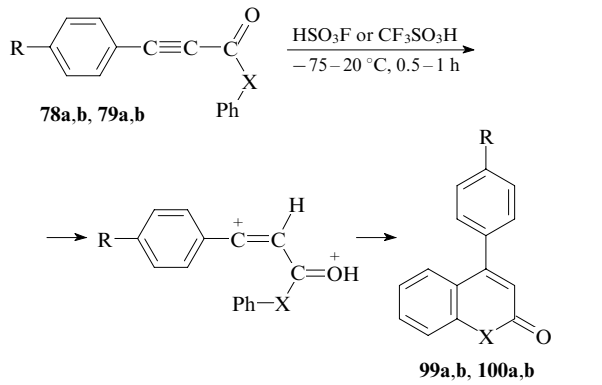
77a–**c** **97a**–**c** **98a**–**c** (94%–97%)

R = H (**a**), 3-Me (**b**), 4-Me (**c**)

3-Phenylpropynoic acid *N*-arylamides **77a**–**c** cyclize in trifluoromethanesulfonic acid through the intermediate formation of cations **97a**–**c** yielding quinolinones **98a**–**c** (Scheme 44, the positions of substituents in the aromatic ring of the parent compound are indicated).[69–71]

Whereas phenyl 3-arylpropynoates **78a**,**b** are converted to coumarins **99a**,**b** in moderate yields (10% and 12%) under these conditions, their sulfur analogues **79a**,**b** afford thiocoumarins **100a**,**b** quantitatively (yields 90% and 86%, respectively) (Scheme 45).[72, 73]

Scheme 45

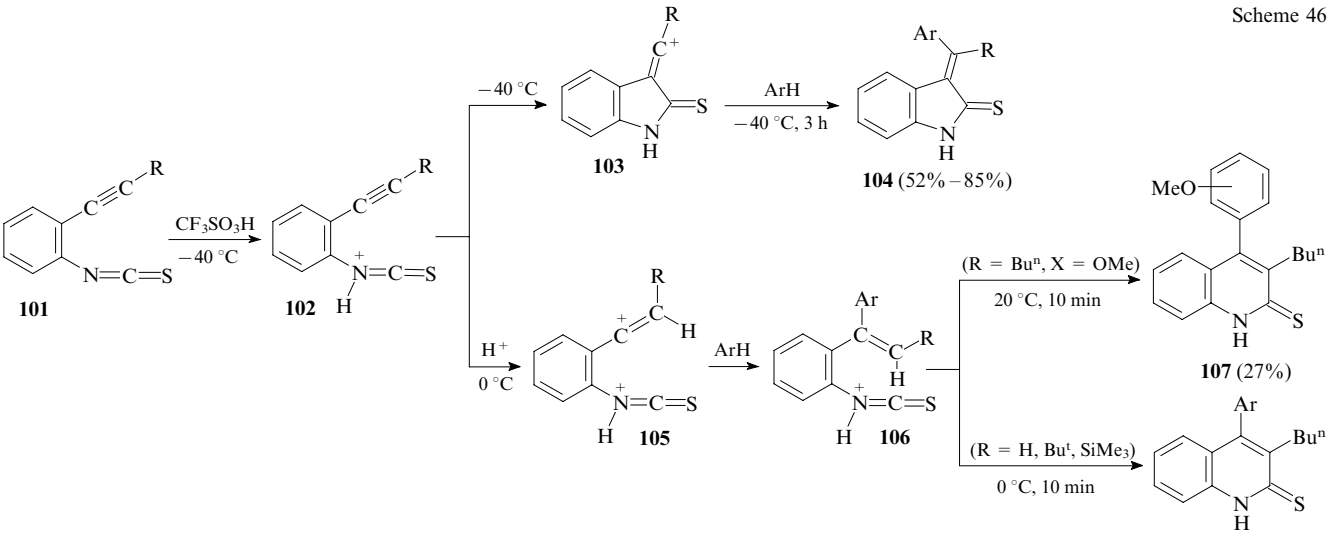


78a,**b**, **79a**,**b** **99a**,**b**, **100a**,**b**

X = O (**78**, **99**), S (**79**, **100**); R = H (**a**), Me (**b**)

It was shown[74] that the C≡C bond participates in intermolecular alkenylation and intramolecular cyclization.

Scheme 46



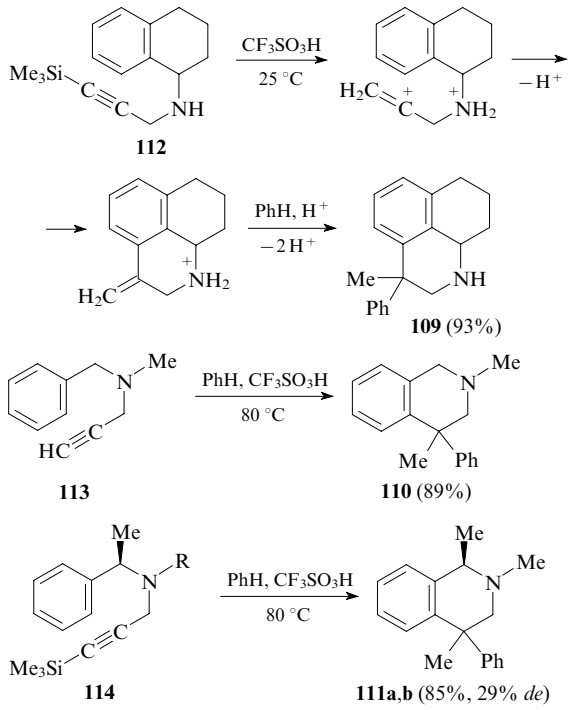
101 **102** **103** **104** (52%–85%) **105** **106** **107** (27%) **108** (55%–99%)

R = H, Me, Bu^n, Bu^t, $SiMe_3$, Bn; Ar = $C_6H_{4-m}X_m$ [X_m = H, Me, Me_2, Me_3, OMe, $(OMe)_2$, Hal]

2-Alkynylphenyl isothiocyanates **101** were considered as examples that react along two different routes depending on the structure and the process temperature (Scheme 46).

Substrates **101** are protonated in CF_3SO_3H at −40 °C at the nitrogen atom of the isothiocyanate moiety affording N-cations **102**, which cyclize to C-cations **103**. The latter react with arenes to give compounds **104** in good yields. At a higher temperature (0 °C), cations **102** are further protonated at a C≡C triple bond. The reaction of dications **105** with arenes gives ions **106**, undergoing intramolecular cyclisization to 4-arylquinoline-2-thiones. Starting from ion **106** (R = Bu^n, X = OMe), compound **107** was obtained as a mixture of *o*- and *p*-isomers in a 37 : 63 ratio. Elimination of R groups at the double bond takes place at the terminal step of the formation of structures **108** (R = H, Bu^t, $SiMe_3$). Tandem reactions involving intramolecular cyclization with vinyl cations followed by hydroarylation of the C=C bond have been decscribed.[61] In this way, compounds **109**–**111** were obtained in the system CF_3SO_3H–benzene using (benzyl)propargylamines **112**–**114** as the starting compounds (Scheme 47).

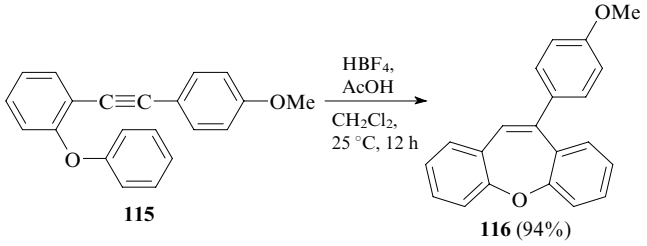
Scheme 47



R = H (**a**), Me (**b**)

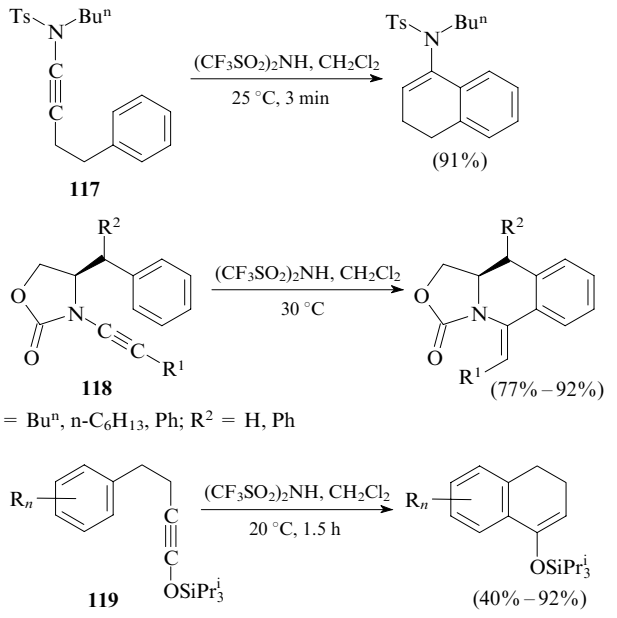
Under the action of tetrafluoroboric and acetic acids, diarylacetylene **115** transforms into dibenzo-[*b*,*f*] oxepine **116** (Scheme 48).[75]

Scheme 48



Cyclization of acetylene derivatives **117**–**119** in the presence of trifluoromethanesulfonimide is a convenient approach to various carbo- and heterocyclic systems, as exemplified in Scheme 49.[76–78]

Scheme 49

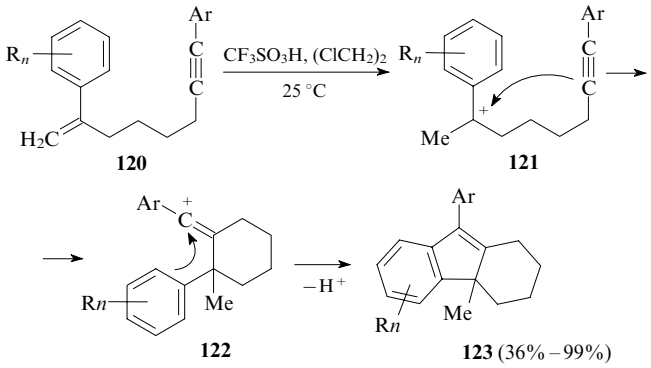


R^1 = Bu^n, n-C_6H_{13}, Ph; R^2 = H, Ph

R_n = 4-Me, 3,5-Me_2, 3-MeO, 4-Br, 3,4-benzo

Cascade cyclization of 1,7-enynes **120** under the action of CF_3SO_3H proceeding through the intermediate formation of cations **121** and **122** yields compounds **123** in 1 h at 25 °C (Scheme 50).[79]

Scheme 50



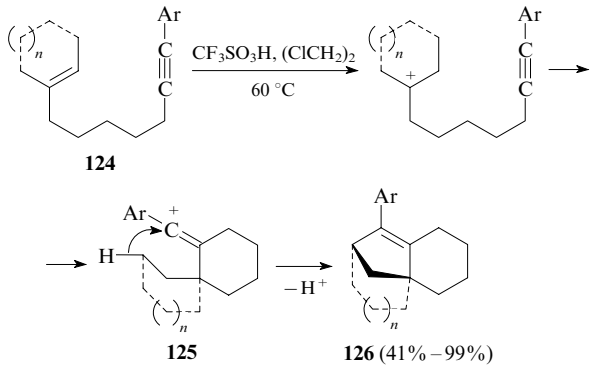
R_n = H, 4-Me, 4-Cl, 3,4-benzo; Ar = Ph, 4-MeC_6H_4, 2-Naph

In a similar reaction involving cyclic and acyclic enynes **124**, cations **125** transform at the terminal step into compounds **126** either through a direct replacement of a proton at a saturated carbon atom or through a number of steps including 1,5-hydride shift (Scheme 51).[80]

Vinyl cations react intramolecularly not only with aromatic π-systems but also with multiple carbon–carbon bonds. The cyclization of 1,5-diynes **127** and 1,5-enynes **128** under the action of trifluoromethanesulfonimide have been investigated.[78, 81]

Protonation of diynes **127** gives rise to cations **129**. In the resonance form **130**, they cyclize at the second C≡C bond affording ions **131**, which detach a halide ion from the

Scheme 51

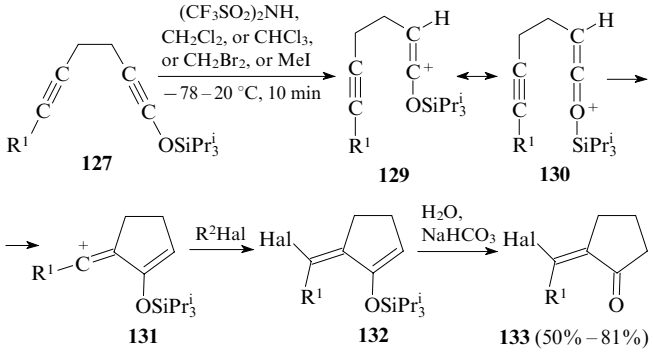


124 **125** **126** (41%–99%)

n = 0–4; Ar = Ph, 4-ClC_6H_4, 4-$CF_3C_6H_4$, 4-$BzOC_6H_4$, 2-Naph

CH_2Cl_2, $CHCl_3$, CH_2Br_2 or CH_3I molecule. Hydrolytic decomposition of the reaction solutions of dienes **132** gives cyclopentanones **133** (Scheme 52).[78, 81]

Scheme 52

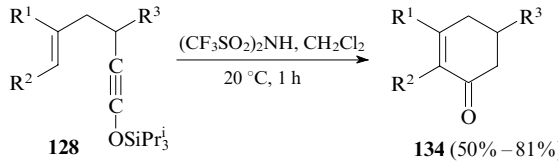


127 **129** **130** **131** **132** **133** (50%–81%)

R^1 = Bu^n, n-C_8H_{17}, $(CH_2)_2OSiPr^i_3$, $(CH_2)_2Ph$, $(CH_2)_3Ph$; Hal = Cl, Br, I

Similarly, cyclohexenones **134** are formed as a result of intramolecular cyclization of enynes **128** (Scheme 53).[78]

Scheme 53

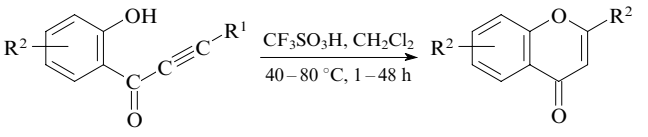


128 **134** (50%–81%)

R^1 = H, Me, Ph; R^2 = H, Me; R^1–R^2 = $(CH_2)_4$; R^3 = H, Bu^n

Oxygen or sulfur atoms may serve as intramolecular nucleophilic centres attacked by the vinyl cations. Thus, *ortho*-hydroxy substituted 1-arylpropynones **135** transform into γ-benzopyranones **136** in the system CF_3SO_3H–CH_2Cl_2.[82] The authors cited [82] suggest that the addition of CF_3SO_3H to a triple bond gives first vinyl triflates, which cyclize subsequently to compounds **136**. An intermediate formation of the corresponding vinyl triflate has been confirmed by NMR spectroscopy using 1-(2-hydroxyphenyl)-3-phenylpropynone as an example (**136**, R^1 = Ph, R^2 = H). However, for more basic and more easily protonated substrates **136** bearing substituents R^1 = 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 3,4,5-$(MeO)_3C_6H_2$, more rapid formation of the vinyl type cation is possible. The latter undergo direct intramolecular interaction of a cationic centre with the OH oxygen atom, thus excluding the vinyl triflate formation step (Scheme 54).

Scheme 54

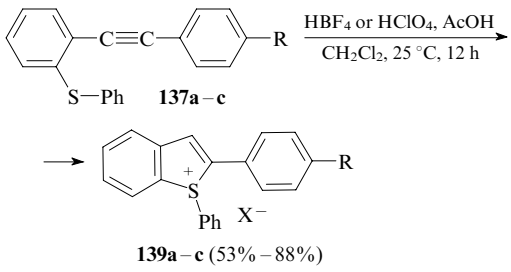


135 **136** (40%–96%)

R^1 = Bu^n, Bu^t, cyclo-C_6H_{11}, Ph, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 3,4,5-$(MeO)_3C_6H_2$; R^2 = H, 4-OMe, 5-OMe, 6-OMe

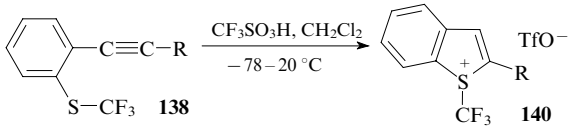
Heterocyclization of *ortho*-sulfanyl-substituted arylacetylenes **137a–c** and **138** under the action of HBF_4, $HClO_4$ or CF_3SO_3H affords benzothiophenylium salts **139a–c** (see Ref. 83) and **140** (see Ref. 84), respectively (Scheme 55).

Scheme 55



137a–c **139a–c** (53%–88%)

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



138 **140**

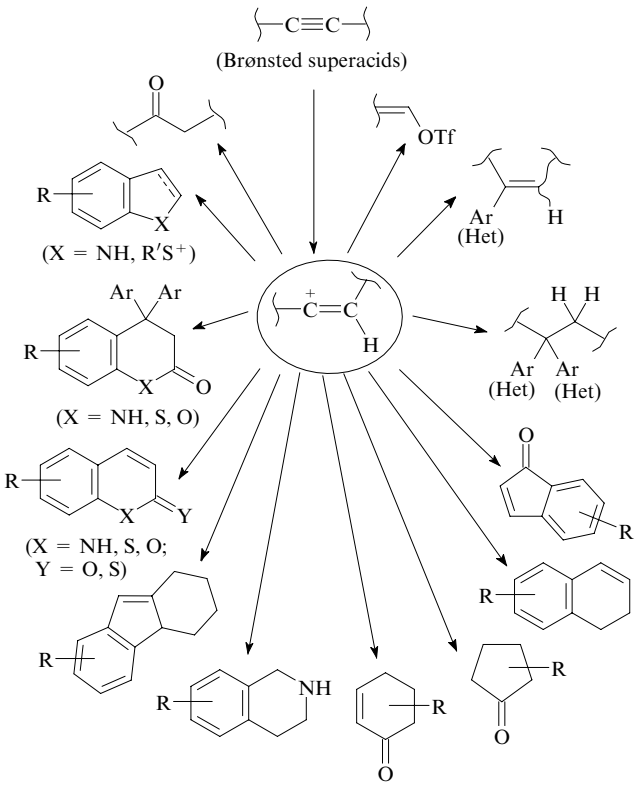
R = Bu^t, cyclo-C_3H_5, Bn, Ph, $C_6H_{5-n}R'_n$ (R'_n = 2-Cl, 4-Me, 3-Br, 4-Br, 4-I, 2,4-F_2, 4-MeO)

VII. Conclusion

Brønsted superacids and conjugated Brønsted–Lewis systems (HSO_3F, CF_3SO_3H, HSO_3F–SbF_5, CF_3SO_3H–SbF_5, HF–SbF_5, HBr–$AlBr_3$, *etc.*) are the unique media (solvents and catalysts) for the protonation of the C≡C bond of acetylene compounds and generation of vinyl type cations.

On the basis of intra- and intermolecular transformations of such cations the following compounds may be obtained: vinyl triflates (fluorosulfonates, fluorides), carbonyl compounds, alkenylarenes (hetarenes), various carbo- and heterocyclic structures, *etc.* (Scheme 56). Many of them are of great importance for the organic synthesis and practical applications.

Scheme 56



A specific property of the superacidic systems such as extremely low nucleophilicity can be used to direct the reaction of the vinyl cation to carbon – carbon bond formation pathways, thus opening new possibilities to obtain organic compounds which are elusive by other synthetic methods. This is the main reason of the steady interest in the chemistry of not only alkynes but also the other classes of the organic compounds in superacids, despite the advances that have already been made in this area on a laboratory and an industrial scales.[5, 6]

Note that the application of Brønsted superacids (especillay HSO_3F and HF) on an industrial scale is connected with the difficulties of their recovery. One trend of the development of this field of chemistry is the replacement of corrosive proton-donating superacids by the environmentally friendly strong Lewis acids, solid (zeolites) and polymer superacids capable of electrophilic activation of various organic substrates.[14, 15, 85 – 88]

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