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Oxidation of Aromatic Compounds: XIV.* Oxidation of Arylethynyl Ketones in the System $CF_3CO_2H–CH_2Cl_2–PbO_2$

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Abstract—Oxidation of arylethynyl ketones $ArC{\equiv}CCOCX_3$ (X = H, F) in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$ was studied on a preparative scale. The oxidation of 4-arylbut-3-yn-2-ones (X = H) involves transfer in total of four electrons, leading to (*E*)-3,4-bis(arylcarbonyl)hex-3-ene-2,5-diones. 4-Aryl-1,1,1-trifluorobut-3-yn-2-ones (X = F) are oxidized with transfer of only two electrons to produce 2-aryl-4-arylcarbonyl-5-trifluoromethyl-3-trifluoroacetylfurans. Possible mechanisms of radical-cation transformations of arylethynyl ketones into the final products are discussed.

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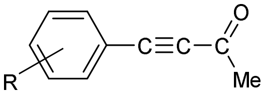
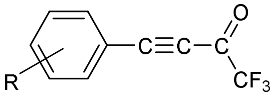
An α,β-acetylenic ketone (propynone) fragment was found in some naturally occurring compounds which exhibit interesting physiological properties [2]. The synthesis of ethynyl ketones [3–7], study of their transformations, and preparation on their base of various compounds, including those possessing biological activity [8], seem to be important. Our studies on one-electron oxidation of 3-arylpropynones, in particular of alkyl 3-arylpropynoates $ArC{\equiv}CCOR$ (R = OAlk) [9] and 1,3-diarylpropynones (R = Ar) [1, 4] allowed us to obtain new difficultly accessible tetracarbonyl derivatives in one step. The present communication continues the series of our publications on such reactions and describes radical-cation transformations of 4-arylbut-3-yn-2-ones **Ia**–**If** and 4-aryl-1,1,1-trifluorobut-3-yn-2-ones **IIa**–**IIi**.

Scheme 1 illustrates the oxidation of compounds **Ia**–**Id** to (*E*)-3,4-bis(arylcarbonyl)hex-3-ene-2,5-diones **IIIa**–**IIId** and of fluorinated analogs **IIa**–**IIc** to 2-aryl-4-arylcarbonyl-5-trifluoromethyl-3-trifluoroacetylfurans **IVa**–**IVc** in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$ through intermediate radical cations **Ia'**–**Id'** and **IIa'**–**IIc'**. The reaction conditions and product yields are given in table. As is seen from Scheme 1, methyl ketones **I** (X = H) and trifluoromethyl ketones **II** (X = F) react along different paths. The oxidation of methyl ketones **Ia**–**Id** having electron-donor methoxy and methyl groups in the aromatic ring (R = MeO, Me) gives tetracarbonyl compounds **IIIa**–**IIId** in up to 72% yield (see table, run nos. 1–4). Compounds **IIIa**–**IIId** were assigned *trans* (*E*) configuration of substituents at the double C=C bond, taking into account that analogous radical cation transformations of other arylpropynone derivatives lead to formation of just *trans* isomers of final dimeric ene structures [1, 4, 9].



Ia–**If**



IIa–**IIi**

I, R = 4-MeO (**a**), 3,4-$(MeO)_2$ (**b**), 3,4-OCH_2O (**c**), 2,4-Me_2 (**d**), 4-Me (**e**), H (**f**); **II**, R = 4-MeO (**a**), 3-F-4-MeO (**b**), 2,4-Me_2 (**c**), 3,4-$(MeO)_2$ (**d**), 2-Me-4,5-CH_2O_2 (**e**), 3,4-$(MeO)_2$-6-NO_2 (**f**), 2,3,5,6-Me_4-4-($CF_3CO–C{\equiv}C$) (**g**), 4-*t*-Bu (**h**), H (**i**).

4-(4-Methylphenyl)but-3-yn-2-one (**Ie**) and 4-phenylbut-3-yn-2-one (**If**) in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$ at 18–20°C in 4 and 30 h, respectively, were completely converted into mixtures of oligomeric products which contained no tetraketones like **III**. The reason is participation in the oxidation process of enol forms of methyl ketones, generated in the presence of trifluoroacetic acid. Enol structures possessing a conjugated enyne fragment are characterized by lower oxidation potentials than initial ketones **Ie** and **If**, and they relatively readily undergo one-electron oxidation which is likely to produce new C–C bonds in a nonselective fashion. Obviously, the rate of oxidation of

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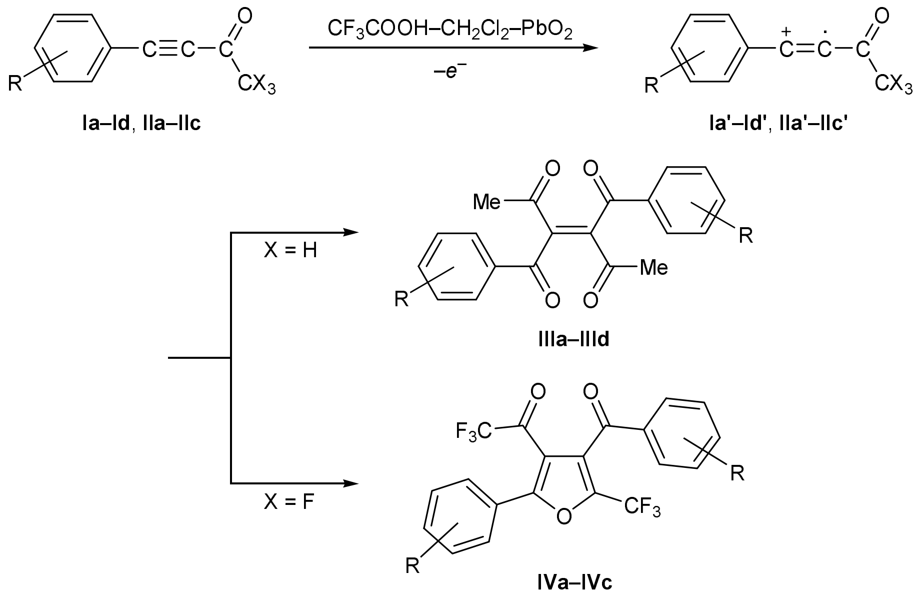
* For communication XIII, see [1].

Scheme 1.



I, X = H; **II**, X = F; **I**, **III**, R = 4-MeO (**a**), 3,4-$(MeO)_2$ (**b**), 3,4-CH_2O_2 (**c**), 2,4-Me_2 (**d**); **II**, **IV**, R = 4-MeO (**a**), 3-F-4-MeO (**b**), 2,4-Me_2 (**c**).

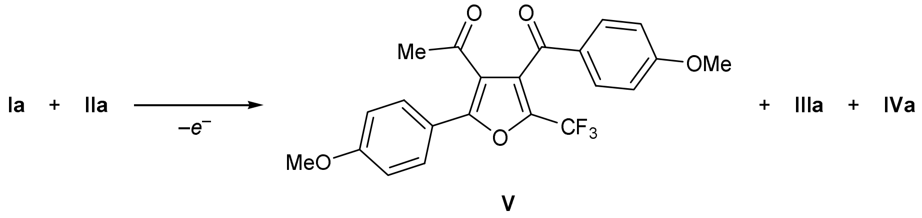
substrates **Ia**–**Id** to compounds **IIIa**–**IIId** is higher than the rate of their enolization.

Trifluoromethyl ketones **IIi** (R = H) and **IIh** (R = 4-Bu-*t*) cannot give rise to enol structures, and they are not oxidized in the system CF_3CO_2H–CH_2Cl_2–PbO_2. Unreacted compounds **IIi** and **IIh** were quantitatively recovered from the reaction mixtures after keeping at 18–20°C for 30 and 60 h, respectively. Introduction of one electron-donor methoxy group into the aromatic ring of trifluoromethyl arylethynyl ketones **II** (compounds **IIa** and **IIb**, R = MeO) or two methyl substituents (**IIc**) reduces the oxidation potential, and the reaction of these compounds with CF_3CO_2H–CH_2Cl_2–PbO_2 in 1–5 h gives furan derivatives **IVa**–**IVc** in 22–66% yield (see table, run nos. 5–7). Further increase in the number of methoxy substituents (**IId**, **IIf**) or introduction of a methylenedioxy group (**IIe**) favors profound oxidation to produce tarry products, and the corresponding substituted furans **IVd**–**IVf** were not isolated. An analogous behavior was observed by us previously for 2,3,4,5-tetraarylfurans [10].

Our preparative experiments on the oxidation of arylethynyl ketones **Ia**–**If** and **IIa**–**IIi** with CF_3CO_2H–CH_2Cl_2–PbO_2 showed that tetraketones **III** are readily obtained from compounds **Ia**–**Id** having one or two methoxy groups or more than one alkyl group in the aromatic ring. The series of trifluoromethyl ketones **II**, from which furan derivatives **IV** can be synthesized, is limited to substrates **IIa**–**IIc** possessing a methoxy group or several alkyl groups in the aromatic ring. Presumably, stronger oxidizing systems should involve inactive compounds **Ie**, **If**, **IIh**, and **IIi** in analogous radical-cation transformations.

We also tried to extend the synthetic potential of the reaction under study by joint oxidation of methyl ketone **Ia** and trifluoromethyl ketone **IIa**. As a result, we obtained a mixture containing compounds **IIIa**, **IVa**, and mixed oxidative dimerization product **V** (Scheme 2; see table, run no. 8). On the other hand, no mixed oxidation product was obtained by joint oxidation of ketones **IIa** and **IIi**, although the latter was taken in a threefold molar excess. In this case, we iso-

Scheme 2.



Oxidation of 4-arylbut-3-yn-2-ones **Ia**–**Id** and **IIa**–**IIc** in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$

Run no.	Initial compound no.	Amounts of reactants				Reaction conditions		Product (yield, %)
		I or **II**, mmol	PbO_2, mmol	CF_3COOH, ml	CH_2Cl_2, ml	temperature, °C	time, h	
1	**Ia**	1.0	1.0	0.4	3	0–2	1.5	**IIIa** (72)
2	**Ib**	0.25	0.25	0.1	2	0–2	1	**IIIb** (41)
3	**Ic**	0.53	0.53	0.25	3	0–2	1	**IIIc** (32)
4	**Id**	1.0	1.0	0.5	5	0–2	1.5	**IIId** (24)
5	**IIa**	0.88	0.88	0.34	2	0–2	1.5	**IVa** (22)
6	**IIb**	1.22	1.22	0.5	3	0–2	1	**IVb** (52)
7	**IIc**	0.44	0.44	0.2	3	18–20	5	**IVc** (66)
8	**Ia**+**IIa**	0.44 + 0.44	0.44	0.2	3	0–2	1	**IIIa** (31), **IVa** (10), **V** (8)
9	**IIa**+**IIi**	0.31 + 0.93	0.31	0.15	3	0–2	1	**IVa** (20)[a]

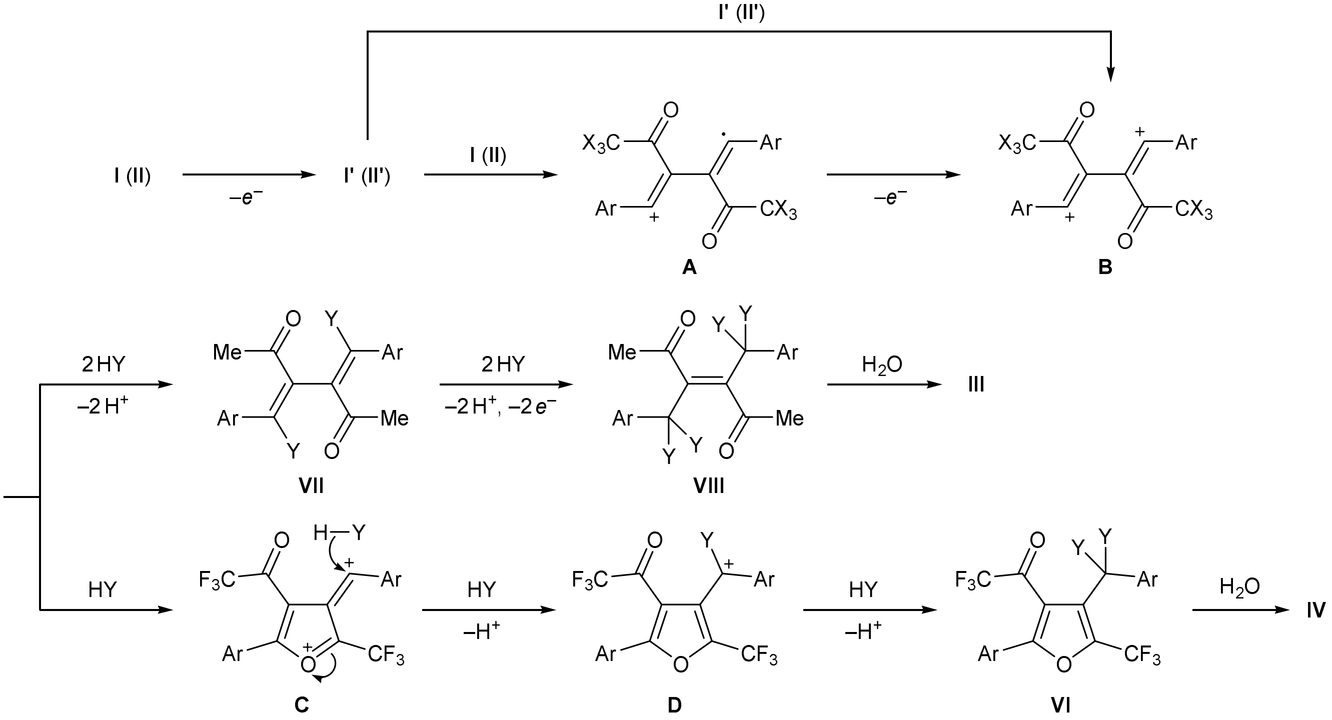
[a] Unreacted initial compound **IIi** was quantitatively recovered from the reaction mixture.

lated only substituted furan **IVa** as oxidative dimerization product of ketone **IIa** (run no. 9).

Intermediate formation of radical cations in the oxidation of arylethynyl ketones **I** and **II** was confirmed by the ESR spectrum of radical cation **IIg'** generated in the system $HSO_3F–PbO_2$ at –75°C (like radical cations derived from 1,3-diarylpropynones studied previously [1]). The ESR spectrum of **IIg'** consists of 13 lines corresponding to interactions of the unpaired electron with 12 protons of the four methyl groups [hyperfine coupling constant a^{H}_{Me} = 11.23 G (12H), g = 2.0026].

Scheme 3 illustrates possible paths of formation of tetraketones **III** and furan derivatives **IV** from ketones **I** and **II**. Initially formed radical cations **I'** and **II'** are capable of reacting with starting compounds **I** and **II** to

Scheme 3.



X = H, F; Y = CF_3COO.

produce dimeric radical cation **A** [11]. The subsequent one-electron oxidation of radical cation **A** gives the key intermediate, dication **B**. The latter may also be formed via dimerization of radical cation **I'** or **II'** [11]. The cationic centers in intermediate **B** derived from trifluoromethyl ketones **II** (X = F) are highly electrophilic due to the presence of electron-acceptor trifluoroacetyl groups; therefore, one of these centers is capable of reacting with such a relatively weakly nucleophilic center as the carbonyl oxygen atom of the $COCF_3$ group in the same molecule. Cyclic intermediate **C** thus formed is then converted into intermediate **D** and structure **VI**, and hydrolysis of the latter finally yields substituted furan **IV**. The formation of heterocyclization product **IV** in the oxidation of trifluoromethyl ketones **II** involves transfer of only two electrons in total.

Dication **B** generated from methyl ketones **I** (X =H) reacts predominantly with external nucleophiles, e.g., trifluoroacetic acid molecule, to produce diene structure **VII** (Scheme 3). Readily oxidizable diene **VII** loses two more electrons, and the subsequent reactions of cationic intermediates with trifluoroacetic acid lead to tetrakis(trifluoroacetate) **VIII** whose hydrolysis yields tetraketone **III**. The overall transformation path of methyl ketones **I** to tetraketones **III** involves transfer of four electrons.

Polycarbonyl compounds **IIIa**–**IIId**, **IVa**–**IVc**, and **V** may be promising as synthons for the preparation of various heterocyclic systems. As examples, Scheme 4 shows the reactions of tetraketone **IIIa** and substituted furan **IVb** with hydrazine. From compound **IIIa** we obtained 2,3,6,7-tetraazanaphthalene derivative **IX**. The reaction of **IVb** with hydrazine afforded cyclic product **X** which was difficult to dehydrate; this is typical of fluorinated ketones [12, 13].

Thus the results of the present work, as well as of the series of our previous studies [1, 4, 9, 14] on electron-transfer reactions of 3-arylpropynones, demonstrated the efficiency of radical-cation activation of 4-arylbut-3-yn-2-ones to oxidative dimerization with formation of new carbon–carbon bonds and prospects in using such reactions in the synthesis of new classes of organic compounds.

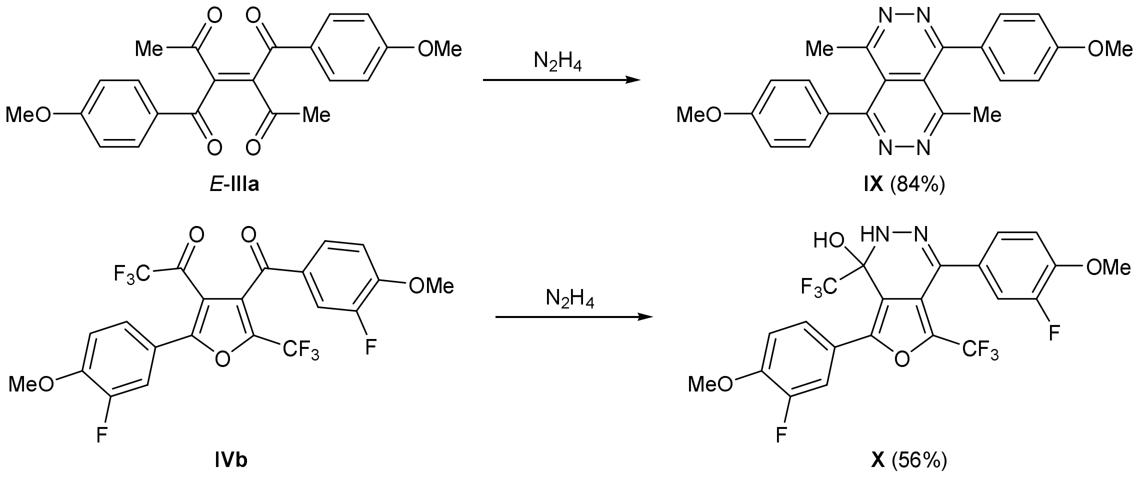
EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-500 spectrometer at 500, 125.76, and 470.7 MHz, respectively, using $CDCl_3$ as solvent. The chemical shifts were referenced to the solvent signal ($CHCl_3$, δ 7.25 ppm; $CDCl_3$, δ_C 77.0 ppm) or $CFCl_3$ (δ_F 0.0 ppm). The IR spectra were obtained from solutions in chloroform on a Specord 75IR instrument. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer. The ESR spectra were recorded on a Varian E-109 spectrometer. The detailed procedure for generation of radical cations in the system $HSO_3F–PbO_2$ and recording their ESR spectra was described previously [15]; the *g* factor was determined relative to diphenylpicrylhydrazyl.

Initial arylethynyl ketones **Ia**–**If**, **IIa**–**IIe**, and **IIg**–**IIi** were synthesized by acetylation and trifluoroacetylation of the corresponding arylacetylene lithium derivatives according to the procedures described in [5] and [16], respectively. Ketone **IIf** was obtained by nitration of **IId** with nitric acid in acetic acid [17].

4-(4-Methoxyphenyl)but-3-yn-2-one (Ia). Yield 68%, mp 43–45°C; published data [18]: mp 45–46°C.

Scheme 4.



^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 3.82 s (3H, OMe), 6.87 d (2H, H$_{arom}$, J = 8.9 Hz), 7.50 d (2H, H$_{arom}$, J = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 32.61, 55.40, 88.23, 91.50, 111.62, 114.36, 135.11, 161.67, 184.63.

4-(3,4-Dimethoxyphenyl)but-3-yn-2-one (Ib). Yield 37%, mp 100–102°C. ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H, Me), 3.88 s (3H, OMe), 3.91 s (3H, OMe), 6.85 d (1H, H$_{arom}$, J = 8.1 Hz), 7.05 s (1H, H$_{arom}$), 7.21 d (1H, H$_{arom}$, J = 8.1 Hz). Found, %: C 71.02; H 6.12. $C_{12}H_{12}O_3$. Calculated, %: C 70.57; H 5.92.

4-(3,4-Methylenedioxyphenyl)but-3-yn-2-one (Ic). Yield 34%, mp 76–78°C. ^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, Me), 6.01 s (2H, OCH_2O), 6.79 d (1H, H$_{arom}$, J = 8.1 Hz), 6.98 s (1H, H$_{arom}$), 7.13 d (1H, H$_{arom}$, J = 8.1 Hz). Found, %: C 70.43; H 4.16. $C_{11}H_8O_3$. Calculated, %: C 70.21; H 4.29.

4-(2,4-Dimethylphenyl)but-3-yn-2-one (Id). Yield 48%, oily substance. IR spectrum, ν, cm^{-1}: 1660 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 2.44 s (6H, Me), 6.99 d (1H, H$_{arom}$, J = 8.0 Hz), 7.06 s (1H, H$_{arom}$), 7.41 d (1H, H$_{arom}$, J = 8.0 Hz). Found, %: C 84.00; H 6.89. $C_{12}H_{12}O$. Calculated, %: C 83.69; H 7.02.

4-(4-Methylphenyl)but-3-yn-2-one (Ie). Yield 62%, oily substance, bp 95°C (2 mm). IR spectrum, ν, cm^{-1}: 1675 (C=O), 2200 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 2.41 s (3H, Me), 7.16 d (2H, H$_{arom}$, J = 7.9 Hz), 7.44 d (2H, H$_{arom}$, J = 7.9 Hz) (cf. [19]).

4-Phenylbut-3-yn-2-one (If). Yield 70%, bp 70°C (2 mm); published data [20]: bp 141°C (25 mm). IR spectrum, ν, cm^{-1}: 1665 (C=O), 2200 (C≡C).

1,1,1-Trifluoro-4-(4-methoxyphenyl)but-3-yn-2-one (IIa). Yield 42%, oily substance. IR spectrum, ν, cm^{-1}: 1690 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, OMe), 6.92 d (2H, H$_{arom}$, J = 8.1 Hz), 7.60 d (2H, H$_{arom}$, J = 8.1 Hz). ^{19}F NMR spectrum: δ_F –74.4 ppm, s (3F, $COCF_3$). ^{13}C NMR spectrum, δ_C, ppm: 55.45 q (J = 145.0 Hz), 84.06 s, 102.48 t (J = 4.7 Hz), 109.62 t (J = 8.5 Hz), 114.74 d.d (J = 162.6, 4.5 Hz), 114.97 q (J = 288.4 Hz), 136.28 d.d (J = 164.5, 7.0 Hz), 163.23 m, 166.95 q (J = 41.8 Hz). Mass spectrum: m/z 228 $[M]^+$. Found, %: C 58.04; H 2.97. $C_{11}H_7F_3O$. Calculated, %: C 57.90; H 3.09.

1,1,1-Trifluoro-4-(3-fluoro-4-methoxyphenyl)-but-3-yn-2-one (IIb). Yield 47%, mp 53–56°C. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 3.94 s (3H, OMe), 6.98 t (1H, H$_{arom}$, J = 8.4 Hz), 7.34 d (1H, H$_{arom}$, J = 9.8 Hz), 7.45 d (1H, H$_{arom}$, J = 8.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: –129.5 t (1F, F$_{arom}$, J = 9.8 Hz), –74.5 s (3F, $COCF_3$). ^{13}C NMR spectrum, δ_C, ppm: 56.28 q (J = 145.8 Hz), 83.61 s, 100.13 t (J = 8.9 Hz), 109.88 t (J = 8.9 Hz), 113.70 d (J = 162.3 Hz), 114.87 q (J = 288.0 Hz), 121.21 d.d.d (J = 166.2, 20.0, 7.2 Hz), 131.94 d.d.d (J = 166.6, 5.9, 3.4 Hz), 151.69 d.t (J = 249.0, 6.0 Hz), 151.97 d.m (J = 10.6 Hz), 166.88 q (J = 42.0 Hz). Mass spectrum: m/z 246 $[M]^+$. Found, %: C 54.69; H 2.50. $C_{11}H_6F_4O_2$. Calculated, %: C 53.67; H 2.46.

4-(2,4-Dimethylphenyl)-1,1,1-trifluorobut-3-yn-2-one (IIc). Yield 42%, oily substance, bp 60–62°C (0.5 mm). IR spectrum, ν, cm^{-1}: 1690 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 2.42 s (3H, Me), 6.94 d (1H, H$_{arom}$, J = 7.6 Hz), 7.02 s (1H, H$_{arom}$), 7.34 d (1H, H$_{arom}$, J = 7.6 Hz). Found, %: C 63.86; H 4.15. $C_{12}H_9F_3O$. Calculated, %: C 63.72; H 4.01.

4-(3,4-Dimethoxyphenyl)-1,1,1-trifluorobut-3-yn-2-one (IId). Yield 55%, mp 61–62°C. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, OMe), 3.94 s (3H, OMe), 6.89 d (1H, H$_{arom}$, J = 8.4 Hz), 7.09 s (1H, H$_{arom}$), 7.35 d (1H, H$_{arom}$, J = 8.4 Hz). Mass spectrum: m/z 258 $[M]^+$. Found, %: C 55.40; H 3.62. $C_{12}H_9F_3O_2$. Calculated, %: C 55.82; H 3.51.

1,1,1-Trifluoro-4-(2-methyl-4,5-methylenedioxyphenyl)but-3-yn-2-one (IIe). Yield 26%, mp 62–64°C. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, Me), 6.02 s (2H, OCH_2O), 6.74 s (1H, H$_{arom}$), 6.98 s (1H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 20.42, 87.59, 101.56, 102.08, 110.00, 110.49, 112.88, 115.04 q (J = 288.9 Hz), 141.5, 145.96, 151.99, 166.80 q (J = 30.9 Hz). Mass spectrum: m/z 256 $[M]^+$. Found, %: C 55.98; H 3.02. $C_{12}H_7F_3O_3$. Calculated, %: C 56.26; H 2.75.

4-(3,4-Dimethoxy-6-nitrophenyl)-1,1,1-trifluoro-but-3-yn-2-one (IIf). Yield 64%, mp 121–123°C. ^{1}H NMR spectrum, δ, ppm: 4.01 s (3H, OMe), 4.02 s (3H, OMe), 7.14 s (1H, H$_{arom}$), 7.77 s (1H, H$_{arom}$). ^{19}F NMR spectrum: δ_F –74.2 ppm, s (3F, $COCF_3$). Mass spectrum, m/z: 303 $[M]^+$. Found, %: C 47.77; H 2.89; N 4.70. $C_{12}H_8F_3NO_5$. Calculated, %: C 47.54; H 2.66; N 4.62.

1,1,1-Trifluoro-4-[2,3,5,6-tetramethyl-4-(4,4,4-trifluoro-3-oxobut-1-ynyl)phenyl]but-3-yn-2-one (IIg). Yield 21%, mp 118–120°C. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.46 s (12H, Me). ^{13}C NMR spectrum, δ_C, ppm: 18.13 q

(J = 128.2 Hz), 92.04, 97.83, 114.96 q (J = 288.7 Hz), 122.4, 139.79, 166.91 q (J = 42.4 Hz). ^{19}F NMR spectrum: δ_F –74.3 ppm, s (6F, $COCF_3$). Found, %: C 57.35; H 3.29. $C_{18}H_{12}F_6O_2$. Calculated, %: C 57.76; H 3.23.

4-(4-*tert*-Butylphenyl)-1,1,1-trifluorobut-3-yn-2-one (IIh). Yield 40%, oily substance. IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.33 s (9H, *t*-Bu), 7.46 d (2H, H_{arom}, J = 7.8 Hz), 7.61 s (1H, H_{arom}, J = 7.8 Hz). Found, %: C 65.86; H 5.43. $C_{14}H_{13}F_3O$. Calculated, %: C 66.14; H 5.15.

1,1,1-Trifluoro-4-phenylbut-3-yn-2-one (IIi). Yield 60%, oily substance; published data [16]: bp 93–94°C (24 mm). IR spectrum, ν, cm^{-1}: 1695 (C=O), 2190 (C≡C). ^{1}H NMR spectrum, δ, ppm: 7.45 t (2H, H_{arom}, J = 7.1 Hz), 7.56 t (1H, H_{arom}, J = 7.1 Hz), 7.67 d (1H, H_{arom}, J = 7.1 Hz). ^{19}F NMR spectrum: δ_F –74.5 ppm, s (3F, $COCF_3$). Mass spectrum: *m/z* 198 $[M]^+$.

General procedure for oxidation of 4-arylbut-3-yn-2-ones Ia–Id to (*E*)-3,4-bis(arylcarbonyl)hex-3-ene-2,5-diones IIIa–IIId and of 4-aryl-1,1,1-trifluorobut-3-yn-2-ones IIa–IIc to 2-aryl-4-arylcarbonyl-5-trifluoromethyl-3-trifluoroacetylfurans IVa–IVc and V in the system CF_3CO_2H–CH_2Cl_2–PbO_2. Compound **Ia–Id** or **IIa–IIc**, 0.25–1.22 mmol, was added to a solution of 0.1–0.5 ml of trifluoroacetic acid in 2–5 ml of methylene chloride under vigorous stirring at 0–20°C. Lead(IV) oxide, 0.25–1.22 mmol, was then added, and the mixture was stirred for 1–5 h (see table). When the reaction was complete, the mixture was poured into 50–250 ml of chloroform. The chloroform solution was washed with water, a saturated aqueous solution of sodium hydrogen carbonate, and water again and dried over Na_2SO_4. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate as eluent. The yields of compounds **IIIa–IIId**, **IVa–IVc**, and **V** were determined for the products isolated by chromatography.

3,4-Bis(4-methoxybenzoyl)hex-3-ene-2,5-dione (IIIa). mp 156–157°C. ^{1}H NMR spectrum, δ, ppm: 2.12 s (6H, Me), 3.86 s (6H, OMe), 6.97 d (4H, H_{arom}, J = 8.8 Hz), 7.93 d (4H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.16 q (J = 129 Hz), 55.55 q (J = 144.8 Hz), 114.41 d.d (J = 162.0, 3.9 Hz), 128.79, 131.22 d.d (J = 161.1, 6.9 Hz), 146.64, 164.54, 192.26, 195.80 q (J = 6.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 380 $[M]^+$ (3), 338 (4), 257 (30), 135 (100), 107 (6), 92 (9), 77 (15), 64 (4), 43 (10). Found, %: C 69.83; H 5.42. $C_{22}H_{20}O_6$. Calculated, %: C 69.46; H 5.30.

(*E*)-3,4-Bis(3,4-dimethoxybenzoyl)hex-3-ene-2,5-dione (IIIb). mp 176–179°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.16 s (6H, Me), 3.96 s (6H, OMe), 3.98 s (6H, OMe), 6.90 d (2H, H_{arom}, J = 8.3 Hz), 7.50 d (2H, H_{arom}, J = 8.3 Hz), 7.61 s (2H, H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 440 (18) $[M]^+$, 287 (24), 165 (100) $[3,4\text{-}MeO_2C_6H_3CO]^+$, 137 (9), 122 (8). Found, %: C 65.49; H 5.47. $C_{24}H_{24}O_8$. Calculated, %: C 65.45; H 5.49.

3,4-Bis(3,4-methylenedioxybenzoyl)hex-3-ene-2,5-dione (IIIc). mp 202–205°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (6H, Me), 6.07 s (4H, OCH_2O), 6.87 d (2H, H_{arom}, J = 8.5 Hz), 7.47 s (2H, H_{arom}), 7.48 d (2H, H_{arom}, J = 8.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 408 $[M]^+$ (11), 336 (2), 324 (2), 271 (17), 149 (100), 121 (20), 65 (18), 57 (12), 43 (19). Found, %: C 64.56; H 4.08. $C_{22}H_{16}O_3$. Calculated, %: C 64.71; H 3.95.

3,4-Bis(2,4-dimethylbenzoyl)hex-3-ene-2,5-dione (IIId). mp 184–185°C. ^{1}H NMR spectrum, δ, ppm: 2.09 s (6H, Me), 2.36 s (6H, Me), 2.68 s (6H, Me), 7.09 d (2H, H_{arom}, J = 7.8 Hz), 7.12 s (2H, H_{arom}), 7.56 d (2H, H_{arom}, J = 7.8 Hz). Mass spectrum, *m/z* (I_{rel}, %): 333 (7), 316 (5), 291 (4), 255 (21), 133 (100), 105 (45), 79 (16), 77 (16). Found, %: C 76.50; H 6.22. $C_{24}H_{24}O_4$. Calculated, %: C 76.57; H 6.43.

4-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-3-trifluoroacetyl-5-trifluoromethylfuran (IVa). mp 115–116°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1705 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, OMe), 3.88 s (3H, OMe), 6.97 d (2H, H_{arom}, J = 8.5 Hz), 7.00 d (2H, H_{arom}, J = 8.5 Hz), 7.64 d (2H, H_{arom}, J = 8.5 Hz), 7.87 d (2H, H_{arom}, J = 8.5 Hz). ^{19}F NMR spectrum, δ_F, ppm: –70.31 s (3F, $COCF_3$), –58.45 s (3F, 5-CF_3). Mass spectrum, *m/z* (I_{rel}, %): 472 $[M]^+$ (35), 453 (22), 383 (12), 236 (3), 135 (100), 107 (10), 92 (13), 77 (22). Found, %: C 56.17; H 3.13. $C_{22}H_{14}F_6O_5$. Calculated, %: C 55.94; H 2.99.

Compound **IVb** was described previously [14].

4-(2,4-Dimethylbenzoyl)-2-(2,4-dimethylphenyl)-3-trifluoroacetyl-5-trifluoromethylfuran (IVc). Oily substance. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 2.38 s (3H, Me), 2.39 s (3H, Me), 2.65 s (3H, Me), 7.1 d (1H, H_{arom}, J = 7.8 Hz), 7.09 d (1H, H_{arom}, J = 7.9 Hz), 7.15 s (2H, H_{arom}), 7.22 d (1H, H_{arom}, J = 7.8 Hz), 7.38 d (1H, H_{arom}, J = 7.9 Hz). ^{19}F NMR spectrum, δ_F, ppm: –78.11 s (3F, $COCF_3$), –66.42 s (3F, 5-CF_3). Mass spectrum, *m/z* (I_{rel}, %): 468 $[M]^+$ (22), 399 (68), 295 (13), 133 (100), 105 (63), 79 (14), 77 (19). Found, %: C 61.59; H 3.73. $C_{24}H_{18}F_6O_3$. Calculated, %: C 61.54; H 3.87.

3-Acetyl-4-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-5-trifluoromethylfuran (V). Oily substance.

^{1}H NMR spectrum, δ, ppm: 2.17 s (3H, Me), 3.88 s (3H, OMe), 3.89 s (3H, OMe), 6.96 d (2H, H_{arom}, J = 8.9 Hz), 7.02 d (2H, H_{arom}, J = 8.6 Hz), 7.65 d (2H, H_{arom}, J = 8.6 Hz), 7.88 d (2H, H_{arom}, J = 8.9 Hz). ^{19}F NMR spectrum: δ_F –58.98 ppm, s (3F, CF_3). Mass spectrum, m/z (I_{rel}, %): 418 $[M]^+$ (46), 403 (13), 383 (9), 309 (5), 152 (9), 135 (100), 107 (11), 92 (13), 77 (21). Found, %: C 62.87; H 4.08. $C_{22}H_{17}F_3O_5$. Calculated, %: C 63.16; H 4.10.

Reactions of compounds **IIIa** and **IVb** with hydrazine to obtain compounds **IX** and **X**, respectively, were carried out according to the procedure reported in [4].

4,8-Bis(4-methoxyphenyl)-1,5-dimethyl-2,3,6,7-tetraazanaphthalene (IX). Yield 84%, mp 258–259°C. ^{1}H NMR spectrum, δ, ppm: 2.48 s (6H, Me), 3.91 s (6H, OMe), 7.1 d (4H, H_{arom}, J = 8.5 Hz), 7.55 d (4H, H_{arom}, J = 8.5 Hz). Mass spectrum, m/z (I_{rel}, %): 372 $[M]^+$ (100), 357 (4), 343 (12), 329 (28), 170 (10), 155 (19), 143 (9), 127 (18), 115 (15), 77 (17). Found, %: C 71.09; H 5.62. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.95; H 5.41.

3,7-Bis(3-fluoro-4-methoxyphenyl)-4-hydroxy-1,4-bis(trifluoromethyl)-4,5-dihydrofuro[3,4-*d*]pyridazine (X). Yield 56%, oily substance. ^{1}H NMR spectrum, δ, ppm: 3.94 s (6H, OMe), 5.27 br.s (1H, OH), 6.93 d.d (2H, H_{arom}, J = 10.8, 8.7 Hz), 7.08 t (2H, H_{arom}, J = 7.6 Hz), 7.29 s (1H, NH), 7.66 t (2H, H_{arom}, J = 8.7 Hz). ^{19}F NMR spectrum, δ_F, ppm: –131.52 t (1F, F_{arom}, J = 9.2 Hz), –130.77 t (1F, F_{arom}, J = 9.9 Hz), –80.28 s (3F, CF_3), –55.92 s (3F, CF_3). Mass spectrum, m/z (I_{rel}, %): 522 (6) $[M]^+$, 504 (87) $[M - H_2O]^+$, 454 (20), 452 (30), 153 (100). Found, %: C 51.35; H 2.37; N 5.49. $C_{22}H_{14}F_8N_2O_4$. Calculated, %: C 50.59; H 2.70; N 5.36.

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