

Oxidation of Aromatic Compounds: XVI.* Radical Cations Derived from Acetylenic Compounds with Electron-Withdrawing Groups: Reactions and ESR Parameters

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Abstract—One-electron oxidation of aryl-substituted acetylenes $\text{ArC}\equiv\text{CX}$ where X is an electron-withdrawing group gives different products, depending on the X substituent. Acetylenic substrates with medium-strength electron-withdrawing substituents, $\text{X} = \text{CO}_2\text{R}$, COAr , COR , $\text{PO}(\text{OEt})_2$, give rise to tetrasubstituted ethenes $\text{X}(\text{ArCO})\text{C}=\text{C}(\text{COAr})\text{X}$. Compounds with strong electron-withdrawing groups ($\text{X} = \text{COCF}_3$, COCO_2R , CN) are converted into furan derivatives. Probable mechanisms of transformations of $\text{ArC}\equiv\text{CX}$ radical cations into the final products are discussed. Radical cations derived from disubstituted acetylenes were characterized by ESR spectroscopy.

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Organic radical cations are formed as intermediates in many chemical transformations, and reactions with participation of radical cations are widely used in the synthesis of new compounds and materials [2–13]. Studies on the properties and reactivity of radical cations are very important from both theoretical and practical viewpoints. Our studies on the oxidation of acetylene derivatives with intermediate formation of radical cations open synthetic routes to new classes of organic compounds [1, 14–21]. The present article reports on reactions of radical cations derived from acetylenic compounds having strong electron-withdrawing groups that are directly attached to the triple-bonded carbon atom and the results of ESR study on such radical cations.

One-electron oxidation of arylacetylenes **I** having various groups X in the system $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ (Scheme 1) gives two types of products, depending on the electron-withdrawing power of the X substituent [16–21]. Table 1 contains such parameters of different groups X as their electronegativities (EN) and Hammett constants σ_p [22–25]. If the substituent X is

a medium-strength electron acceptor [$\text{X} = \text{CO}_2\text{R}$, COAr , COR , $\text{PO}(\text{OEt})_2$, $EN = 7.1-7.5$, $\sigma_p \leq 0.57$], the oxidation of the corresponding substrates **I** leads to the formation of tetrasubstituted ethenes **II** [16–20].

Table 1. Group electronegativities (EN) and Hammett constants σ_p for electron-withdrawing groups X

Group X	EN [22]	σ_p [23]
COMe	7.1	0.38–0.51
COPh	– ^a	0.42–0.51
CO ₂ Me	7.5	0.38–0.48
PO(OEt) ₂	– ^a	0.57 ^b
COCF ₃	7.6	0.80
CF ₃	7.7	0.48–0.58
CN	7.9	0.63–0.72
SO ₂ Ph	– ^a	0.71 ^c
SO ₂ Me	9.0	0.67–0.75 ^c
SO ₂ CF ₃	9.4	0.91
NO ₂	9.5	0.73–0.93

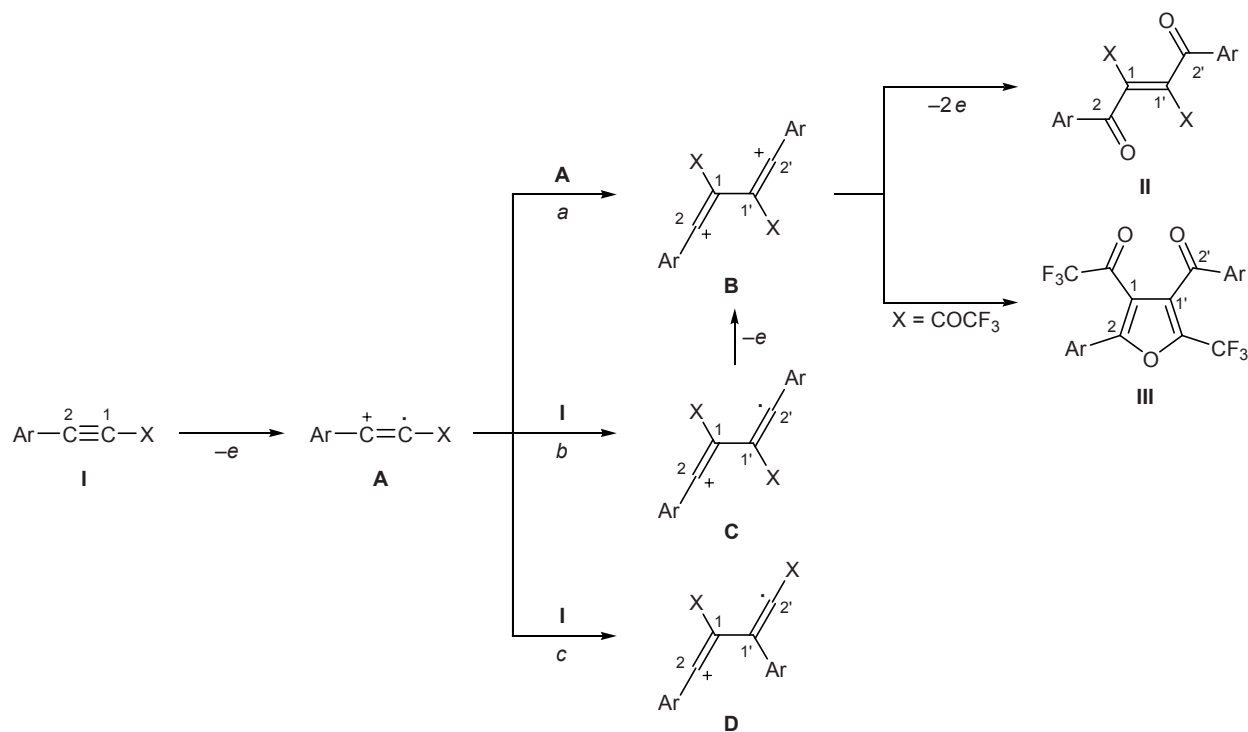
^a No data.

^b Data of [24].

^c Data of [25].

* For communication XV, see [1].

Scheme 1.



II, X = CO₂R, COAr, COR, PO(OR)₂.

Stronger acceptors (e.g., X = COCF₃) give rise to furan derivatives **III** [21].

We proposed in [21] that the key intermediate formed along the transformation of initial compounds **I** into products **II** and **III** is dication **B** which can be generated in two ways. Among the latter, the most probable is that involving combination of two radical cations **A** (path *a* in Scheme 1). According to [26], radical cations like **A**, in which the electron-withdrawing (X) and electron-donating groups (alkyl- or methoxyaryl) are conjugated through double C=C or triple C≡C bonds, are expected to feature sharp separation of the unpaired electron and positive charge between the the C¹ and C² atoms. The radical center on the C¹ atom is essentially stabilized by the electron-withdrawing group X, while the cationic center on C² is stabilized by the electron-donating aryl group, as shown in Scheme 1 for one resonance structure of radical cation **A**. This separation makes the C¹ atom in **A** a reactive vinyl type radical center, and new carbon-carbon bond is formed with participation of just that carbon atom in the combination of two species **A** (path *a* in Scheme 1). Such dimerizations are typical for various radical cations [27–29].

Another reaction path of radical cation **A** is its reaction with neutral precursor **I**. In this case formation

of two intermediate radical cations **C** and **D** is possible as a result of C¹–C^{1'} and C¹–C^{2'} couplings, respectively (paths *b* and *c* in Scheme 1). The unpaired electron in intermediates **C** and **D** is delocalized over different structural fragments, aryl group and electron-withdrawing substituent X, respectively.

Vinyl radicals are stabilized by aryl and electron-withdrawing groups in the α-position, and they have linear structure with the *sp*-hybridized radical center [30, 31]. Both electron-donating and electron-withdrawing substituents increase thermodynamic stability of radical species [32, 33]. However, attack by vinyl [34] and trichloromethyl radicals [35] on double C=C bonds in ethenes having electron-withdrawing groups follows mainly a path leading to intermediate species in which the radical center is directly conjugated with the electron-withdrawing group, i.e., like path *c* in Scheme 1. The effect of electron-donating substituents on delocalization of unpaired electron in these reactions is not significant [35]. The same factors may determine the stability of radical cation intermediates **A**, **C**, and **D** and pathways of their subsequent transformations, especially taking into account high degree of separation of the positive charge and unpaired electron density therein [26]. Presumably, path *c* is preferred in the reaction of radical cation **A** with initial

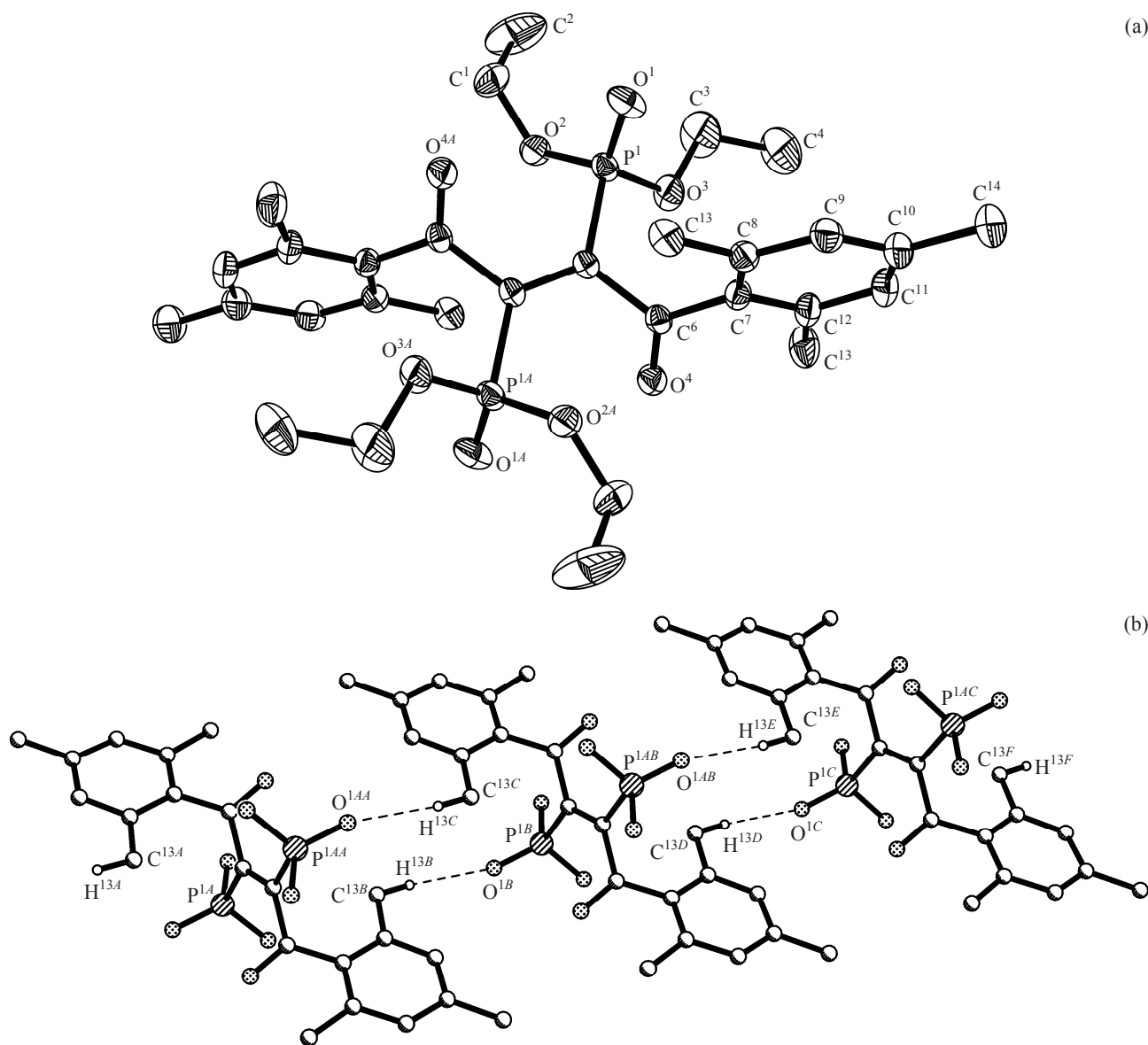


Fig. 1. (a) Structure of the molecule of tetraethyl 1,4-dioxo-1,4-bis(2,4,6-trimethylphenyl)but-2-ene-2,3-diyl diphosphonate (**V**) and (b) packing of molecules **V** in crystal according to the X-ray diffraction data.

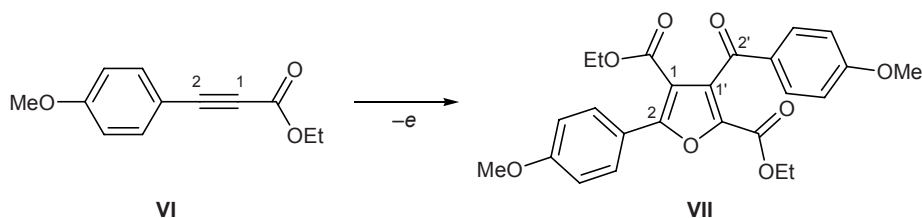
molecule **I**. This path leads to the formation of radical cation **D** in which the radical center is localized on the $C^{1'}$ atom directly linked to the acceptor group **X**. However, the process does not follow path *c*, for final products **II** and **III** cannot be formed in this case.

The contribution of path *b* with formation of intermediate **C** (in which the unpaired electron on $C^{2'}$ is conjugated with the donor alkyl- or methoxy-substituted aromatic ring) to the overall reaction pattern of radical cation **A** is likely to be insignificant. The mechanism of subsequent transformations of dication **B** into products **II** and **III** was discussed in [21]. The *trans* (*E*) structure of tetracarbonyl compounds **II** ($X =$

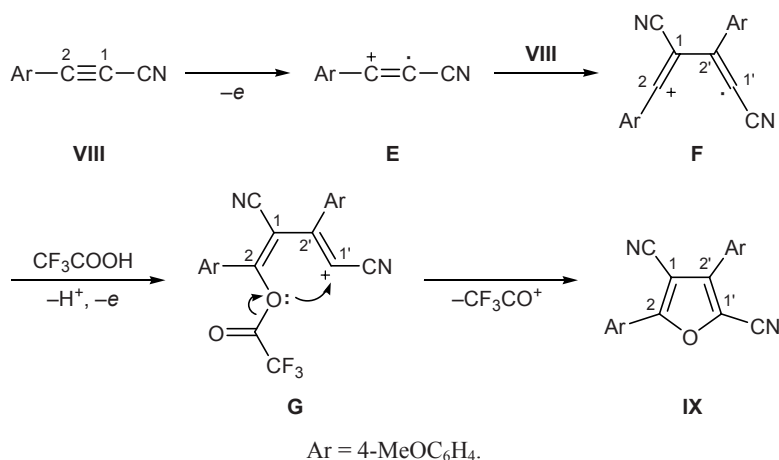
CO_2R , $COAr$; Scheme 1) was proved by X-ray analysis [16, 19]. The formation of *trans*-(*E*)-dioxo diphosphonates **II** [$X = PO(OEt)_2$; Scheme 1] [20] was confirmed by the X-ray diffraction data for tetraethyl 1,4-dioxo-1,4-bis(2,4,6-trimethylphenyl)but-2-ene-2,3-diyl diphosphonate (**V**) (Fig. 1) obtained by oxidation of diethyl (2,4,6-trimethylphenylethynyl)phosphonate (**IV**).

In the present work we examined one-electron oxidation of acetylenic compounds **I** having other electron-withdrawing groups **X** than those given in Scheme 1. The oxidation of ethyl 4-(4-methoxyphenyl)-2-oxobut-3-ynoate (**VI**, $X = COCO_2Et$) in the

Scheme 2.



Scheme 3.



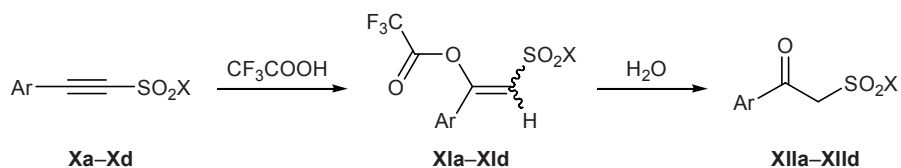
system $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ gave furan derivative **VII** (Scheme 2) via formation of new $\text{C}^1-\text{C}^{1'}$ bond, as in the reaction with trifluoromethyl ketones **I** ($\text{X} = \text{COCF}_3$; Scheme 1). Despite the lack of quantitative data characterizing electron-withdrawing power of the COCO_2Et group, we believe that this group should be analogous to COCF_3 , taking into account similar electronegativities and Hammett constants of the CF_3 and CO_2Me groups (Table 1).

Introduction of an even stronger electron-withdrawing cyano group into acetylenic substrate **I** ($\text{X} = \text{CN}$; Table 1) gives rise to a radically new mode of carbon-carbon bonding under conditions of one-electron oxidation. 3-(4-Methoxyphenyl)propenenitrile (**VIII**) in the system $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ is converted into substituted furan **IX** (Scheme 3) via formation of $\text{C}^1-\text{C}^{2'}$ bond. This reaction path may be interpreted as follows. Radical cation **E** reacts with substrate molecule **VIII** to give intermediate **F** (in a way similar to

path *c* in Scheme 1) in which the radical center on $\text{C}^{1'}$ is essentially stabilized due to electron-withdrawing effect of the cyano group (see above). The subsequent transformations through intermediate species **G** give furan **IX**.

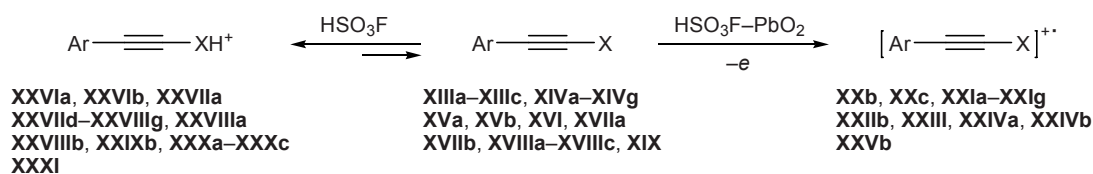
The oxidation of compounds **I** with $\text{X} = \text{CO}_2\text{R}$, COAr , COR , and $\text{PO}(\text{OEt})_2$ involves in total transfer of four electrons, leading to products **II** (Scheme 1). The oxidation of compounds **I**, **VI**, and **VIII** having much more powerful electron-withdrawing groups ($\text{X} = \text{COCF}_3$, COCO_2R , CN ; Table 1) is accompanied by transfer of only two electrons, and the products are furan derivatives **III**, **VII**, and **IX** (Schemes 1–3) [21]. Further rise in the acceptor power of the substituent [$\text{X} = \text{SO}_2\text{Ph}$, SO_2Me , SO_2CF_3 ; $EN = 9.0-9.4$, $\sigma_p = 0.67-0.91$; Table 1) radically changes the reactivity of acetylenic substrates in the reaction under study. Acetylenic sulfones **Xa-Xd** gave no oxidation products in the heterogeneous system $\text{PbO}_2-\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2$

Scheme 4.



$\text{X} = \text{Ph}$, $\text{R} = 4\text{-MeC}_6\text{H}_4$ (**a**), $2,4\text{-Me}_2\text{C}_6\text{H}_3$ (**b**), $4\text{-MeOC}_6\text{H}_4$ (**c**); $\text{X} = \text{CF}_3$, $\text{R} = 3,4\text{-Me}_2\text{C}_6\text{H}_3$ (**d**).

Scheme 5.



XIII, XX, XXVI, X = COMe, R = 4-MeC₆H₄ (**a**), 2,4,6-Me₃C₆H₂ (**b**), 2,3,5,6-Me₄C₆H (**c**), Me₅C₆ (**d**); **XIV, XXI, XXVII**, X = CPh, R = 2,4,6-Me₃C₆H₂ (**a**), 2,3,5,6-Me₄C₆H (**b**), Me₅C₆ (**c**), 2,3,5,6-Me₄-4-PhCOC≡CC₆ (**d**), 2,3,5,6-Me₄-4-O₂NC₆ (**e**), 4-MeOC₆H₄ (**f**), 4-MeO-3-O₂NC₆H₃ (**g**); **XV, XXII, XXVIII**, X = COCF₃, R = 2,3,5,6-Me₄-4-CF₃COC≡CC₆; **XVI, XXIII**, X = CO₂H, R = 4-MeOC₆H₄; **XVII, XXIV, XXIX**, X = CO₂Me, R = 4-MeOC₆H₄ (**a**); X = CO₂Et, R = 4-MeO-3-O₂NC₆H₃ (**b**); **XVIII, XXV, XXX**, X = COCO₂Et, R = Ph (**a**), 2,4,6-Me₃C₆H₂ (**b**), 4-O₂NC₆H₄ (**c**); **XIX, XXXI**, X = SO₂Ph, R = Ph.

(20°C, 20 h; the reaction mixture was treated with water) but were converted into oxo sulfones **XIIa–XIIId** (Scheme 4). In this case, lead(IV) oxide was not consumed during the process due to high oxidative potential of compounds **Xa–Xd**. Benzoylmethyl sulfones **XIIa–XIIId** were also formed from acetylenic sulfones **Xa–Xd** on keeping in a mixture of trifluoroacetic acid with methylene chloride in the absence of PbO₂, other conditions being equal (20°C, 2 h; treatment with water). Monitoring of the reaction course by thin-layer chromatography confirmed slow transformation of sulfones **Xa–Xd** in a mixture of anhydrous CF₃CO₂H and CH₂Cl₂. These data suggest initial addition of trifluoroacetic acid at the triple bond in molecule **Xa–Xd** with formation of trifluoroacetate **XIa–XIId**, followed by hydrolysis to produce final oxo sulfone **XIIa–XIIId** (Scheme 4). Such addition reactions are typical of acetylenic sulfones [36–38]. They may

follow both electrophilic [36] and nucleophilic mechanism of addition at a triple carbon–carbon bond [36–38]. The nucleophilic mechanism seems to be more probable, taking into account activating effect of the electron-withdrawing sulfonyl group [36]. Presumably, acetylenic nitro compounds ArC≡CX (X = NO₂) in the system CF₃CO₂H–CH₂Cl₂–PbO₂ should react in a way similar to sulfones **Xa–Xd** since the nitro group is a powerful electron acceptor (Table 1). However, such substrates were not studied.

Radical cations derived from acetylenic compounds were detected and characterized by ESR spectroscopy in the oxidation with HSO₃F–PbO₂ at –80°C. Radical cations **XXb, XXc, XXIa–XXIg, XXII, XXIII, XXIVa, XXIVb**, and **XXVb** were generated from compounds **XIIIb, XIIIc, XIVa–XIVg, XV, XVI, XVIIa, XVIIb**, and **XVIIIb**, respectively (Scheme 5; Table 2, Fig. 2). The parameters of radical cations

Table 2. ESR spectra of radical cations **XXb, XXc, XXIIb, XXIIc, XXIIe, XXIIg, XXIII, XXIVa, XXIVb, XXVb**, and **XXXIV**, generated from compounds **XIIIb, XIIIc, XIVb, XIVc, XIVe, XIVf, XVI, XVIIa, XVIIb, XVIIIb**, and **XXXIII**, respectively, in the system HSO₃F–PbO₂ at –80°C

Radical cation no.	Hyperfine coupling constants, ^a G	Pattern	g Factor
XXb	$a_{o-\text{Me}}^{\text{H}} = 11.7$ (6H), $a_{m-\text{Me}}^{\text{H}} = 10.5$ (6H), $a_{p-\text{H}}^{\text{H}} = 0.8$ (1H)	Multiplet, 13 line groups	2.0025
XXc	$a_{o-\text{Me}}^{\text{H}} = 11.4$ (6H), $a_{m-\text{Me}}^{\text{H}} = 10.4$ (6H), $a_{p-\text{Me}}^{\text{H}} = 1.0$ (3H)	Multiplet, 13 line groups	2.0030
XXIIb	$a_{o-\text{Me}}^{\text{H}} = 11.6$ (6H), $a_{m-\text{Me}}^{\text{H}} = 10.4$ (6H), $a_{p-\text{H}}^{\text{H}} = 0.8$ (1H)	Multiplet, 13 line groups	1.9977
XXIIc	$a_{o-\text{Me}}^{\text{H}} = 11.2$ (6H), $a_{m-\text{Me}}^{\text{H}} = 10.2$ (6H), $a_{p-\text{Me}}^{\text{H}} = 0.5$ (3H)	Multiplet, 13 line groups	2.0029
XXIIe	$a_{\text{Me}}^{\text{H}} = 11.5$ (12H)	Tridecet	2.0024
XXIIg	$a_{\text{OMe}}^{\text{H}} = a_{m-\text{H}}^{\text{H}} = 4.5$ (5H)	Sextet	2.0046
XXIII	$a_{\text{OMe}}^{\text{H}} = a_{m-\text{H}}^{\text{H}} = 4.0$ (5H)	Sextet	2.0038
XXIVa	$a_{\text{OMe}}^{\text{H}} = a_{m-\text{H}}^{\text{H}} = 4.0$ (5H)	Sextet	2.0032
XXIVb	$a_{\text{OMe}}^{\text{H}} = a_{m-\text{H}}^{\text{H}} = 4.5$ (4H)	Quintet	2.0036
XXVb	$a_{p-\text{Me}}^{\text{H}} = 12.6$ (3H), $a_{o-\text{Me}}^{\text{H}} = a_{m-\text{H}}^{\text{H}} = 2.1$ (8H)	Quartet of nonets	2.0031
XXXIV	$a_{o-\text{Me}}^{\text{H}} = 11.6$ (6H), $a_{m-\text{Me}}^{\text{H}} = 10.6$ (6H), $a_{p-\text{H}}^{\text{H}} = 1.0$ (1H), $a_{\text{CH}=\text{H}}^{\text{H}} = 0.4$ (1H)	Multiplet, 13 line groups	2.0026

^a *ortho*, *meta*, and *para* Positions with respect to the ethynyl group.

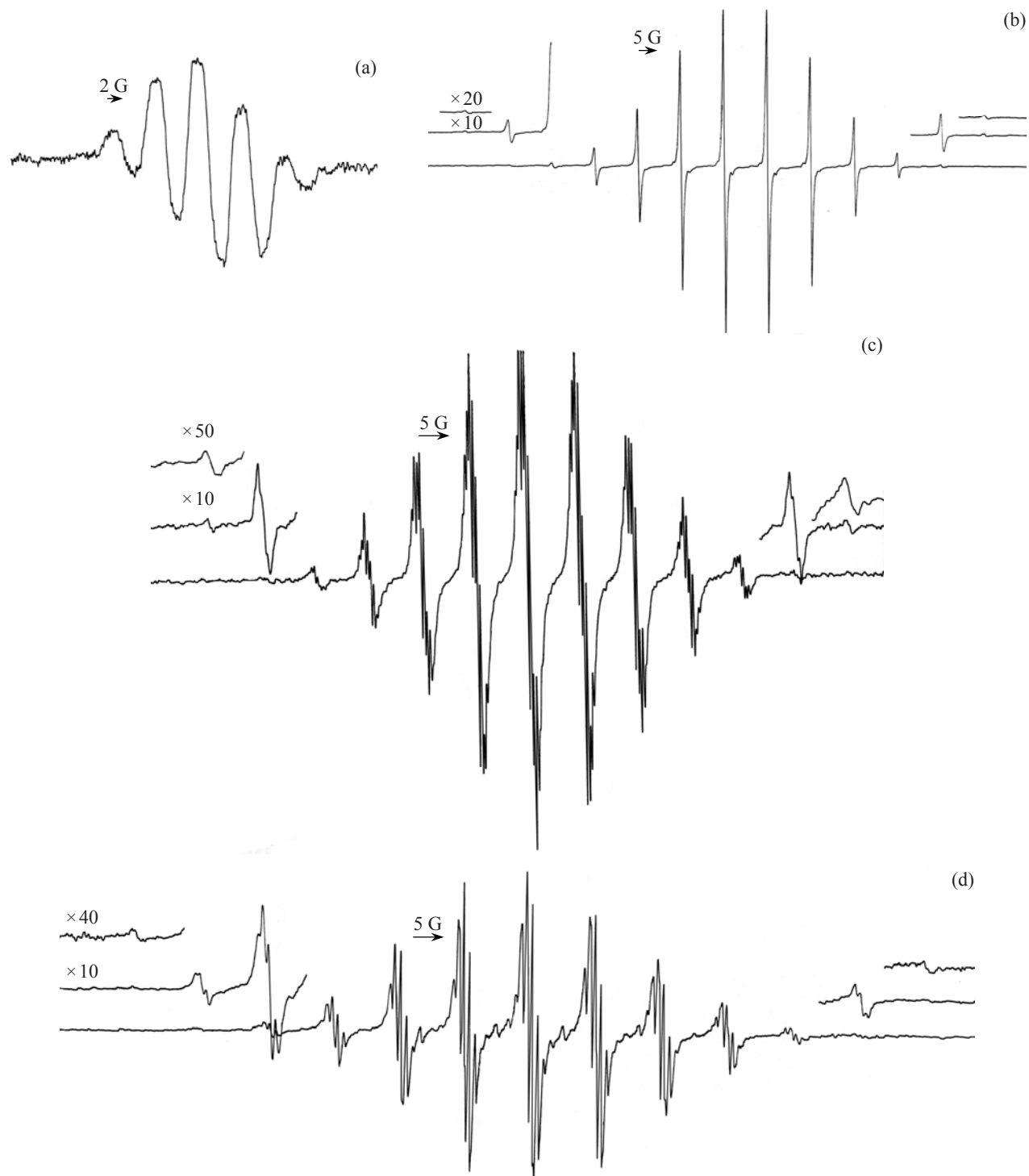


Fig. 2. ESR spectra of radical cations (a) **XXIVb**, (b) **XXIe**, (c) **XXIc**, and (d) **XXXIV** generated by oxidation of compounds **XVIIb**, **XIVe**, **XIVc**, and **XXXIII**, respectively, in the system $\text{HSO}_3\text{F}-\text{PbO}_2$ at -80°C .

XXIa, **XXId**, **XXIg**, and **XXII** were reported previously [19, 21].

Fluorosulfonic acid is a superacid capable of protonating triple-bonded carbon atoms in fairly basic acetylenic compounds with formation of vinyl type

cations and their subsequent transformation into vinyl fluorosulfonates or other products [39–43]. Therefore, we examined the stability of the acetylenic substrates under study toward fluorosulfonic acid. Compounds **XIIIa**, **XIIIb**, **XIVa**, **XIVd–XIVg**, **XV**, **XVIIb**,

Table 3. ^1H NMR spectra of cations **XXVIa**, **XXVIb**, **XXVIIIf**, **XXVIII**, **XXXa–XXXc**, and **XXXI** generated from acetylenic compounds **XIIIa**, **XIIIb**, **XIVf**, **XV**, **XVIIIa–XVIIIc**, and **XIX**, respectively, in HSO_3F at -80°C via protonation at the electron-withdrawing group

Ion no.	Chemical shifts δ , ppm
XXVIa	2.53 s (3H, MeCO), 3.08 s (3H, Me), 7.50 d (2H, H_{arom} , $J = 7.6$ Hz), 7.93 d (2H, H_{arom} , $J = 7.6$ Hz)
XXVIb	2.62 s (3H, MeCO), 2.75 s (6H, Me), 2.96 s (6H, Me), 8.60 s (1H, H_{arom})
XXVIIe	4.33 s (3H, OMe), 7.45 t (2H, m -H, $J = 7.4$ Hz), 7.85 d (2H, o -H, $J = 7.4$ Hz), 8.21 d (2H, H_{arom} , $J = 6.8$ Hz), 8.59 t (1H, p -H, $J = 7.4$ Hz), 8.71 d (2H, H_{arom} , $J = 6.8$ Hz)
XXVIII	2.67 s (Me)
XXXa	1.55 t (3H, Me, $J = 6.0$ Hz), 4.82 q (2H, OCH_2 , $J = 6.0$ Hz), 7.75–8.94 m (5H, H_{arom})
XXXb	1.56 t (3H, Me, $J = 6.1$ Hz), 2.55 s (3H, Me), 2.83 s (6H, Me), 4.82 q (2H, OCH_2 , $J = 6.1$ Hz), 7.57 s (2H, H_{arom})
XXXc	1.75 t (3H, Me, $J = 6.0$ Hz), 5.33 q (2H, OCH_2 , $J = 6.0$ Hz), 8.17 d (2H, H_{arom} , $J = 7.9$ Hz), 8.67 d (2H, H_{arom} , $J = 7.9$ Hz)
XXXI	7.44–8.17 m (Ph)

Table 4. ^{13}C NMR spectra of acetylenic compounds **XIIIa** and **XV** (CDCl_3 , 25°C) and the corresponding cationic species **XXVIa** and **XXVIII** formed by protonation at the carbonyl oxygen atom in HSO_3F at -80°C

Compound (ion) no.	Chemical shifts δ_{C} , ppm								
	ArCH ₃	CH ₃ or CF ₃	C=O ^a	C ¹	C ²	C ⁱ	C ^o	C ^m	C ^p
XIIIa	21.66	32.64	184.54	88.14	90.95	116.76	133.05	129.41	141.43
XXVIa	22.34	29.49	200.62	94.22	113.18	139.47	131.51	138.73	153.28
XV	18.13	114.96 q ($J_{\text{CF}} = 287$ Hz)	166.57 q ($J_{\text{CF}} = 42$ Hz)	92.04	97.83	122.40	139.78	–	–
XXVIII^b	19.04	115.83 q ($J_{\text{CF}} = 282$ Hz)	173.96 q ($J_{\text{CF}} = 44$ Hz)	99.51	126.64	136.87	146.70	–	–

^a C=OH⁺ in HSO_3F .^b Dication.

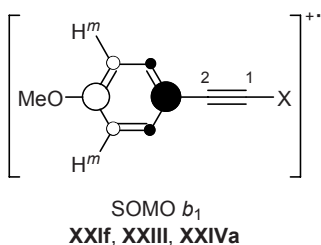
XVIIIa–XVIIIc, and **XIX** in HSO_3F at -80°C underwent protonation at the electron-withdrawing group to give cations **XXVIa**, **XXVIb**, **XXVIIa**, **XXVIIId–XXVIIg**, **XXVIII**, **XXIXb**, **XXXa–XXXc**, and **XXXI**, respectively (Scheme 5). Tables 3 and 4 contain the ^1H and ^{13}C NMR parameters of ions **XXVIa**, **XXVIb**, **XXVIIIf**, **XXVIII**, **XXXa–XXXc**, and **XXXI** in HSO_3F ; the corresponding parameters of **XXVIIa**, **XXVIIId**, **XXVIIe**, **XXVIIg**, and **XXIXb** were reported in [39, 40]. For comparison, the ^{13}C NMR spectra of precursors **XIIIa** and **XV** (CDCl_3 , 25°C) are given in Table 4.

The ^1H NMR spectra of solutions of acetylenic compounds **XIIIa**, **XIIIb**, **XIVf**, **XV**, **XVIIIa–XVIIIc**, and **XIX** in HSO_3F (Table 3) lacked signals in the region δ 6.40–6.90 ppm, which are typical of vinyl protons in the products of alkyne transformations in HSO_3F [40, 41]. Protonated species **XXVIa**, **XXVIb**,

XXVIIIf, **XXVIII**, **XXXa–XXXc**, and **XXXI** occur in equilibrium with their neutral precursors **XIIIa**, **XIIIb**, **XIVf**, **XV**, **XVIIIa–XVIIIc**, and **XIX** and are stable under conditions ensuring their “long life” (-80°C). Unprotonated initial compounds **XIIIa–XIIIc**, **XIVa–XIVg**, **XVa**, **XVb**, **XVI**, **XVIIa**, **XVIIb**, **XVIIIa–XVIIIc**, and **XIX** undergo one-electron oxidation to radical cations **XX–XXV** by the action of PbO_2 [12, 13, 19] (Scheme 5).

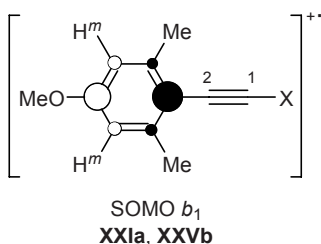
Radical cations derived from acetylenic compounds are very unstable and highly reactive intermediates [44, 45]. We succeeded in detecting relatively stable radical cation species in the system $\text{HSO}_3\text{F–PbO}_2$ (-80°C) only for substrates **XIIIb**, **XIIIc**, **XIVa–XIVg**, **XV**, **XVI**, **XVIIa**, **XVIIb**, and **XVIIIb** having methoxy or alkyl groups in the aromatic ring (Table 2, Fig. 2). The ESR spectra of p -methoxyphenyl-substituted radical cations **XXIf**, **XXIII**, and **XXIVa** dis-

played sextets with hyperfine coupling constants (HCC) a^H of 4–4.5 G (Table 2). The spectral pattern is determined by interaction of the unpaired electron with three protons of the methoxy group and two aromatic protons in the *meta* positions with the same HCCs (cf. the ESR spectra of methoxybenzenes [12, 44, 46, 47]). These radical cations are characterized by SOMO b_1 (singly occupied molecular orbital that is the former highest occupied molecular orbital of the neutral molecule [2, 3]). According to published data, radical cations with such SOMO feature considerable spin density transfer to the C¹ atom of the acetylene fragment [44].



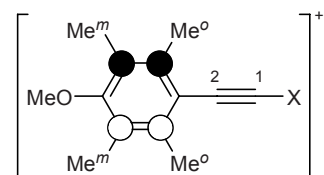
XXIf, X = CPh; **XXIII**, X = CO₂H; **XXIVa**, X = CO₂Me.

Replacement of one hydrogen atom in the *meta* position of *p*-methoxyphenyl derivatives **XIVg** and **XVIIb** by a nitro group simplifies the ESR spectra of the corresponding radical cations **XXIg** and **XXIVb** which show quintet signals (Fig. 2a). The unpaired electron in radical cations **XXIa** and **XXVb** derived from 2,4,6-trimethylphenylacetylenes also occupies SOMO b_1 [19] (Table 2).



XXIa, X = CPh; **XXVb**, X = CO₂Et.

The SOMO in radical cations **XXb**, **XXc**, **XXIb–XXIe**, and **XXII** having tetra- and pentamethyl-substituted aromatic rings is characterized by a_2 symmetry with a small contribution of the acetylenic bond (Table 2; Fig. 2b, c). The HCC for protons in the *ortho*-methyl groups is a^H = 11.2–11.7 G, and that for protons in the *meta*-methyl groups is a^H = 10.2–10.5 G (Table 2; cf. [12, 44, 48, 49]). The ESR spectrum of radical cation **XXXIV** derived from fluorosulfonate **XXXIII** which was formed by reaction of trifluoro-

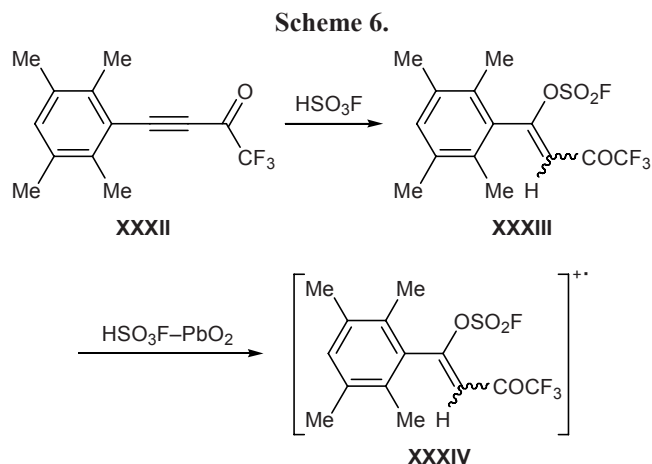


SOMO a_2

XXb, XXc, XXIb–XXIe, XXII

X = COMe, CPh, COCF₃; R = H, Me, O₂N, etc.

methyl ketone **XXXII** with CF₃SO₃H at –80°C [40, 41] (Scheme 6) showed an additional coupling with the vinyl proton, a^H = 0.4 G (Table 2, Fig. 2d).



Differences in the spin density distribution (i.e., different types of SOMO) in radical cations derived from acetylenic substrates are responsible for different paths of transformation of alkynes under conditions of one-electron oxidation. Substrates giving rise to radical cations with b_1 type of SOMO and reactive carbon atoms at the triple bond are converted into oxidative dimerization products **II** and **III** (Scheme 1) in good yields [16–21]. Radical cations having SOMO a_2 , where the acetylenic bond contributes little to delocalization of spin density, react along other pathways with formation of considerable amounts of tarry products, while the yields of structures like **II** and **III** are small [19, 21].

Thus the results of our studies [16–21] on the transformations of radical cations derived from acetylenic compounds with electron-withdrawing groups demonstrated the possibility of obtaining new synthetically important polyfunctional compounds via one-electron oxidation of alkynes. Initially formed radical cations were characterized by ESR spectroscopy, and mechanisms were proposed for their subsequent transformations into oxidative dimerization products.

EXPERIMENTAL

The IR spectra were recorded from solutions in chloroform on a Specord 75IR spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-500 spectrometer at 500 and 125.76 MHz, respectively, using CDCl_3 as solvent and reference (CHCl_3 , δ 7.25 ppm; CDCl_3 , δ_{C} 77.0 ppm). The ^1H and ^{13}C NMR spectra of solutions in HSO_3F were obtained on a Bruker Avance 400 instrument at 400 and 100 MHz, respectively, using methylene chloride as internal reference (δ 5.32, δ_{C} 77.0 ppm). The mass spectra (electron impact, 70 eV) were recorded on an MKh-1321 mass spectrometer with direct sample admission into the ion source; batch inlet probe temperature 100–120°C. X-Ray analysis was performed on a Smart Apex automatic diffractometer (graphite monochromator, MoK_α irradiation, ω - θ scanning). The ESR spectra of radical cations **XXb**, **XXc**, **XXIa–XXIg**, **XXII**, **XXIII**, **XXIVa**, **XXIVb**, and **XXVb** in the system $\text{HSO}_3\text{F-PbO}_2$ were measured at -80°C on a Bruker spectrometer; the spectra were simulated using WINEPR SimFonia program. The procedure for generation of radical cations **XXVIa**, **XXVIb**, **XXVIIa**, **XXVIIId–XXVIIg**, **XXVIII**, **XXIXb**, **XXXa–XXXc**, and **XXXI** in HSO_3F was reported previously [39, 40].

The procedures for the synthesis and properties of diethyl (2,4,6-trimethylphenylethynyl)phosphonate (**IV**) [20], 4-arylbut-3-yn-2-ones **XIIIa–XIIIc** [21, 43], 1,3-diarylprop-2-yn-1-ones **XIVa**, **XIVb**, **XIVd**, and **XIVg** [19, 39], 1,1,1-trifluoro-4-[2,3,5,6-tetramethyl-4-(4,4,4-trifluoro-3-oxobut-1-yn-1-yl)phenyl]but-3-yn-2-one (**XV**) [21], 3-arylpropynoic acids and their esters **XVI**, **XVIIa**, and **XVIIb** [16, 17, 40], and ethyl 4-aryl-2-oxobut-3-ynoates **VI** and **XVIIIb** [43] were described previously.

3-(4-Methoxyphenyl)propynenitrile (VIII) was synthesized according to the procedure described in [50]. Yield 10%, mp 76–78°C; published data [50]: mp 78–80°C. IR spectrum, ν , cm^{-1} : 2210 ($\text{C}\equiv\text{C}$), 2270 ($\text{C}\equiv\text{N}$). ^1H NMR spectrum, δ , ppm: 3.85 s (3H, OCH_3), 6.99 d (2H, H_{arom} , $J = 8.1$ Hz), 7.54 d (2H, H_{arom} , $J = 8.1$ Hz).

1-Aryl-2-(phenylsulfonyl)ethynes **Xa–Xc** and **XIX** were synthesized as described in [51].

2-(4-Methylphenyl)ethynyl phenyl sulfone (Xa). Yield 60%, mp 87–88°C; published data [52]: mp 87–88°C. IR spectrum: ν 2190 cm^{-1} ($\text{C}\equiv\text{C}$). ^1H NMR spectrum, δ , ppm: 2.37 s (3H, CH_3), 7.17 d (2H, H_{arom} , $J = 8.0$ Hz), 7.41 d (2H, H_{arom} , $J = 8.0$ Hz), 7.59 t (2H,

H_{arom} , $J = 7.6$ Hz), 7.67 t (1H, H_{arom} , $J = 7.6$ Hz), 8.07 d (2H, H_{arom} , $J = 7.6$ Hz).

2-(2,4-Dimethylphenyl)ethynyl phenyl sulfone (Xb). Yield 56%, mp 85–88°C. ^1H NMR spectrum, δ , ppm: 2.32 s (3H, CH_3), 2.33 s (3H, CH_3), 6.97 d (1H, H_{arom} , $J = 7.9$ Hz), 7.02 s (1H, H_{arom}), 7.34 d (1H, H_{arom} , $J = 7.9$ Hz), 7.58 t (2H, H_{arom} , $J = 7.6$ Hz), 7.67 t (1H, H_{arom} , $J = 7.6$ Hz), 8.07 d (2H, H_{arom} , $J = 7.6$ Hz). Found, %: C 71.15; H 5.30. $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}$. Calculated, %: C 71.08; H 5.22.

2-(4-Methoxyphenyl)ethynyl phenyl sulfone (Xc). Yield 73%, mp 89–90°C; published data [52]: mp 103–105°C. IR spectrum: ν 2170 cm^{-1} ($\text{C}\equiv\text{C}$). ^1H NMR spectrum, δ , ppm: 3.82 s (3H, OCH_3), 6.86 d (2H, H_{arom} , $J = 8.7$ Hz), 7.46 d (2H, H_{arom} , $J = 8.7$ Hz), 7.58 t (2H, H_{arom} , $J = 7.6$ Hz), 7.66 t (1H, H_{arom} , $J = 7.6$ Hz), 8.06 d (2H, H_{arom} , $J = 7.6$ Hz).

2-(3,4-Dimethylphenyl)ethynyl trifluoromethyl sulfone (Xd) was synthesized according to the procedure reported in [38]. Yield 35%, oily substance. ^1H NMR spectrum, δ , ppm: 2.29 s (3H, CH_3), 2.33 s (3H, CH_3), 7.22 d (1H, H_{arom} , $J = 7.8$ Hz), 7.43 d (1H, H_{arom} , $J = 7.8$ Hz), 7.45 s (1H, H_{arom}). Found, %: C 50.31; H 3.40. $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_2\text{S}$. Calculated, %: C 50.38; H 3.46.

Phenyl phenylethynyl sulfone (XIX). Yield 64%, mp 67–68°C; published data [52]: mp 68–69°C. IR spectrum: ν 2190 cm^{-1} ($\text{C}\equiv\text{C}$). ^1H NMR spectrum, δ , ppm: 7.36 t (2H, H_{arom} , $J = 7.5$ Hz), 7.47 t (1H, H_{arom} , $J = 7.5$ Hz), 7.52 d (2H, H_{arom} , $J = 7.5$ Hz), 7.60 t (2H, H_{arom} , $J = 7.7$ Hz), 7.68 t (1H, H_{arom} , $J = 7.7$ Hz), 8.08 d (2H, H_{arom} , $J = 7.7$ Hz).

3-(2,3,4,5,6-Pentamethylphenyl)-1-phenylprop-2-yn-1-one (XIVc) was synthesized according to the procedure described in [18]. Yield 28%, mp 156–158°C. IR spectrum, ν , cm^{-1} : 1620 ($\text{C}=\text{O}$), 2170 ($\text{C}\equiv\text{C}$). ^1H NMR spectrum, δ , ppm: 2.23 s (6H, CH_3), 2.26 s (6H, CH_3), 2.56 s (3H, CH_3), 7.22 t (2H, H_{arom} , $J = 7.1$ Hz), 7.62 t (1H, H_{arom} , $J = 7.1$ Hz), 8.24 d (2H, H_{arom} , $J = 7.1$ Hz). Mass spectrum, m/z (I_{rel} , %): 276 [M]⁺ (84), 261 (58), 246 (15), 233 (29), 218 (10), 199 (20), 141 (20), 105 (100), 77 (55). Found, %: C 87.01; H 7.25. $\text{C}_{20}\text{H}_{20}\text{O}$. Calculated, %: C 86.92; H 7.29. M 276.15.

Ethyl 4-aryl-2-oxobut-3-ynoates **XVIIIa** and **XVIIIc** were synthesized according to the procedure described in [53].

Ethyl 2-oxo-4-phenylbut-3-ynoate (XVIIIa). Yield 25%, mp 31–32°C; published data [53]: oily

substance. IR spectrum, ν , cm^{-1} : 1680 (C=O), 1730 (C=O), 2195 (C \equiv C). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.40 t (3H, CH_3 , $J = 7.3$ Hz), 4.39 q (2H, OCH_2 , $J = 7.3$ Hz), 7.40 t (2H, H_{arom} , $J = 7.8$ Hz), 7.50 t (1H, H_{arom} , $J = 7.8$ Hz), 7.65 d (2H, H_{arom} , $J = 7.8$ Hz). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 13.91, 63.22, 87.01, 97.88, 119.02, 128.76, 131.82, 133.72, 159.20, 169.55.

Ethyl 4-(4-nitrophenyl)-2-oxobut-3-ynoate (XVIIIc). Yield 20%, mp 80–82°C. IR spectrum, ν , cm^{-1} : 1680 (C=O), 1720 (C=O), 2200 (C \equiv C). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.42 t (3H, CH_3 , $J = 7.1$ Hz), 4.41 q (2H, OCH_2 , $J = 7.1$ Hz), 7.40 d (2H, H_{arom} , $J = 8.3$ Hz), 8.27 d (2H, H_{arom} , $J = 8.3$ Hz). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 13.91, 63.60, 89.20, 93.25, 123.84, 125.56, 134.29, 149.03, 158.73, 169.20. Found, %: C 58.51; H 3.65; N 5.75. $\text{C}_{12}\text{H}_9\text{NO}_5$. Calculated, %: C 58.30; H 3.67; N 5.67.

1,1,1-Trifluoro-4-(2,3,5,6-tetramethylphenyl)but-3-yn-2-one (XXXII) was synthesized according to the procedure described in [54]. Yield 42%, mp 61–63°C. ^1H NMR spectrum, δ , ppm: 2.24 s (6H, CH_3), 2.41 s (6H, CH_3), 7.11 s (1H, H_{arom}). Found, %: C 66.09; H 5.12. $\text{C}_{14}\text{H}_{13}\text{F}_3\text{O}$. Calculated, %: C 66.14; H 5.15.

Tetraethyl 1,4-dioxo-1,4-bis(2,4,6-trimethylphenyl)but-2-ene-2,3-diylidiphosphonate (V) was synthesized from diethyl 2-(2,4,6-trimethylphenyl)ethynylphosphonate (IV) [20]. A 0.60×0.50×0.40-mm single crystal of V for X-ray analysis (Fig. 1) was obtained by slow evaporation of a solution of V in hexane–ethyl acetate at room temperature over a period of several days. Monoclinic crystal system; $\text{C}_{15}\text{H}_{21}\text{O}_4\text{P}$; unit cell parameters [at 293(2) K]: $a = 10.835(3)$, $b = 16.750(4)$, $c = 8.631(2)$ Å; $\beta = 97.378(5)^\circ$; $V = 1553.4(6)$ Å 3 ; $Z = 4$; space group $P2(1)/c$; $d_{\text{calc}} = 1.267$ g/cm 3 ; $\mu = 0.187$ mm $^{-1}$; $1.90 \leq \theta \leq 23.99^\circ$. Total of 7531 reflections were measured, 2429 of which were independent ($R_{\text{int}} = 0.0264$); divergence factors $R_1 = 0.0602$ [for reflections with $I > 2\sigma(I)$], $wR_2 = 0.1497$ (for all reflections). The structure was solved by the direct method and was refined by the least-squares procedure with respect to F_{hkl}^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were visualized from the Fourier difference syntheses, and their positions were refined in isotropic approximation. All calculations were performed using SHELXTL v. 6.10 software package [55].

The procedure for the oxidation of acetylenic compounds VI and VIII to substituted furans VII and

IX, respectively, in the system $\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ was described in [21].

Ethyl 4-(2-ethoxy-1,2-dioxoethyl)-3-(4-methoxybenzoyl)-5-(4-methoxyphenyl)furan-2-carboxylate (VII) was obtained by oxidation of 56 mg (0.24 mmol) of compound VI with 58 mg (0.24 mmol) of PbO_2 in a mixture of 0.1 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 3 ml of CH_2Cl_2 at 20°C (reaction time 1.5 h). Yield 14 mg (24%), oily substance. IR spectrum, ν , cm^{-1} : 1680, 1730 (C=O). ^1H NMR spectrum, δ , ppm: 0.98 t (3H, CH_3 , $J = 7.0$ Hz), 1.06 t (3H, CH_3 , $J = 7.1$ Hz), 3.87 s (6H, CH_3O), 3.93 q (2H, OCH_2 , $J = 7.1$ Hz), 4.12 q (2H, OCH_2 , $J = 7.0$ Hz), 6.94 d (2H, H_{arom} , $J = 8.7$ Hz), 6.99 d (2H, H_{arom} , $J = 8.6$ Hz), 7.77 d (2H, H_{arom} , $J = 8.7$ Hz), 7.90 d (2H, H_{arom} , $J = 8.6$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 13.53 q ($J = 126.6$ Hz), 13.56 q ($J = 127.5$ Hz), 55.47 q ($J = 144.51$ Hz), 55.50 q ($J = 144.7$ Hz), 61.65 t.q ($J = 149.2$, 4.5 Hz), 62.54 t.q ($J = 148.3$, 4.2 Hz), 113.83 d.d ($J = 161.8$, 4.5 Hz), 114.21 d.d ($J = 161.8$, 4.7 Hz), 118.85 s, 120.43 t ($J = 7.9$ Hz), 130.37 t ($J = 7.4$ Hz), 130.63 d.d ($J = 162.5$, 7.0 Hz), 131.70 d.d ($J = 161.1$, 7.0 Hz), 132.41 s, 139.88 s, 157.39 t ($J = 2.7$ Hz), 161.82 t ($J = 2.5$ Hz), 162.21 m, 164.10 m, 162.30 s, 180.52 s, 188.00 t ($J = 3.8$ Hz). Mass spectrum, m/z (I_{rel} , %): 480 [M] $^+$ (15), 407 (61), 135 (100). Found, %: C 64.85; H 5.08. $\text{C}_{27}\text{H}_{24}\text{O}_9$. Calculated, %: C 65.00; H 5.03. M 480.14.

2,4-Bis(4-methoxyphenyl)furan-3,5-dicarbonitrile (IX) was obtained by oxidation of 160 mg (1.0 mmol) of compound VIII with 245 mg (1.0 mmol) of PbO_2 in a mixture of 0.4 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 4 ml of CH_2Cl_2 at 20°C (reaction time 2 h). Yield 16 mg (10%), mp 132–134°C. ^1H NMR spectrum, δ , ppm: 3.81 s (3H, OCH_3), 3.86 s (3H, OCH_3), 6.85 d (2H, H_{arom} , $J = 8.9$ Hz), 6.98 d (2H, H_{arom} , $J = 8.5$ Hz), 7.31 d (2H, H_{arom} , $J = 8.5$ Hz), 7.43 d (2H, H_{arom} , $J = 8.9$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 55.37, 55.39, 109.15, 110.07 (C \equiv N), 111.49 (C \equiv N), 114.45, 114.94, 120.02, 120.25, 122.22, 128.50, 128.90, 130.46, 154.86, 160.49, 161.28. Mass spectrum, m/z (I_{rel} , %): 330 [M] $^+$ (100), 315 (18), 276 (17), 190 (12), 135 (20). Found, %: C 72.83; H 4.35; N 8.55. $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3$. Calculated, %: C 72.72; H 4.27; N 8.48. M 330.10.

Keto sulfones XIIIa–XIII d were obtained from ethynyl sulfones Xa–Xd according to the procedure analogous to the oxidation of acetylenic compounds but without PbO_2 [21].

1-(4-Methylphenyl)-2-(phenylsulfonyl)ethanone (XIIIa) was obtained from 100 mg (0.39 mmol) of

compound **Xa** in a mixture of 0.15 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 2 ml of CH_2Cl_2 at 20°C (reaction time 2 h). Yield 48 mg (45%), mp $125\text{--}126^\circ\text{C}$. IR spectrum: $\nu(\text{C}=\text{O})$ 1690 cm^{-1} . ^1H NMR spectrum, δ , ppm: 2.41 s (3H, CH_3), 4.70 s (2H, CH_2), 7.27 d (2H, H_{arom} , $J = 8.1$ Hz), 7.54 t (2H, H_{arom} , $J = 7.6$ Hz), 7.65 t (1H, H_{arom} , $J = 7.6$ Hz), 7.83 d (2H, H_{arom} , $J = 8.1$ Hz), 7.88 d (2H, H_{arom} , $J = 7.6$ Hz). Found, %: C 65.65; H 5.10. $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}$. Calculated, %: C 65.67; H 5.14.

1-(2,4-Dimethylphenyl)-2-(phenylsulfonyl)ethanone (XIb) was obtained from 50 mg (0.19 mmol) of compound **Xb** in a mixture of 0.1 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 2 ml of CH_2Cl_2 at 20°C (reaction time 2 h). Yield 42 mg (76%), mp $100\text{--}102^\circ\text{C}$. IR spectrum: ν 1680 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 2.35 s (3H, CH_3), 2.40 s (3H, CH_3), 4.68 s (2H, CH_2), 7.05–7.08 m (2H, H_{arom}), 7.51–7.54 m (2H, H_{arom}), 7.63–7.66 m (2H, H_{arom}), 7.86 d (2H, H_{arom} , $J = 8.0$ Hz). Found, %: C 66.59; H 5.62. $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$. Calculated, %: C 66.64; H 5.59.

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (XIc) was obtained from 55 mg (0.20 mmol) of compound **Xc** in a mixture of 0.1 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 2 ml of CH_2Cl_2 at 20°C (reaction time 2 h). Yield 46 mg (80%), mp $108\text{--}110^\circ\text{C}$. IR spectrum: ν 1670 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 3.88 s (3H, OCH_3), 4.67 s (2H, CH_2), 6.94 d (2H, H_{arom} , $J = 8.9$ Hz), 7.54 t (2H, H_{arom} , $J = 7.6$ Hz), 7.65 t (1H, H_{arom} , $J = 7.6$ Hz), 7.88 d (2H, H_{arom} , $J = 7.6$ Hz), 7.92 d (2H, H_{arom} , $J = 8.9$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 55.60, 63.48, 114.09, 128.56, 128.91, 129.14, 131.86, 134.12, 138.85, 164.59, 186.12. Found, %: C 62.12; H 4.90. $\text{C}_{15}\text{H}_{14}\text{O}_4\text{S}$. Calculated, %: C 62.05; H 4.86.

1-(3,4-Dimethylphenyl)-2-(trifluoromethylsulfonyl)ethanone (XIId) was obtained from 116 mg (0.44 mmol) of compound **Xd** in a mixture of 0.2 ml of $\text{CF}_3\text{CO}_2\text{H}$ and 3 ml of CH_2Cl_2 at 20°C (reaction time 10 h). Yield 50 mg (40%), oily substance. ^1H NMR spectrum, δ , ppm: 2.34 s (3H, CH_3), 2.35 s (3H, CH_3), 4.80 s (2H, CH_2), 7.29 d (1H, H_{arom} , $J = 8.1$ Hz), 7.69 d (1H, H_{arom} , $J = 8.1$ Hz), 7.73 s (1H, H_{arom}). Mass spectrum, m/z (I_{rel} , %): 280 [$\text{M}]^+$ (16), 210 (11), 133 (100), 119 (15), 105 (25), 91 (13). Found, %: C 47.21; H 4.06. $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_3\text{S}$. Calculated, %: C 47.14; H 3.96. M 280.04.

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