Russian Journal of Organic Chemistry, Vol. 41, No. 10, 2005, pp. 1485–1492. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 10, 2005, pp. 1516–1523.

Protonation of 3-Arylpropynoic Acid Derivatives in Superacids

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Received November 12, 2004

Abstract—According to the ^{1}H and ^{13}C NMR data, 3-arylpropynoic acids and their esters XC_6H_n–C≡C–CO_2R (R = H, Me, Et) having electron-withdrawing substituents in the benzene ring (X = NO_2, CN, COMe, CO_2Me) exist in HSO_3F at –80 to 0°C as XC_6H_n–C≡C–C^+(OH)OR ions. Derivatives with other substituents (X = H, F, Me, MeO) in HSO_3F or CF_3SO_3H above –40°C undergo protonation at the acetylenic carbon atom neighboring to the acid group to give unstable vinyl-type XC_6H_n–C^+=CH–CO_2R cations which are then transformed into mixtures of stereoisomeric (*Z* and *E*) fluorosulfonates or triflluoromethanesulfonates XC_6H_n–CY=CH–CO_2R (Y = OSO_2F, OSO_2CF_3), the *E* isomer prevailing.

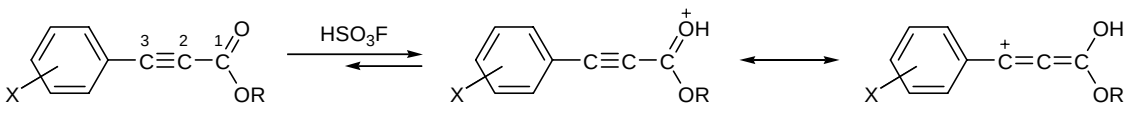
We recently initiated studies on protonation and subsequent transformations of acetylenic compounds in superacidic media [1–6], which opened new prospects in the application of superacids [7] in synthetic organic chemistry. Stang [8, 9] and Olah [10] were the first to report on the addition of superacids (HSO_3F and CF_3SO_3H) to alkyl- and dialkylacetylenes with formation of the corresponding vinyl fluorosulfonates and trifluoromethanesulfonates. The transformations in HSO_3F of acetylenic compounds with strong electron-withdrawing substituents were studied using propynoic, 2-butynoic, and 3-phenylpropynoic acids as examples [10]; however, the mechanism of formation of fluorosulfonates thus obtained and their stereochemical structure were not determined.

Despite apparent simplicity of processes involving addition of superacids at a triple carbon–carbon bond, study of the reaction mechanism and development of synthetic procedures on the basis of this reaction are important for the preparation of fluorosulfonates and trifluoromethanesulfonates [11]. Trifluoromethanesulfonates possessing various functional groups attract specific interest from the viewpoint of their use in Pd-catalyzed reactions leading to formation of new C–C bonds [12–14]. In particular, access to such compounds may be opened via addition of CF_3SO_3H to 3-arylpropynoic acid derivatives.

The present communication reports on the behavior of 3-arylpropynoic acid derivatives in superacids (HSO_3F and CF_3SO_3H), reactivity of the O- and C-protonated species thus formed, and stereochemical aspects of the addition of HSO_3F and CF_3SO_3H at the triple bond of the substrate.

^{1}H and ^{13}C NMR monitoring of the reactions of 3-arylpropynoic acids **Ia**–**Ie** and the corresponding ethyl esters **If**–**In** with HSO_3F at –80°C revealed

Scheme 1.



Ia–In **IIa–IIn** **IIIa–IIIn**

I, **IIa**–**IIh**, **IIk**–**IIm**, **IIIa**–**IIIh**, **IIIk**–**IIIm**, R = H, X = 3-O_2N (**a**), 4-O_2N (**b**), 4-NC (**c**), 4-F (**d**), 4-MeO-3-O_2N (**e**); R = Et, X = 3-O_2N (**f**), 4-O_2N (**g**), 4-NC (**h**), 4-MeCO (**i**), 4-MeOCO (**j**), 3,4-$(O_2N)_2$ (**k**), 4-MeO-3-O_2N (**l**), 2,5-Me_2-4-O_2N (**m**), 4-EtOCOC≡C (**n**); **IIi**, **IIj**, **IIn**, **IIIi**, **IIIj**, **IIIn**, R = Et, X = 4-MeC^+(OH) (**i**), 4-$MeOC^+$(OH) (**j**), 4-$EtOC^+$(OH)C≡C (o).

1070-4280/05/4110-1485

formation of stable cations **IIa**–**IIn** via protonation of the carbonyl oxygen atom (Scheme 1). The ^{1}H and ^{13}C NMR spectra of protonated acids **IIa**–**IIe** in HSO_3F at –80 and 0°C are given in Tables 1 and 2, and Tables 3 and 4 contain the ^{1}H and ^{13}C NMR data for protonated ethyl 3-arylpropynoates **IIf**–**IIn** in HSO_3F at –80°C. For comparison, the NMR spectra of precursors **Ia**–**Ic** and **If**–**In** in $CDCl_3$ or CD_3OD at 25°C are also given in Tables 2 and 4. The ^{13}C signals were assigned by analysis of their multiplicity in the proton-coupled spectra of ions **IIa**, **IIg**, and **IIh** and neutral compounds **Ia**–**Ic** and **If**–**In** (Tables 2 and 4 contain only proton-decoupled ^{13}C NMR spectra of the latter).

Protonated esters **IIf**–**IIn** in HSO_3F at –80°C showed in the ^{1}H NMR spectra a broadened singlet in the δ region 13.5–14.5 ppm from proton on the carbonyl oxygen atom (Table 3). The corresponding signal of protonated acids **Ia**–**Ie** was not detected even at –80°C due to fast exchange with the acidic medium (Table 1), while protonated esters **If**–**In** did not display that signal at 0°C. Diester **In** in HSO_3F undergoes protonation at both carbonyl groups to give dication **IIn** (Scheme 1; Tables 3, 4).

In the examined ^{1}H NMR spectra of **IIa**–**IIc**, **IIe**, **IIf**–**IIh**, and **IIk**–**IIm** in HSO_3F we observed no signal from proton that added to electron-withdrawing groups (X = NO_2, CN) in the benzene ring; an analogous pattern was typical of protonation of 1,3-diarylpropynones in superacids [2]. Compounds **IIi** and **IIj** (X = 4-COMe and 4-CO_2Me) take up an additional proton at the X substituent, and the corresponding signal is present in the ^{1}H NMR spectra (Table 3). The different behaviors in HSO_3F of the NO_2 and CN groups in structures **IIa**–**IIc**, **IIe**, **IIf**–**IIh**, and **IIk**–**IIm**, on the one hand, and COMe and CO_2Me groups in **IIi** and **IIj**, on the other, are reflected in Scheme 1.

Table 1. ^{1}H NMR spectra of ions **IIa**–**IIe** generated from 3-arylpropynoic acids **Ia**–**Ie** in HSO_3F

Ion no.	Temperature, °C	Chemical shifts δ, ppm (*J*, Hz)
IIa	–80	7.97 s (1H), 8.41 s (1H), 8.74 s (1H), 8.89 s (1H)
	0	7.94 t (1H, *J* = 8.1), 8.35 d (1H, *J* = 8.1), 8.70 d (1H, *J* = 8.1), 8.84 s (1H)
IIb	–80	8.20 s (2H), 8.58 s (2H)
	0	8.17 d (2H, *J* = 8.6), 8.55 d (2H, *J* = 8.6)
IIc	–80	8.17 d (2H, *J* = 6.6), 8.31 d (2H, *J* = 6.6)
	0	8.13 d (2H, *J* = 7.3), 8.20 d (2H, *J* = 7.3)
IId	–80	7.35 s (2H), 8.00 s (2H)
IIe	–80	4.49 s (3H, OMe), 7.71 d (1H, *J* = 6.5), 8.52 d (1H, *J* = 6.5), 9.09 s (1H)

Insofar as HSO_3F at –80°C is characterized by a high viscosity, in most cases signals from aromatic protons and protons in the CH_2 and CH_3 groups of the ester fragment of ions **IIf**–**IIn** appeared in the ^{1}H NMR spectra as broadened singlets with unresolved fine structure (Tables 1, 3). In the spectra recorded at 0°C we observed well resolved multiplets typical of aromatic systems (Table 1).

The C^1 signal in the ^{13}C NMR spectra of ions **IIa**–**IIc** and **IIf**–**IIn** in HSO_3F is located at δ_C 165.7–168.5 ppm, i.e., in a weaker field (by 11–13 ppm) than the corresponding signal of neutral acids and esters **Ia**–**Ic** and **If**–**In** in $CDCl_3$ or CD_3OD (Tables 2, 4). Likewise, the spectra of protonated species **IIa**–**IIc** and **IIf**–**IIn** are characterized by an appreciably more downfield position of the C^3 signal (δ_C 99–108 ppm in HSO_3F against δ_C 79–85 ppm in the spectra of **Ia**–**Ic** and **If**–**In** in $CDCl_3$ and CD_3OD; $\delta\Delta_C$ = 17–24 ppm; Tables 2, 4). These data suggest delocalization of the positive charge over the arylethynyl fragment, i.e., a considerable contribution of canonical structures **IIIa**–**IIIn** to the charge distribution (Scheme 1). The position of the C^1 signal in the ^{13}C NMR spectra of **IIa**–**IIc** and **IIf**–**IIn** in HSO_3F (δ_C 165.7–168.5 ppm) indicates formation of protonated species **IIa**–**IIn** rather than the corresponding acylium (arylpropynoyl) ions which are characterized by a C^1 signal located at δ_C 124 ppm [15].

NMR analysis of the protonation of 3-arylpropynoic acid derivatives showed that compounds **Ia**–**Ic**, **If**–**Ik**, **Im**, and **In** containing strong electron-withdrawing substituents in the aromatic ring (X = NO_2, CN, COMe, CO_2Me, etc.) in HSO_3F exist as stable ions **IIa**–**IIc**, **IIf**–**IIk**, **IIm**, and **IIn** even at 0°C. Their ^{1}H NMR spectra lacked signals in the δ region 6–7 ppm, which could be assigned to vinyl protons in products of HSO_3F addition at the triple bond.

Compounds **Id**, **Ie**, and **Il** (X = 4-F, 4-MeO-3-NO_2) in HSO_3F at –80°C also give rise to the corresponding O-protonated species **IId**, **IIe**, and **III** (Scheme 1). However, raising the temperature to –40°C leads to rearrangement into C-protonated vinyl-type cations Ar–C^+=CH–CO_2R which are then converted into mixtures of isomeric *E*- and *Z*-fluorosulfonates **IVd**, **IVe**, and **IVl** (Scheme 2). Likewise, 3-phenylpropynoic acid (**Io**), its methyl ester **Ip**, and *para*-fluoro-substituted ester **Iq** in HSO_3F above –40°C are converted into

Table 2. ^{13}C NMR spectra of 3-arylpropynoic acids **Ia**–**Ic** in $CDCl_3$ or CD_3OD (25°C) and ions **IIa**–**IIc** generated therefrom in HSO_3F (–80 and 0°C)

Comp. no.	Solvent	Temperature, °C	Chemical shifts δ, ppm (*J*, Hz)						
			$C^1{=}O$[a]	C^2	C^3	C^i	C^o	C^m	C^p
Ia	$CDCl_3$	25	156.62	81.58	84.89	121.08	127.86, 138.47	148.14, 129.90	125.57
IIa	HSO_3F[b]	–80	168.03 s	76.86 s	106.73 s	118.23 d (9.2)	131.61 d (175.0), 144.40 d.t (168.0, 6)	146.45 m (4.0), 132.49 d (171.2)	131.01 d (171.0)
		0	168.47 s	76.86 s	108.04 t (5.6)	118.36 d (9.6)	131.38 d.t (174.5, 5.6), 143.71 d.t (169.7, 6)	147.39 m (4.8), 132.54 d (171.3)	130.98 d.m (170.1, 3.6)
Ib	CD_3OD	25	156.76	86.34	84.84	121.08	135.81	125.84	150.97
IIb	HSO_3F	–80	167.93	78.05	105.68	124.61	125.58	137.25	149.03
		0	168.37	78.27	106.86	124.45	125.67	137.20	149.98
Ic	CD_3OD	25[c]	156.82	85.90	84.65	126.88	134.59	134.59	116.01
IIc	HSO_3F	–80[d]	168.04	78.25	105.40	125.29	136.29	136.38	108.36
		0[e]	168.48	78.33	107.01	124.47	135.78	136.35	111.03

[a] In HSO_3F, signal from the protonated carboxy group.
[b] Proton-coupled spectrum.
[c] δ_C CN 119.85 ppm.
[d] δ_C CN 106.83 ppm.
[e] δ_C CN 110.24 ppm.

Table 3. ^1H NMR spectra of ions **IIf**–**IIn** generated from ethyl 3-arylpropynoates **If**–**In** in HSO_3F at –80°C

Ion no.	Chemical shifts, δ, ppm (*J*, Hz)			
	$OC\mathbf{H}_2CH_3$[a]	$CH_2C\mathbf{H}_3$[a]	H_{arom}, X	$^+C^1$–OH
IIf	5.07	1.66	7.97 s (1H), 8.39 s (1H), 8.73 s (1H), 8.87 s (1H)	13.6 s
IIg	5.08	1.66	8.16 s (2H), 8.56 s (2H)	13.7 s
IIh	5.06	1.65	8.13 s (2H), 8.25 s (2H)	13.9 s
IIi[b]	5.09	1.66	3.45 s (3H, Me), 8.18 s (2H), 8.63 s (2H)	14.46 s
IIj[c]	5.07	1.65	4.69 s (3H, OMe), 8.17 s (2H), 8.32 s (2H)	13.5 s
IIk	5.09	1.65	8.25 d (1H, *J* = 8.2), 8.41 d (1H, *J* = 8.2), 8.61 s (1H)	14 s
IIl	5.05	1.64	4.52 s (3H, OMe), 7.73 d (1H, *J* = 8.2), 8.52 d (1H, *J* = 8.2), 9.02 s (1H)	13.6 s
IIm	5.09	1.66	2.71 s (3H, Me), 2.75 s (3H, Me), 8.02 s (1H), 8.73 s (1H)	13.8 s
IIn	5.05	1.64	8.01 s (4H)	13.52 s

[a] The CH_2 and CH_3 signals appeared as singlets (for details, see text).
[b] The protonated acetyl group in the benzene ring gave a singlet at δ 14.4 ppm.
[c] The protonated methoxycarbonyl group in the benzene ring gave a singlet at δ 13.7 ppm.

E/*Z*-fluorosulfonates **IVo**–**IVq**. Isomeric trifluoromethanesulfonates **Vo** and **Vp** are formed From compounds **Io** and **Ip** in CF_3SO_3H at 0°C (Scheme 2).

The addition of superacids to compounds **Id**, **Ie**, **Il**, and **Io**–**Iq** was monitored, and the *E*/*Z*-isomer ratios in products **IVd**, **IVe**, **IVl**, **IVo**–**IVq**, **Vo**, and **Vp** were determined, by NMR spectroscopy (the reactions were carried out in NMR ampules). The results are collected in Table 5. No vinyl-type cations were detected, though they should be formed as unstable intermediates via protonation of the triple carbon–carbon bond in the substrates by HSO_3F or CF_3SO_3H. The isomer structure of compounds **IVd**, **IVe**, **IVl**, **IVo**–**IVq**, **Vo**, and **Vp** was assigned by analysis of the ^1H NMR spectra of the isomer mixtures. Comparison of the ^1H NMR spectrum of *E*-**IVo** [10] with that of isomer mixture *E*-**IVo**/*Z*-**IVo** showed that signal from the vinyl proton in the *E* isomer is located in a stronger field than the

Table 4. ^{13}C NMR spectra of ethyl 3-arylpropynoates **If–In** ($CDCl_3$, 25°C) and ions **IIf–IIn** derived therefrom in fluorosulfonic acid at –80°C

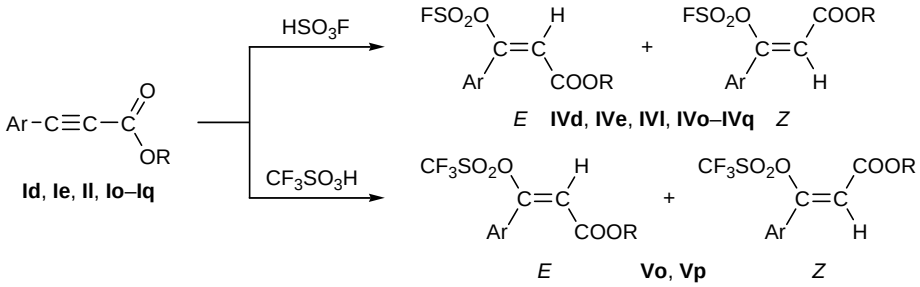
Comp. no.	Solvent	Chemical shifts δ_C, ppm (*J*, Hz)						
		C^1	C^2	C^3	C_{arom}	OCH_2	CH_3	X
If	$CDCl_3$	153.03	82.13	82.22	121.28, 124.97, 127.32, 129.71, 138.10, 147.89	62.27	13.80	
IIf	HSO_3F	166.02	81.97	102.96	118.64, 130.58, 131.32, 132.41, 144.27, 146.30	78.32	12.78	
Ig	$CDCl_3$	153.05	84.04	82.52	123.58, 126.10, 133.51, 148.34	62.39	13.89	
IIg	HSO_3F[a]	166.00 s	82.04 s	102.46 s	125.31 s, 125.70 d (173.7), 136.98 d (171.3), 148.61 s	78.33 t (152.40)	12.74 q (129.59)	
Ih	$CDCl_3$	153.10	83.51	82.89	113.8, 124.21, 132.06, 133.05	62.29	13.82	117.61 (CN)
IIh	HSO_3F[a]	165.90 s	81.79 s	102.00 s	109.30 s, 124.78 s, 135.64 d.d (173.0, 10.0), 135.78 d.d (173.3, 10.4)	77.98 t (130.39)	12.66 q (127.58)	108.28 s (CN)
Ii	$CDCl_3$	153.26	82.62	84.06	123.85, 128.01, 132.70, 137.75	62.01	13.76	26.33 (CH_3), 196.61 (C=O)
IIi	HSO_3F	165.98	79.21	101.55	129.54, 132.49, 135.96	78.59	12.64	26.28 (CH_3), 222.73 ($C=OH^+$)
Ij	$CDCl_3$	153.48	82.56	84.30	123.98, 129.46, 131.53, 132.62	62.14	13.90	52.24 (CH_3), 165.85 (C=O)
IIj	HSO_3F	166.07	82.28	102.49	126.36, 132.03, 136.28	78.60	12.76	64.03 (CH_3), 181.85 ($C=OH^+$)
Ik	$CDCl_3$	152.56	85.47	79.69	125.53, 125.95, 128.76, 137.11, 142.77	62.85	13.87	
IIk	HSO_3F	165.93	78.24	99.06	123.26, 127.84, 132.46, 141.55, 142.56, 144.57	79.08	12.76	
Il	$CDCl_3$	153.47	81.15	83.04	111.74, 113.87, 130.04, 138.36, 139.37, 154.28	62.16	13.92	56.73 (OMe)
IIl	HSO_3F	165.74	81.89	101.39	112.28, 118.09, 131.42, 137.21, 151.11, 164.06	78.34	12.73	61.43 (OMe)
Im	$CDCl_3$	153.29	86.66	81.90	124.37, 125.32, 130.70, 137.99, 140.79, 149.39	62.25	13.89	19.42 (CH_3), 19.49 (CH_3)
IIm	HSO_3F	165.99	82.80	99.95	129.16, 129.81, 140.64, 140.89, 145.16, 145.96	78.83	12.76	19.51 (CH_3), 21.63 (CH_3)
In	$CDCl_3$	153.45	82.78	84.19	121.66, 132.73	62.14	13.90	
IIn	HSO_3F	166.05	81.62	104.94	121.57, 135.86	78.06	12.78	

[a] Proton-coupled spectrum.

corresponding signal of the *Z* isomer (Table 5). An additional support to the above assignment was obtained by NOESY experiment ($CDCl_3$, 25°C) performed for isomer mixture *E*-**Vp**/*Z*-**Vp** which was isolated in a preparative amount by addition of trifluoromethanesulfonic acid to methyl 3-phenylpropynoate (**Ip**) (see Experimental). The minor isomer (*Z*-**Vp**), though its fraction in the mixture was as small as 5% (Table 5, run no. 9), showed a strong correlation between the vinyl proton (δ 6.73 ppm in HSO_3F) and *ortho*-protons in the benzene ring. No analogous correlation was found for the major component (*E*-**Vp**, δ 6.62 ppm in HSO_3F; Table 5). The existence of such correlation in the NOESY spectrum indicates spatially close location of the corresponding structural fragments, which is possible only in the *Z* isomer.

As follows from the data in Table 5, isomer mixtures **IVd**, **IVe**, **IVl**, **IVo–IVq**, **Vo**, and **Vp** contain mainly the *E* isomers whose fraction reaches 95%; they result from *syn*-addition of superacids HSO_3F and CF_3SO_3H at the triple carbon–carbon bond. The *E*/*Z*-isomer ratio depends on the temperature: raising the

Scheme 2.



R = H, Ar = 4-FC_6H_4 (**d**), 4-MeO-3-$O_2NC_6H_3$ (**e**), C_6H_5 (**o**); R = Et, Ar = 4-MeO-3-$O_2NC_6H_3$ (**l**); R = Me, Ar = C_6H_5 (**p**), 4-FC_6H_4 (**q**).

temperature to 0°C (the reaction was performed at –40°C) induces *E*–*Z* isomerization (cf. run nos. 1, 2 and 5, 6 in Table 5). Isomer mixtures **IVe** and **IVl**, which were obtained in HSO_3F at 0°C, contained the corresponding *Z* isomers as the major components; presumably, the reason is the presence of an electron-donor methoxy group in the *para*-position with respect to the double C=C bond, which facilitates isomerization. Furthermore, when a mixture of trifluoromethanesulfonates *E*-**Vp** and *Z*-**Vp** (initial isomer ratio 95:5; Table 5, run no. 9) was stored for three months without a solvent at room temperature, the isomer ratio changed to 21:79. The data on *E*–*Z* isomerization of compounds **IVd**, **IVo**, and **Vp** indicate that addition of HSO_3F and CF_3SO_3H to 3-arylpropynoic acid derivatives initially gives the corresponding *E* isomers as kinetically controlled products (*syn*-addition at the triple bond) which are then transformed into thermodynamically more stable *Z* isomers (*anti*-addition products). Olah and Spear [10] postulated that addition of HSO_3F to acetylenecarboxylic acids initially gives *anti*-adducts (*Z* isomers) which then undergo fast isomerization into *syn*-adducts (*E* isomers).

The known methods for the synthesis of vinyl trifluoromethanesulfonates are based on reactions of carbonyl compounds with trifluoromethanesulfonic anhydride in the presence of bases [9, 11]. The main disadvantage of these procedures is low regio- and stereoselectivity. The addition of HSO_3F and CF_3SO_3H to 3-arylpropynoic acid derivatives, described in the present article, can be regarded as a simple, effective, and selective synthetic route to fluorosulfonates and trifluoromethanesulfonates like **IV** and **V**.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra of solutions in $CDCl_3$ and CD_3OD were recorded on Bruker AM-500 (500, 125.76, and 470 MHz, respectively) and Bruker AVANCE 300 spectrometers (300, 75, and 300 MHz, respectively). The chemical shifts were measured relative to the solvent signals (^1H: $CHCl_3$, δ 7.25 ppm;

Table 5. Addition of fluorosulfonic and trifluoromethanesulfonic acids to compounds **Id**, **Ie**, **Il**, and **Io**–**Iq**[a]

Run no.	Initial compound no.	Superacid, temperature	Products	*E*/*Z*-Isomer ratio	$\delta_{2\text{-H}}$, ppm
1	**Id**	HSO_3F, –40°C	*E*-**IVd**/*Z*-**IV**d	87:13	6.58/6.65
2	**Id**	HSO_3F, 0°C	*E*-**IVd**/*Z*-**IV**d	65:35	6.57/6.61
3	**Ie**	HSO_3F, 0°C	*Z*-**IVe**	100	6.85
4	**Il**	HSO_3F, 0°C	*E*-**IVl**/*Z*-**IVl**	20:80	6.78/6.87
5	**Io**	HSO_3F, –40°C	*E*-**IVo**/*Z*-**IVo**	90:10	6.65/6.72
6	**Io**	HSO_3F, 0°C	*E*-**IVo**/*Z*-**IVo**	76:24	6.62/6.71
7	**Io**	CF_3SO_3H, 0°C	*E*-**Vo**/*Z*-**Vo**	93:7	6.61/6.70
8	**Ip**	HSO_3F, 0°C	*E*-**IVp**/*Z*-**IVp**	78:22	6.64/6.71
9	**Ip**	CF_3SO_3H, 0°C	*E*-**Vp**/*Z*-**Vp**	95:5	6.62/6.73
10	**Iq**	HSO_3F, –30°C	*E*-**IVq**/*Z*-**IVq**	89:11	6.60/6.70

[a] In an NMR ampule (see Experimental).

CD_3OD, δ 3.31 ppm; ^{13}C: $CDCl_3$, δ_C 77.0 ppm; CD_3OD, δ_C 49.0 ppm) or $CFCl_3$ (^{19}F: δ_F 0.0 ppm). The ^1H and ^{13}C NMR spectra of cationic species in superacids (HSO_3F and CF_3SO_3H) were recorded on a Bruker AVANCE 400 spectrometer at 400 and 100 MHz, respectively, using methylene chloride as internal reference (δ 5.32 ppm, δ_C 77.0 ppm). The IR spectra were obtained from solutions in $CHCl_3$ on a Specord 75IR spectrophotometer. The mass spectra (electron impact, 70 eV) were run on MKh-1321 and TSQ 700 Finigan MAT instruments. NOESY experiment was performed with a solution of 50 mg of isomer mixture *E*-**Vp**/*Z*-**Vp** in 1 ml of $CDCl_3$ at 25°C using a Bruker AVANCE 400 instrument.

Initial ethyl 3-arylpropynoates **If–In** were synthesized by the procedures reported in [16, 17]. 3-Arylpropynoic acids **Ia–Ie** were obtained by hydrolysis of the corresponding ethyl esters in the system KOH–EtOH–H_2O. Methyl 3-arylpropynoates **Ip** and **Iq** were prepared by methylation of the corresponding 3-arylpropynoic acids with dimethyl sulfate according to [18]. The properties of compounds **Il**, **Ip**, and **Iq** were reported by us previously [17].

3-(3-Nitrophenyl)propynoic acid (Ia). mp 145–147°C; published data [19]: mp 141–142°C.

3-(4-Nitrophenyl)propynoic acid (Ib). mp 198–200°C; published data [19]: mp 198°C. ^1H NMR spectrum (500 MHz, CD_3OD), δ, ppm: 7.81 d (2H, H_{arom}, J = 8.8 Hz), 8.28 d (2H, H_{arom}, J = 8.8 Hz).

3-(4-Cyanophenyl)propynoic acid (Ic). Sublimes at 200°C. ^1H NMR spectrum (500 MHz, CD_3OD), δ, ppm: 7.74 d (2H, H_{arom}, J = 8.3 Hz), 7.79 d (2H, H_{arom}, J = 8.3 Hz). Mass spectrum: *m*/*z* 171 $[M]^+$. Found, %: C 69.97; H 3.09; N 8.00. $C_{10}H_5NO_2$. Calculated, %: C 70.18; H 2.94; N 8.18.

3-(4-Fluorophenyl)propynoic acid (Id). mp 155–157°C. ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.01–7.07 m (2H, H_{arom}), 7.54–7.59 m (2H, H_{arom}), ~13 br.s (1H, OH). Found, %: C 65.89; H 3.11. $C_9H_5FO_2$. Calculated, %: C 65.86; H 3.07.

3-(4-Methoxy-3-nitrophenyl)propynoic acid (Ie). mp 189–191°C. Mass spectrum: *m*/*z* 221 $[M]^+$. Found, %: C 54.18; H 3.02; N 6.47. $C_{10}H_7NO_5$. Calculated, %: C 54.31; H 3.19; N 6.33.

Ethyl 3-(3-nitrophenyl)propynoate (If). Oily substance. IR spectrum, ν, cm^{-1}: 1350, 1525, 1710 (C=O), 2220 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.29 t (3H, Me, J = 7.1 Hz), 4.24 q (2H, CH_2, J = 7.1 Hz), 7.55 d.d (1H, H_{arom}, J = 8.3, 7.7 Hz), 7.81 d.d.d (1H, H_{arom}, J = 7.7, 1.4, 1.1 Hz), 8.22 d.d.d (1H, H_{arom}, J = 8.3, 2.2, 1.1 Hz), 8.31 d.d (1H, H_{arom}, J = 2.2, 1.4 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 219 (13) $[M]^+$, 174 (75) $[M - OEt]^+$, 147 (100), 128 (55), 101 (23), 100 (21), 74 (34). Found, %: C 60.15; H 4.09; N 6.44. $C_{11}H_9NO_4$. Calculated, %: C 60.28; H 4.14; N 6.39.

Ethyl 3-(4-nitrophenyl)propynoate (Ig). mp 124–126°C; published data: mp 120–122°C [20]. IR spectrum, ν, cm^{-1}: 1350, 1520, 1710 (C=O), 2230 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.30 t (3H, Me, J = 7.1 Hz), 4.26 q (2H, CH_2, J = 7.1 Hz), 7.68 d (2H, H_{arom}, J = 8.9 Hz), 8.18 d (2H, H_{arom}, J = 8.9 Hz).

Ethyl 3-(4-cyanophenyl)propynoate (Ih). mp 67–68°C; published data [20]: mp 66–68°C. IR spectrum, ν, cm^{-1}: 1710 (C=O); 2220, 2235 (C≡C, C≡N). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.29 t (3H, Me, J = 7.2 Hz), 4.25 q (2H, CH_2, J = 7.2 Hz), 7.60 d (2H, H_{arom}, J = 8.6 Hz), 7.63 d (2H, H_{arom}, J = 8.6 Hz).

Ethyl 3-(4-acetylphenyl)propynoate (Ii). mp 82.0–82.5°C. IR spectrum, ν, cm^{-1}: 1690, 1710 (C=O); 2220, 2250 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.24 t (3H, Me, J = 7.1 Hz), 2.49 s (3H, Me), 4.19 q (2H, CH_2, J = 7.1 Hz), 7.53 d (2H, H_{arom}, J = 8.5 Hz), 7.83 d (2H, H_{arom}, J = 8.5 Hz). Found, %: C 72.14; H 5.61. $C_{13}H_{12}O_3$. Calculated, %: C 72.21; H 5.59.

Ethyl 3-(4-methoxycarbonylphenyl)propynoate (Ij). mp 46–48°C [20]. IR spectrum, ν, cm^{-1}: 1710, 1730 (C=O); 2215, 2250 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.30 t (3H, Me, J = 7.1 Hz), 3.87 s (3H, OMe), 4.25 q (2H, CH_2, J = 7.1 Hz), 7.58 d (2H, H_{arom}, J = 8.5 Hz), 7.97 d (2H, H_{arom}, J = 8.5 Hz).

Ethyl 3-(3,4-dinitrophenyl)propynoate (Ik). mp 72–73°C. IR spectrum, ν, cm^{-1}: 1360, 1550, 1710 (C=O), 2245 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.34 t (3H, Me, J = 7.1 Hz), 4.30 q (2H, CH_2, J = 7.1 Hz), 7.91 d.d (1H, H_{arom}, J = 8.4, 1.6 Hz), 7.95 d (1H, H_{arom}, J = 8.4 Hz), 8.06 d (1H, H_{arom}, J = 1.6 Hz). Found, %: C 49.88; H 3.00; N 10.43. $C_{11}H_8N_2O_6$. Calculated, %: C 50.01; H 3.05; N 10.60.

Ethyl 3-(4-methoxy-3-nitrophenyl)propynoate (Il). mp 86–87°C. IR spectrum, ν, cm^{-1}: 1355, 1525, 1700 (C=O), 2220 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.31 t (3H, Me, J = 7.1 Hz), 3.96 s (3H, OMe), 4.25 q (2H, CH_2, J = 7.1 Hz), 7.08 d (1H, H_{arom}, J = 8.7 Hz), 7.70 d.d (1H, H_{arom}, J = 8.7,

2.1 Hz), 8.00 d (1H, H_{arom}, J = 2.1 Hz). Found, %: C 57.69; H 4.41; N 5.74. $C_{12}H_{11}NO_5$. Calculated, %: C 57.83; H 4.45; N 5.62.

Ethyl 3-(2,5-dimethyl-4-nitrophenyl)propynoate (Im). mp 68–69°C. IR spectrum, ν, cm^{-1}: 1350, 1520, 1710 (C=O), 2230 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.31 t (3H, Me, J = 7.1 Hz), 2.45 s (3H, Me), 2.47 s (3H, Me), 4.25 q (2H, CH_2, J = 7.1 Hz), 7.43 s (1H, H_{arom}), 7.76 s (1H, H_{arom}). Found, %: C 63.21; H 5.32; N 5.74. $C_{13}H_{13}NO_4$. Calculated, %: C 63.15; H 5.30; N 5.66.

Ethyl 3-[(4-ethoxycarbonylethynyl)phenyl]-propynoate (In). mp 92–94°C. IR spectrum, ν, cm^{-1}: 1700 (C=O), 2215, 2250 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 1.30 t (3H, Me, J = 7.1 Hz), 4.25 q (2H, CH_2, J = 7.1 Hz), 7.52 s (4H, H_{arom}). Found, %: C 71.26; H 5.20. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22.

General procedure for generation of ions IIa–IIn in HSO_3F and preparation of *E*/*Z*-isomeric fluorosulfonates IVd, IVe, IVl, and IVo–IVq in HSO_3F and trifluoromethanesulfonates Vo and Vp in CF_3SO_3H *in situ*. An NMR ampule was charged with 0.8–1 ml of HSO_3F (mp –89°C) and cooled to approximately –110°C (using ethanol–liquid nitrogen), and 5–30 mg of compound **Ia**–**In** was added. The temperature was raised to –78°C, and a Teflon capillary (1 mm i.d.) was immersed into the ampule till its bottom. A slight stream of argon was passed through the capillary over a period of 5–15 min to obtain a homogeneous solution. The capillary was withdrawn, and methylene chloride (internal reference) was added. The ^1H and ^{13}C NMR spectra of ionic species **IIa**–**IIn** were recorded at –80 and 0°C (Tables 1–4). The ^1H NMR spectra of isomeric fluorosulfonates **IVd**, **IVe**, **IVl**, and **IVo**–**IVq** were recorded in HSO_3F at –40 and 0°C (Table 5). Solutions of *E*/*Z*-isomeric trifluoromethanesulfonates **Vo** and **Vp** in CF_3SO_3H were prepared in a similar way, by adding 5–30 mg of substrate **Io** or **Ip** to 0.8–1 ml of CF_3SO_3H (mp –34°C) placed in an NMR ampule and frozen at –78°C, followed by homogenization at 0°C. The ^1H and ^{13}C NMR spectra of compounds *E*/*Z*-**Vo** and *E*/*Z*-**Vp** were recorded at 0°C (Table 5).

The synthesis and properties of fluorosulfonates *E*/*Z*-**IVq** were described by us previously [6].

Trifluoromethanesulfonates *E*/*Z*-Vp. A solution of 0.2 g (1.25 mmol) of methyl 3-phenylpropynoate (**Ip**) in 10 ml of anhydrous methylene chloride was cooled to –30°C, 1.1 ml (12.5 mmol) of CF_3SO_3H was added dropwise over a period of 5 min under vigorous stirring, and the mixture was allowed to warm up to 0°C and was stirred for an additional 0.5 h. When the reaction was complete, the mixture was added dropwise to a suspension of $KHCO_3$ in MeOH, cooled to –20°C. The resulting mixture was diluted with water and extracted with diethyl ether. The extract was washed with water and dried over Na_2SO_4, and the solvent was distilled off to obtain 230 mg (59%) of a mixture of isomeric trifluoromethanesulfonates *E*-**Vp** and *Z*-**Vp** (95:5) as a light yellow oily material. Compounds *E*-**Vp** and *Z*-**Vp** decomposed on attempted chromatographic separation in a column charged with silica gel. On storage at room temperature without a solvent, isomer *E*-**Vp** was gradually converted into *Z*-**Vp**. The spectral parameters of particular isomers *E*-**Vp** and *Z*-**Vp** were derived from the spectra of their mixture.

Methyl (*E*)-3-phenyl-3-trifluoromethylsulfonyloxy-2-propenoate (*E*-Vp). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.69 s (3H, OMe), 6.19 s (1H, =CH–), 7.41–7.57 m (5H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 52.06 (OMe), 113.07 (=C^2), 118.25 q (CF_3, J_{CF} = 318 Hz), 128.19 (C^m), 129.07 (C^o), 130.42 (C^i), 131.60 (C^p), 159.12 (C^3), 163.75 (C=O). ^{19}F NMR spectrum (300 MHz, $CDCl_3$): δ_F –74.17 ppm, s (CF_3).

Methyl (*Z*)-3-phenyl-3-trifluoromethylsulfonyloxy-2-propenoate (*Z*-Vp). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.84 s (3H, OMe), 6.25 s (1H, =CH–), 7.36–7.58 m (5H, H_{arom}).

Mass spectrum of isomer mixture *E*/*Z*-**Vp**, *m*/*z* (I_{rel}, %): 310 (82) $[M]^+$, 279 (45), 245 (14), 215 (28), 177 (27), 149 (89), 121 (62), 105 (97), 77 (100). Found, %: C 43.05; H 3.31. $C_{11}H_9F_3O_5S$. Calculated, %: C 42.58; H 2.92.

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