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Oxidation of Aromatic Compounds: XII.* Regio- and Stereoselective Oxidative Dimerization of Alkyl 3-Arylpropynoates in the System $CF_3CO_2H–CH_2Cl_2–PbO_2$

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Abstract—Regio- and stereoselective oxidative dimerization of alkyl 3-arylpropynoates in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$ (1–30 h, 0–20°C) leads to dialkyl (*E*)-2,3-bis(arylcarbonyl)-2-butene-1,4-dioates with *trans* arrangement of the substituents at the double bond.

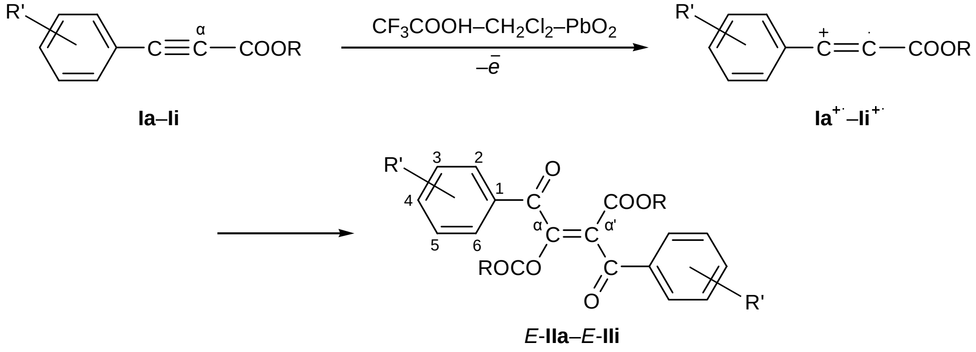
We previously showed that one-electron oxidation of acetylene derivatives with lead(IV) oxide in weakly nucleophilic acidic media (HSO_3F, CF_3CO_2H) leads to formation of oxidative dimerization products [2–6]. The next step in studying reactions of this sort was examination of stereo- and regioselectivity relations holding in the formation of new carbon–carbon bonds via transformations of radical cations derived from alkyl 3-arylpropynoates [1]. The present communication reports on the oxidation of alkyl 3-arylpropynoates in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$.

Scheme 1 illustrates the transformation of alkyl 3-arylpropynoates **Ia**–**Ii** through intermediate radical cations $\mathbf{Ia}^{+\cdot}$–$\mathbf{Ii}^{+\cdot}$ to dialkyl (*E*)-2,3-bis(arylcarbonyl)-2-butene-1,4-dioates *E*-**IIa**–*E*-**IIi**, which is promoted by the system $CF_3COOH–CH_2Cl_2–PbO_2$. The reaction conditions and products yields are given in Table 1.

The structure of compounds *E*-**IIa**–*E*-**IIi** was rigorously established by X-ray analysis and NMR spectroscopy. X-Ray diffraction study of the product obtained by oxidation of methyl 3-(4-methoxyphenyl)propynoate (**Ie**) showed that it has the structure of dimethyl 2,3-bis(4-methoxybenzoyl)-2-butene-1,4-dioate (**IIe**) having *E*-configuration at the double C=C bond [1]. The structure of molecule *E*-**IIe** suggests that oxidative dimerization of alkyne **Ie** involves formation of a new C–C bond between acetylenic carbon atoms in the α-position with respect to the carbonyl group (Scheme 1). This pattern is typical of radical cations derived from arylpropynone systems such as esters **Ia**–**Ii** and symmetrically substituted 1,3-diarylpropynones which were studied by us previously [5].

Comparison of the ^1H NMR spectrum of dimethyl *trans*-2,3-dibenzoyl-2-butene-1,4-dioate (*E*-**IIa**) with

Scheme 1.



R = Me, R' = H (**a**), 4-Me (**b**), 3,4-Me_2 (**c**), 4-F (**d**), 4-MeO (**e**), 3,4-$(MeO)_2$ (**f**); R = Et, R' = 4-MeO (**g**), 3-F-4-MeO (**h**), 4-MeO-3-NO_2 (**i**).

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* For communication XI, see [1].

Table 1. Conditions of oxidation of alkyl 3-arylpropynoates **Ia**–**Ii** in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$ and yields of products *E*-**IIa**–*E*-**IIi**

Initial comp. no.	Amounts of reactants				Reaction conditions		Product (yield, %)
	I, mmol	PbO_2, mmol	CF_3CO_2H, ml	CH_2Cl_2, ml	temperature, °C	time, h	
Ia	6.25	6.25	2.4	5.0	18–20	30	*E*-**IIa** (4)
Ib	1.72	1.72	0.7	3.0	18–20	5	*E*-**IIb** (23)
Ic	1.33	1.33	0.5	2.5	0–2	3	*E*-**IIc** (18)
Id	2.81	2.81	1.1	5.0	18–20	20	*E*-**IId** (9)
Ie	2.10	2.10	0.8	4.0	0–2	2	*E*-**IIe** (55)
If	2.11	2.11	0.8	4.0	0–2	1	*E*-**IIf** (40)
Ig	0.49	0.49	0.2	1.5	0–2	2	*E*-**IIg** (37)
Ih	0.45	0.45	0.2	2.0	0–2	1	*E*-**IIh** (38)
Ii	0.50	0.50	0.2	1.0	18–20	12	*E*-**IIi** (19)

that reported in [7] for *cis* isomer *Z*-**IIa** revealed some distinguishing features. In the ^{1}H NMR spectra recorded in $CDCl_3$, the signal from the methoxy group of isomer *E*-**IIa** is located at δ 3.56 ppm (see Experimental), while the corresponding signal of isomer *Z*-**IIa** appears at δ 3.79 ppm [7]. The observed difference (Δδ = 0.23 ppm) results from different magnetically anisotropic effects of the surrounding molecular fragments on the MeO protons in the *cis* and *trans* isomers of **IIa**. Taking into account the above specificity of the MeO signal, dimethyl esters **IIb**–**IIf** were also assigned *trans* configuration at the double bond: signals from the methoxy protons in these compounds were located in the narrow range from δ 3.56 to 3.59 ppm (see Experimental and Table 2).

In the ^{1}H NMR spectra of diethyl esters **IIg**–**IIi**, magnetic anisotropy of the environment is reflected most clearly in the positions of signals from the OCH_2 protons of the ester groups. We revealed the following relations holding in the positions of signals from the OMe and OCH_2 groups in the spectra of **Ia**–**Ii** and *E*-**IIa**–*E*-**IIi**. The difference between the chemical shifts of the ester methoxy protons in compounds **Ia**–**If** and oxidation products *E*-**IIa**–*E*-**IIf** turned out to be constant, $\Delta\delta_E$(MeO) = –0.25±0.01 ppm (Table 2). For example, the chemical shift of the MeO protons in initial alkyne **Ic** is $\delta_{\mathbf{Ic}}$ = 3.82 ppm, and the corresponding value for *E*-**IIc** is $\delta_{E\text{-}\mathbf{IIc}}$ = 3.57 ppm; the difference $\Delta\delta_E$(MeO) is $\delta_{E\text{-}\mathbf{IIc}}$(MeO) – $\delta_{\mathbf{Ic}}$(MeO) = –0.25 ppm. The same pattern is typical of the other pairs of compounds **Ia**–**If** and *E*-**IIa**–*E*-**IIf** (Table 2). By contrast, the corresponding difference for the *cis* isomer of **IIa** (*Z*-**IIa**) is $\Delta\delta_Z$(MeO) = $\delta_{Z\text{-}\mathbf{IIa}}$(MeO) – $\delta_{\mathbf{Ia}}$(MeO) = –0.05 ppm {$\delta_{\mathbf{Ia}}$(MeO) = 3.84 ppm, $\delta_{Z\text{-}\mathbf{IIa}}$(MeO) = 3.79 ppm [7]}. As follows from the data in Table 2, a similar difference in the chemical shifts of the OCH_2 protons, $\Delta\delta_E(OCH_2)$ = –0.21±0.04 ppm, is observed for ethyl esters **Ig**–**Ii** and their oxidative dimerization products *E*-**IIg**–*E*-**IIi**.

The yield of the product and the reaction time strongly depend on the substituents in the aromatic ring of esters **Ia**–**Ii**. In the oxidation of methyl 3-phenylpropynoate (**Ia**), the yield of dimerization product *E*-**IIa** in 30 h was as poor as 4%. The reaction with *para*-fluoro-substituted ester **Id** also required a long time (20 h), and the yield of *E*-**IId** was 9%. Introduction of alkyl (compounds **Ib** and **Ic**) or methoxy groups (**Ie**–**Ii**) into the aromatic ring leads to considerable shortening of the reaction time (to 1 h for compounds **If** and **Ih**) and increase in the yield up to 40–55% (Table 1). We failed to obtain the expected oxidative dimerization product from methyl 3-(3,5-dimethylphenyl)propynoate (**Ij**). Despite complete consumption of PbO_2 (equimolar amount, 2 h, 0–2°C), we isolated only a small amount of tarry products. Presumably, radical cation $\mathbf{Ij}^{+\cdot}$ possesses an a_2-like highest occupied molecular orbital, and the alkyne chain contributes little to delocalization of the positive charge and unpaired electron. As a result, the oxidation involves methyl groups in the substrate.

Thus alkyl 3-arylpropynoates undergo regio- and stereoselective transformation into dialkyl (*E*)-2,3-bis-(arylcarbonyl)-2-butene-1,4-dioates in the system $CF_3CO_2H–CH_2Cl_2–PbO_2$. This reaction may be regarded as a new efficient one-pot synthesis of difficultly accessible polyfunctional compounds [7, 8].

Table 2. Chemical shifts ($CDCl_3$) of the MeO and OCH_2 protons in the ester fragments of compounds **Ia**–**Ii** and *E*-**IIa**–*E*-**IIi**

Pairs of compounds	δ(MeO), ppm		$\Delta\delta_E$(MeO) = $\delta_{E\text{-}\mathbf{II}}$(MeO)–$\delta_{\mathbf{I}}$(MeO), ppm
	I	*E*-**II**	
Ia–*E*-**IIa**	3.84	3.56	–0.28
Ib–*E*-**IIb**	3.82	3.56	–0.26
Ic–*E*-**IIc**	3.82	3.57	–0.25
Id–*E*-**IId**	3.83	3.59	–0.24
Ie–*E*-**IIe**	3.81	3.56	–0.25
If–*E*-**IIf**	3.81	3.56	–0.25
			Average value $\Delta\delta_E$(MeO) = –0.25 ± 0.01

Pairs of compounds	$\delta(OCH_2)$, ppm		$\Delta\delta_E(OCH_2) = \delta_{E\text{-}\mathbf{II}}(OCH_2) - \delta_{\mathbf{I}}(OCH_2)$, ppm
	I	*E*-**II**	
Ig–*E*-**IIg**	4.26	4.02	–0.24
Ih–*E*-**IIh**	4.26	4.04	–0.22
Ii–*E*-**IIi**	4.25	4.08	–0.17
			Average value $\Delta\delta_E(OCH_2)$ = –0.21 ± 0.04

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer (500 MHz for ^1H and 125.76 MHz for ^{13}C) using $CDCl_3$ as solvent and internal reference (δ 7.25 ppm, δ_C 77.0 ppm). The IR spectra were obtained on a Specord 75-IR instrument from samples prepared as solutions in $CHCl_3$ and KBr pellets. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer with direct sample admission into the ion source (batch inlet probe temperature 100–120°C).

Methyl 3-arylpropynoates **Ia**–**If** and **Ij** were synthesized by esterification of the corresponding 3-arylpropynoic acids with dimethyl sulfate according to the procedure described in [9]; the acids were prepared from the corresponding cinnamic acids as reported in [10]. Ethyl 3-arylpropynoates **Ig**–**Ii** were obtained by reactions of aryl iodides with ethyl propynoate [11, 12]. The properties of compounds **Ie** and *E*-**IIe** and the X-ray diffraction data for *E*-**IIe** were reported previously [1].

Methyl 3-phenylpropynoate (Ia). Oily substance. Published data [13]: bp 128°C (4 mm). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1700, 2200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (3H, OMe), 7.37 d.d (2H, H_{arom}, J = 7.5, 7.4 Hz), 7.45 t (1H, H_{arom}, J = 7.4 Hz), 7.58 d (2H, H_{arom}, J = 7.5 Hz) .

Methyl 3-(4-methylphenyl)propynoate (Ib). mp 65–68°C; published data [13]: mp 68–70°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1700, 2220. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, Me), 3.82 s (3H, OMe), 7.16 d (2H, H_{arom}, J = 7.8 Hz), 7.46 d (2H, H_{arom}, J = 7.8 Hz).

Methyl 3-(3,4-dimethylphenyl)propynoate (Ic). mp 41–43°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1705, 2220. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (3H, Me), 2.28 s (3H, Me), 3.82 s (3H, OMe), 7.12 d (1H, H_{arom}, J = 7.7 Hz), 7.32 d (1H, H_{arom}, J = 7.7 Hz), 7.36 s (1H, H_{arom}). Found, %: C 76.33; H 6.38. M^+ 188. $C_{12}H_{12}O_2$. Calculated, %: C 76.57; H 6.42. M 188.23.

Methyl 3-(4-fluorophenyl)propynoate (Id). mp 56–57°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.83 s (3H, OMe), 7.07 d.d (2H, H_{arom}, J = 8.9, 8.5 Hz), 7.58 d.d (2H, H_{arom}, J = 8.9, 5.3 Hz). Found, %: C 67.31; H 4.00. M^+ 178. $C_{10}H_7FO_2$. Calculated, %: C 67.42; H 3.96. M 178.16.

Methyl 3-(3,4-dimethoxyphenyl)propynoate (If). mp 82–84°C; published data [9]: mp 81–82°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1695, 2210. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 s (3H, OMe), 3.89 s (3H, OMe), 3.90 s (3H, OMe), 7.05 d (1H, H_{arom}, J = 8.4 Hz), 7.19 d (1H, H_{arom}, J = 1.7 Hz), 7.26 d.d (1H, H_{arom}, J = 8.4, 1.7 Hz).

Ethyl 3-(4-methoxyphenyl)propynoate (Ig). Oily substance. Published data [14]: bp 140°C (5 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, Me, J = 7.2 Hz), 3.80 s (3H, OMe), 4.26 q (2H, OCH_2, *J* = 7.2 Hz), 6.85 d (2H, H_{arom}, *J* = 8.7 Hz), 7.51 d (2H, H_{arom}, *J* = 8.7 Hz).

Ethyl 3-(3-fluoro-4-methoxyphenyl)propynoate (Ih). mp 72.5–73.5°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1700, 2220. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, Me, *J* = 7.2 Hz), 3.89 s (3H, OMe), 4.26 q (2H, OCH_2, *J* = 7.2 Hz), 6.91 d.d (1H, H_{arom}, *J* = 8.5, 8.5 Hz), 7.27 d.d (1H, H_{arom}, *J* = 11.2, 1.9 Hz), 7.33 d.d.d (1H, H_{arom}, *J* = 8.5, 2.2, 1.9 Hz). Found, %: C 64.82; H 4.78. M^+ 222. $C_{12}H_{11}FO_3$. Calculated, %: C 64.86; H 4.99. *M* 222.21.

Ethyl 3-(4-methoxy-3-nitrophenyl)propynoate (Ii). mp 86–87°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, Me, *J* = 7.2 Hz), 3.96 s (3H, OMe), 4.25 q (2H, OCH_2, *J* = 7.2 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 57.89; H 4.48; N 5.36. M^+ 249. $C_{12}H_{11}NO_5$. Calculated, %: C 57.83; H 4.45; N 5.62. *M* 249.22.

Methyl 3-(3,5-dimethylphenyl)propynoate (Ij). mp 26–27°C. IR spectrum ($CHCl_3$), ν, vm^{-1}: 1700, 2200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (6H, 2Me), 3.80 s (3H, OMe), 7.17 s (1H, H_{arom}), 7.23 s (2H, H_{arom}). Found, %: C 76.70; H 6.31. M^+ 188. $C_{12}H_{12}O_2$. Calculated, %: C 76.57; H 6.42. *M* 188.23.

Oxidation of alkyl-3-arylpropynoates Ia–Ii to dialkyl (*E*)-2,3-bis(arylcarbonyl)-2-butene-1,4-dioates *E*-IIa–*E*-IIi. Alkyl 3-arylpropynoate **Ia**–**Ii**, 0.45–6.25 mmol, was added at 0–20°C under vigorous stirring to a solution of 0.2–2.4 ml of trifluoroacetic acid in 1–5 ml of methylene chloride. Lead(IV) oxide, 0.45–6.25 mmol, was then added, and the mixture was stirred for 1–30 h (Table 1). When the reaction was complete, the mixture was poured into 50–250 ml of chloroform. The chloroform solution was washed in succession with water, a saturated aqueous solution of sodium hydrogen carbonate, and water again, dried over Na_2SO_4, and evaporated. The residue was subjected to column chromatography on silica gel using petroleum ether–chloroform (40 : 70) as eluent. The yields of compounds *E*-**IIa**–*E*-**IIi** were determined from the weights of fractions isolated by chromatography (Table 1).

Dimethyl (*E*)-2,3-dibenzoyl-2-butene-1,4-dioate (*E*-IIa). mp 161–162°C. IR spectrum (KBr), ν, cm^{-1}: 1676, 1730. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.56 s (6H, 2OMe), 7.52 d.d (4H, H_{arom}, *J* = 8.0, 7.4 Hz), 7.63 t.t (2H, H_{arom}, *J* = 7.4, 1.0 Hz), 7.99 d.d (4H, H_{arom}, *J* = 8.0, 1.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 53.30 q (MeO, *J* = 148.5 Hz), 128.74 d.d.d (C^2, *J* = 161.1, 7.3, 6.3 Hz), 128.94 d.d (C^3, *J* = 162.3, 7.6 Hz), 134.04 d.t (C^4, *J* = 161.5, 7.2 Hz), 135.46 t (C^1, *J* = 7.2 Hz), 142.27 s (C=C), 162.84 q (C=O, ester, *J* = 4.0 Hz), 190.87 t (C=O, ketone, *J* = 4.5 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 352 (3) M^+, 321 (2) $[M – OMe]^+$, 105 (100) $[PhCO]^+$, 77 (32) $[Ph]^+$, 51 (6). Found, %: C 68.15; H 4.58. M^+ 352. $C_{20}H_{16}O_6$. Calculated, %: C 68.18; H 4.58. *M* 352.34.

Dimethyl (*E*)-2,3-bis(4-methylbenzoyl)-2-butene-1,4-dioate (*E*-IIb). mp 224–226°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (6H, 2Me), 3.56 s (6H, 2OMe), 7.31 d (4H, H_{arom}, *J* = 8.3 Hz), 7.88 d (4H, H_{arom}, *J* = 8.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.81 q.t (Me, *J* = 126.7, 4.0 Hz), 53.21 q (MeO, *J* = 148.4 Hz), 128.90 d.d (C^2, *J* = 160.2, 6.4 Hz), 129.67 d.d.q (C^3, *J* = 159.8, 5.9, 4.7 Hz), 133.16 t (C^1, *J* = 7.4 Hz), 142.18 s (C=C), 145.10 t.q (C^4, *J* = 6.5, 6.5 Hz), 162.98 q (C=O, ester, *J* = 4.0 Hz), 190.57 t (C=O, ketone, *J* = 3.7 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 380 (10) M^+, 349 (7) $[M – OMe]^+$, 119 (100) $[MeC_6H_4CO]^+$, 91 (12) $[MeC_6H_4]^+$. Found, %: C 69.60; H 5.21. M^+ 380. $C_{22}H_{20}O_6$. Calculated, %: C 69.46; H 5.30. *M* 380.40.

Dimethyl (*E*)-2,3-bis(3,4-dimethylbenzoyl)-2-butene-1,4-dioate (*E*-IIc). mp 218–219°C. IR spectrum (KBr), ν, cm^{-1}: 1673, 1732. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.33 s (6H, 2Me), 2.34 s (6H, 2Me) 3.57 s (6H, 2OMe), 7.26 d (2H, H_{arom}, *J* = 8.0 Hz), 7.71 d.d (2H, H_{arom}, *J* = 8.0, 1.6 Hz), 7.79 d (2H, H_{arom}, *J* = 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.80 q.d (Me, *J* = 126.7, 4.6 Hz), 20.17 q.d (Me, *J* = 126.7, 4.6 Hz), 53.24 q (MeO, *J* = 148.8 Hz), 126.75 d.d (C^6, *J* = 160.6, 5.9 Hz), 129.55 d.d.q (C^2, *J* = 158.1, 5.5 Hz), 130.19 d.q (C^5, *J* = 158.5, 4.7 Hz), 133.53 d (C^1, *J* = 7.6 Hz), 137.45 m (C^3, *J* = 5.0 Hz), 142.25 s (C=C), 143.94 m (C^4, *J* = 5.0 Hz), 163.06 q (C=O, ester, *J* = 4.0 Hz), 190.82 t (C=O, ketone, *J* = 4.2 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 408 (9) M^+, 134 (10), 133 (100) $[Me_2C_6H_3CO]^+$, 95 (6), 79 (9), 77 (7). Found, %: C 70.37; H 6.03. M^+ 408. $C_{24}H_{24}O_6$. Calculated, %: C 70.57; H 5.92. *M* 408.45.

Dimethyl (*E*)-2,3-bis(4-fluorobenzoyl)-2-butene-1,4-dioate (*E*-IId). mp 207–208°C. IR spectrum (KBr), ν, cm^{-1}: 1684, 1728. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.59 s (6H, 2OMe), 7.20 d.d (4H, H_{arom}, *J* = 8.9, 8.4 Hz), 8.00 d.d (4H, H_{arom}, *J* = 8.9, 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 53.45 q (MeO, *J* = 148.8 Hz), 116.28 d.d.d (C^3, *J* = 165.7, 22.0, 3.4 Hz), 131.45 d.d.d (C^2, *J* = 163.2, 9.8, 7.1 Hz), 131.98 m (C^1, *J* = 5.0 Hz), 142.07 s (C=C), 162.69 q

(C=O, ester, J = 3.8 Hz), 166.27 d.t.t (C^4, J = 256.9, 10.5, 5.0 Hz), 189.32 t (C=O, ketone, J = 3.6 Hz). Mass spectrum, m/z (I_{rel}, %): 388 (5) M^+, 357 (2), $[M - OMe]^+$, 123 (100) $[FC_6H_4CO]^+$, 95 (25), 75 (5). Found, %: C 61.89; H 3.67. M^+ 388. $C_{20}H_{14}F_2O_6$. Calculated, %: C 61.86; H 3.63. M 388.32.

Dimethyl (*E*)-2,3-bis(3,4-dimethoxybenzoyl)-2-butene-1,4-dioate (*E*-IIf). mp 197–198°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670, 1715. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.56 s (6H, $2CO_2Me$), 3.94 s (6H, 2OMe), 3.96 s (6H, 2OMe), 6.90 d (2H, H_{arom}, J = 8.3 Hz), 7.50 d.d (2H, H_{arom}, J = 8.3, 1.5 Hz), 7.60 d (2H, H_{arom}, J = 1.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 53.32 q (MeO, J = 148.5 Hz), 56.07 q (MeO, J = 144.8 Hz), 56.21 q (MeO, J = 145.3 Hz), 109.74 d.d (C^2, J = 160.5, 7.2 Hz), 110.38 d (C^5, J = 160.5 Hz), 124.62 d.d (C^6, J = 161.4, 6.7 Hz), 128.90 d (C^1, J = 8.1 Hz), 142.04 s (C=C), 149.60 m (C^3, J = 5.0 Hz), 154.28 m (C^4, J = 5.0 Hz), 163.20 q (C=O, ester, J = 3.9 Hz), 189.53 t (C=O, ketone, J = 4.8 Hz). Mass spectrum, m/z (I_{rel}, %): 472 (14) M^+, 413 (5) $[M - CO_2Me]^+$, 236 (2) M^{2+}, 165 (100) $[(MeO)_2C_6H_3CO]^+$, 137 (7) $[(MeO)_2C_6H_3]^+$, 122 (4), 107 (14), 94 (3), 79 (6). Found, %: C 59.84; H 5.17. M^+ 472. $C_{24}H_{24}O_{10}$. Calculated, %: C 61.01; H 5.12. M 472.45.

Diethyl (*E*)-2,3-bis(4-methoxybenzoyl)-2-butene-1,4-dioate (*E*-IIg). Oily substance. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1675, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 t (6H, 2Me, J = 7.1 Hz), 3.88 s (6H, 2OMe), 4.02 q (4H, $2OCH_2$, J = 7.1 Hz), 6.98 d (4H, H_{arom}, J = 8.9 Hz), 7.96 d (4H, H_{arom}, J = 8.9 Hz). Mass spectrum, m/z (I_{rel}, %): 440 (5) M^+, 395 (1) $[M - OEt]^+$, 367 (1) $[M - CO_2Et]^+$, 136 (9), 135 (100) $[MeOC_6H_4CO]^+$, 107 (4), 92 (5), 77 (9), 64 (2). Found, %: C 65.49; H 5.55. M^+ 440. $C_{24}H_{24}O_8$. Calculated, %: C 65.45; H 5.49. M 440.45.

Diethyl (*E*)-2,3-bis(3-fluoro-4-methoxybenzoyl)-2-butene-1,4-dioate (*E*-IIh). mp 137–139°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 t (6H, 2Me, J = 7.0 Hz), 3.96 s (6H, 2Me), 4.04 q (4H, J = 7.0 Hz), 7.03 d.d (2H, H_{arom}, J = 8.4, 7.9 Hz), 7.71 d (2H, H_{arom}, J = 8.4 Hz), 7.74 d (2H, H_{arom}, J = 11.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.32 q (MeO, J = 145.8 Hz), 13.42 t.q (OCH_2, J = 127.6, 2.5 Hz), 62.79 q.t (MeO, J = 149.2, 4.2 Hz), 112.53 d (C^5, J = 161.9 Hz), 115.76 d.d.d (C^2, J = 164.0, 19.1, 7.6 Hz), 126.70 d.d.d (C^6, J = 162.3, 7.2, 3.0 Hz), 129.13 d.d (C^1, J = 7.7 Hz), 141.75 s (C=C), 152.26 d.d.d.d (C^3, J = 249.1, 7, 7, 1.5 Hz), 152.68 m (C^4, J = 5.0 Hz), 162.41 q (C=O, ester, J = 3.2 Hz), 188.72 t (C=O, ketone, J = 5.0 Hz). Mass spectrum, m/z (I_{rel}, %): 476 (10) M^+, 154 (10), 153 (100) $[MeOFC_6H_3CO]^+$, 125 (7) $[MeOFC_6H_3]^+$, 110 (4), 95 (6). Found, %: C 60.68; H 4.73. M^+ 476. $C_{24}H_{22}F_2O_8$. Calculated, %: C 60.50; H 4.65. M 476.43.

Diethyl (*E*)-2,3-bis(4-methoxy-3-nitrobenzoyl)-2-butene-1,4-dioate (*E*-IIi). mp 232–234°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 t (6H, 2Me, J = 7.1 Hz), 4.06 s (6H, 2OMe), 4.08 q (4H, $2OCH_2$, J = 7.1 Hz), 7.21 d (2H, H_{arom}, J = 8.7 Hz), 8.13 d.d (2H, H_{arom}, J = 8.7, 2.1 Hz), 8.46 d (2H, H_{arom}, J = 2.1 Hz). Mass spectrum, m/z (I_{rel}, %): 530 (6) M^+, 485 (2) $[M - OEt]^+$, 457 (2) $[M - CO_2Et]^+$, 181 (10), 180 (100) $[MeO(NO_2)C_6H_3CO]^+$, 133 (6), 106 (9), 105 (18), 104 (17), 76 (8). Found, %: C 54.31; H 4.19. M^+ 530. $C_{24}H_{22}N_2O_{12}$. Calculated, %: C 54.34; H 4.18. M 530.44.

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