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Oxidation of Aromatic Compounds: XIII.* Oxidation of Unsymmetrically Substituted 1,3-Diarylpropynones in a System CF_3CO_2H-CH_2Cl_2-PbO_2

A.V. Vasil'ev[1], A.P. Rudenko[1], S.A. Aristov[1], and G.K. Fukin[2]

[1]*St. Petersburg StateAcademy of Forestry Engineering, St. Petersburg, 194021Russia*
e-mail: aleksvasil@hotmail.com
[2]*Razuvaev Institute of Organometallic Chemistry, Russian Academy of Science, Nizhnii Novgorod, Russia*

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Abstract— Oxidation of unsymmetrically sunstituted 1,3-diarylpropynones in a system trifluoroacetic acid-dichloromethane-lead(IV) oxide proceeds through intermediate formation of cation radicals and occurs regio- and stereoselectively affording *E*-1,1,2,2-tetraaroylethenes. The highest yield of these compounds was obtained from 1,3-diarylpropynones containing electron-donor methoxy and methyl groups in the aromatic ring conjugated with the triple bond.

Alkynes are extensively used for preparation of versatile carbonyl synthons [2]. One-electron oxidation reactions of acetylene compounds open a way to new classes of synthetically valuable polycarbonyl systems [1, 3–6].

This study is carried out in extension of an investigation series on cation-radical reactions of alkynes and deals with the regio- and stereoslectivity of carbon-carbon bonds formation at oxidative dimerization of unsymmetrically substituted 1,3-diarylpropynones **Ia–Ik**.

Scheme 1 shows initial 1,3-diarylpropynones **Ia–Ik** that are oxidized via an intermediate formation of cation-radicals **IIa–IIk** to the final reaction products, *E*-1,1,2,2-tetraaroylethenes **IIIa–IIIg** (see the table).

The structure and composition of compounds **IIIa–IIIg** were established from the data of elemental analysis, ^{1}H and ^{13}C NMR and mass spectra, and from the X-ray diffraction study. The exact *trans*-position of aroyl groups at the C=C bond was determined by X-ray diffraction analysis by an example of compound **IIIc** (Fig. 1). The

Oxidation conditions of 1,3-diarylpropynones **Ia–Ij** in a system CF_3CO_2H–CH_2Cl_2–PbO_2 at 18–20°C, and yields of oxidation products **IIIa–IIIg**

Run no.	Compd.no.	Amount of reagents brought into reaction				Reaction time, h	Reaction products (yield, %)
		I, mmol	PbO_2, mmol	CF_3CO_2H, ml	CH_2Cl_2, ml		
1	**Ia**	1.5	1.5	0.6	2	5	**IIIa** (48)
2	**Ib**	1.7	1.7	0.5	3	3	**IIIb** (52)
3	**Ic**	2.0	2.0	0.8	5	2	**IIIc** (31)
4	**Id**	0.6	0.6	0.2	2	2	**IIId** (6)
5	**Ie**	1.3	1.3	0.5	4	1	**IIIe**(62)
6	**If**	0.4	0.4	0.2	2	6	**IIIf** (38)
7	**Ig**	0.7	0.7	0.4	5	2	**IIIg** (56)
8	**Ih**	2.0	2.0	0.8	3	20	**III**a (8)
9	**Ii**	1.7	1.7	0.7	3	20	**IIIe** (8)
10	**Ij**	1.0	1.0	0.4	5	2	**Ij** (80)

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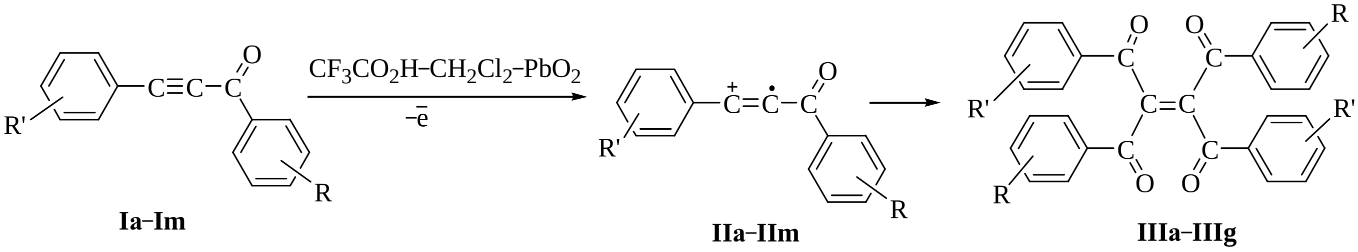
* For communication XII see [1].

Scheme 1.



R = H, R' = 4-Me (**a**), 3,4-Me_2 (**b**), 2,4,6-Me_3 (**c**), 2,3,5,6-Me_4 (**d**), 4-MeO (**e**); 2,3,5,6-$Me_4C_6C(O)C\equiv C$ (**j**), 4-MeO-3-NO_2 (**k**);
R = 4-F, R' = 4-Me (**f**); R = 4-NO_2, R' = 4-MeO (**g**); R' = H, R = 4-Me (**h**), 4-MeO (**i**).

trans-structure of tetraaroylethenes **IIIa–IIIg** was additionally proved by their chemical reaction with hydrazine (see below).

The performed preparative oxidation of 1,3-diarylpropynones **Ia–Ij** revealed the following regular trends in the reaction. Substarates **Ia–Ic, Ie–Ig** containing electron-donor methoxy and methyl groups in the aromatic ring conjugated with the triple bond are cleanly converted into **IIIa–IIIc, IIIe–IIIg** within 1–6 h in 31–62% yields (see the table). An increased number of alkyl groups results in a lower yield of the final oxidation products, for instance, in the case of tetramethyl derivative **Id** the yield decreases to 6% (cf. runs nos. *1*–*6*). The reason is that alkyl groups suffer oxidation by side reactions furnishing tarry compounds and thus reducing the yield of the target tetraaroylethenes.

The oxidation of diarylpropynone **I** that are isomeric having the same substituents R, (R') in *o*-, *m*-, or *p*-position but in different aromatic rings results in tetraaroylethenes **III** with identical structures. Thus isomers **Ia** and **Ih** afford the same tetraketone **IIIa** (runs nos. *1* and *8*). Analogous-ly, the oxidation of isomeric methoxy-substituted deriva-tives **Ie** and **Ii** furnished compound **IIIe** (runs nos. *5* and *9*). It should be mentioned that aryl-3-phenylpropinones **Ih** and **Ii** not activated by electron-donor substituents R' require a prolonged oxidation time (20 h) and afford oxidation products **IIIa** and **IIIe** in a small yield, 8% (runs nos. *8* and *9*) at conversion of the initial compound reaching only 30%.

The formation of cation-radicals **II** from diarylpropynones **I** was registered at one-electron oxidation of compounds **Ic, Ij,** and **Ik** with lead(IV) dioxide in HSO_3F at –75°C. Substrates **Ic, Ij,** and **Ik** in HSO_3F at –75°C exist as stable forms O-protonated at the carbonyl group [7]. However the one-electron oxidation in the system $HSO_3F–PbO_2$ undergo nonprotonated compounds present in insignificant concentration (cf. with data in [8, 9] on the ESR studies and electrochemistry of cataion-radicals of acetophenones in superacids).

The ESR spectrum of cation-radical **IIj** contains thirteen equidistant lines with a hyperfine coupling constant a^{H}_{Me} 11.5 Gs (12H). This pattern is due to the interaction

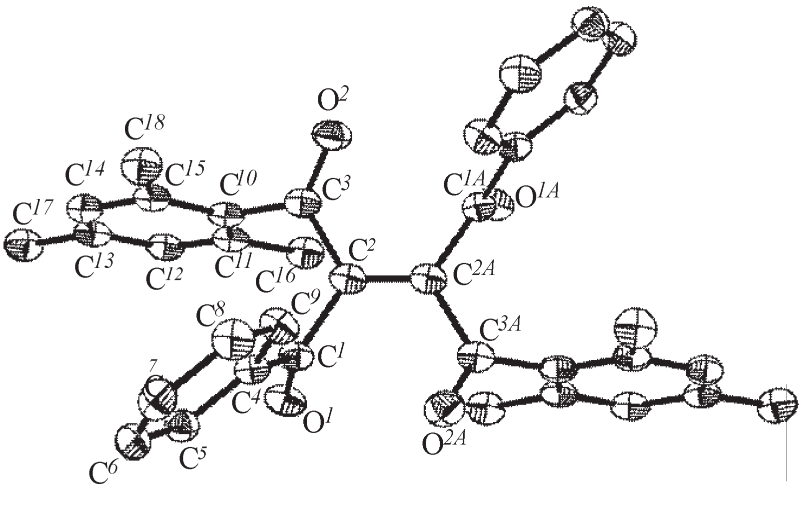


Fig. 1. Molecular structure of *E*-1,2-bis(2,4,6-trimethyl-phenylcarbonyl)-1,2-bis(phenylcarbonyl)ethene (**IIIc**).

of the unpaired electron with twelve protons of the four methyl groups (*g*-factor is equal to 2.0033). The character of the spectrum evidences the presence in the cation radical **IIj** of a singly occupied molecular orbital (SOMO) a_2 (previous HOMO of the neutral molecule [10]). Therewith the methyl substituents are considerably involved in the distribution of the spin-positive density. As a result the oxidation of compound **Ij** did not furnish the corresponding tetraaroylethene. In the reaction the equimolar amount of PbO_2 was totally consumed, and beside a small quantity of oily oligomeric products initial compound **Ij** was recovered in an 80% yield (run no. *10*). The reaction proceeded through the oxidation of “active” methyl groups not involving the acetylene moieties of the molecule.

ESR spectra of cation-radicals **IIc** and **IIk** are shown on Fig. 2. The ESR spectrum of cation-radical **IIc** is a quartet of nonets with constants $a^{\mathrm{H}}_{\ddot{\imath}\text{-Me}}$ 12 (3H) and $a^{\mathrm{H}}_{O\text{-Me}} = a^{\mathrm{H}}_{m\text{-arom}}$ 2.4 Gs (8H) (Fig. 2a) and corresponds to SOMO b_1. The spin-positive density in the cation-radical **IIc** is essentially delocalized onto the *para*-methyl group (the principal quartet splitting in the spectrum) and on the triple bond C≡C governing the reactivity of the latter. Actually, the oxidation of compound **Ic** results in formation of tetraketone **IIIc** in a 31% yield (run no.*3*) in contrast to the above mentioned substrate **Ij**.

The comparison of the ESR spectrum of cation-radical **IIc** with ESR spectra of cation-radicals of the structurally related mesityene derivatives containing an electron-acceptor group in the aromatic ring [8] reveales the transformation of SOMO a_2 (characteristic of the latter) into SOMO b_1 for the species **IIc**. In cation-radical **IIc** the involvement of the acetylene bond into the delocalization of the spin-positive density becomes favorable even disregarding the electron-acceptor character of the C≡CC(O)Ph group.

ESR spectrum of cation-radical **IIk** is a quintet (intensity ratio of the lines equals to 1:4:6:4:1) with a hyperfine coupling constant $a^{\mathrm{H}}_{\mathrm{MeO}} = a^{\mathrm{H}}_{m\text{-arom}}$ 4.5 Gs (4H) (*g*-factor 2.0037) and also corresponds to SOMO b_1 for this species (Fig. 2b).

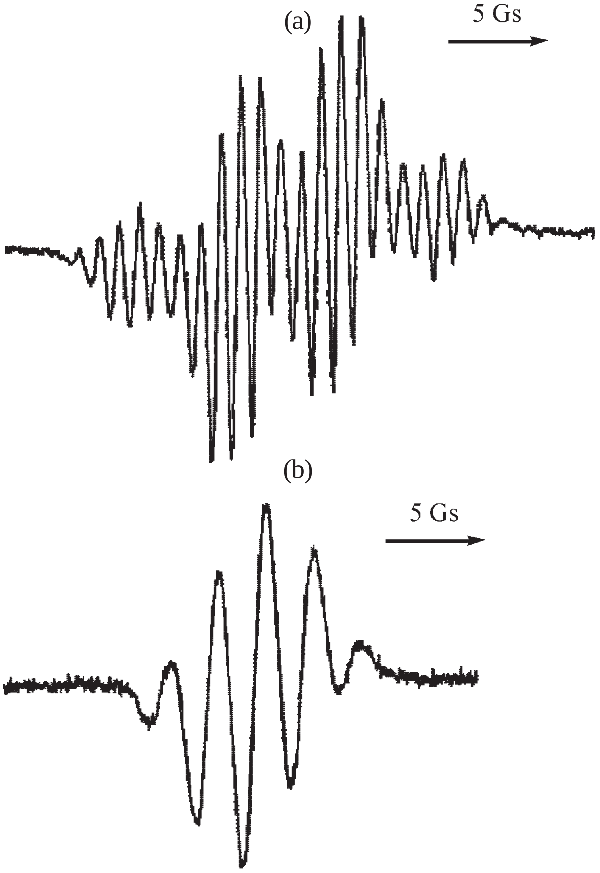


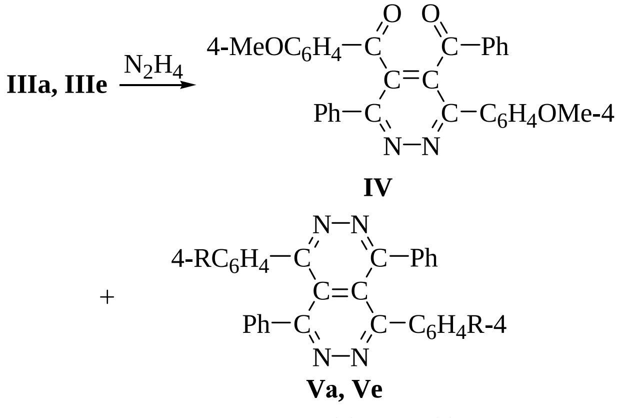
Fig. 2. ESR spectra of cation-radicals **IIc** (*a*) and **IIk** (*b*) registered at oxidation of compounds **Ic** and **Ik** in the system HSO_3F–PbO_2 at –75°C.

The reaction of tetraaroylethenes **IIIa** and **IIIe** with hydrazine gave rise to heterocyclic derivatives of pyridazine **IV** and 2,3,6,7-tetraazanaphthalene **Va** and **Ve** series (Scheme 2). The synthesis of pyridazine **IV** is possible only from *trans*-compound **IIIe**. In the case of a *cis*-isomer *Z*-**IIIe** presumably should have formed two different isomeric pyridazines that was not the case. Therefore the data on the structure of the products obtained in reaction of compounds **IIIa** and **IIIe** with hydrazine additionally confirm the *trans*-configuration of tetraketones **IIIa–IIIg**.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{19}F NMR spectra were registered on spectrometer Bruker AM-500 (operating frequencies

Scheme 1.



V, R = Me (**a**), MeO (**e**).

500, 125.76, and 470.7 MHz respectively) from solutions in $CDCl_3$ and $(CD_3)_2CO$. As internal references were used the residual signals of $CHCl_3$ (δ 7.25 ppm) and $(CD_3)_2CO$ (δ 2.05 ppm) in the ^{1}H NMR spectra, signal of $CDCl_3$ solvent (δ 77.0 ppm) in the ^{13}C NMR spectra, and signal of $CFCl_3$ (δ 0.0 ppm) in the ^{19}F NMR spectrum. IR spectra were recorded on spectrophotometer Specord 75IR from solutions in $CHCl_3$. Molecular weights were determined by mass spectrometry on MKh-1321 instrument at ionizing voltage 70 V at direct admission of samples into the ion source heated to 100–120°C. ESR spectra of cation-radicals were measured on spectrometer Varian E-109; the procedure of cation-radicals generation and registering their ESR spectra in the system $HSO_3F–PbO_2$ was described in detail in [8]; the *g*-factor value was estimated with respect to diphenylpicrylhydrazyl. The X-ray diffraction study of compound **IIIc** was performed on a diffractometer Smart Apex.

Initial 1,3-diarylpropynones **Ia–Ij** were prepared from the corresponding arylacetylenes and aroyl chlorides by procedure [4]. The properties of compounds **Ia, Ic, Ie, Ij**, and **Ik** were published in [7].

3-(3,4-Dimethylphenyl)-1-phenylpropynone (Ib). Yield 30%, mp 77–79°C. IR spectrum, ν, cm^{-1}:1630, 1635 (C=O), 2200 (C≡C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.31 s (3H, Me), 2.33 s (3H, Me), 7.27 d (1$\mathrm{H_{arom}}$, *J* 7.7 Hz), 7.48–7.74 m (5$\mathrm{H_{arom}}$), 8.22–8.24 m (2$\mathrm{H_{arom}}$). Found, %: C 87.24; H 5.93. M^+ 234. $C_{17}H_{14}O$. Calculated, %: C 87.15; H 6.02. *M* 234.10.

3-(2,3,5,6-Tetramethylphenyl)-1-phenylpropynone (Id). Yield 35%, mp 108–110°C. IR spectrum, ν, cm^{-1}:1620 (C=O), 2190 (C≡C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.24 s (6H, 2Me), 2.47 s (6H, 2Me), 7.10 s (1$\mathrm{H_{arom}}$), 7.62 t (2$\mathrm{H_{arom}}$, *J* 7.5 Hz), 7.73 t (1$\mathrm{H_{arom}}$, *J* 7.5 Hz), 8.24 d (2$\mathrm{H_{arom}}$, *J* 7.5 Hz). Found, %: C 87.05; H 6.98. M^+ 262. $C_{19}H_{18}O$. Calculated, %: C 86.99; H 6.92. *M* 262.14.

3-(4-Methylphenyl)-1-(4-fluorophenyl)propynone (If). Yield 46%, mp 95–97°C. IR spectrum, ν, cm^{-1}: 1625 (C=O), 2195 (C≡C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.41 s (3H, Me), 7.34–7.38 m (4$\mathrm{H_{arom}}$), 7.68 d (2$\mathrm{H_{arom}}$, *J* 7.9 Hz), 8.28–8.32 m (2$\mathrm{H_{arom}}$). Found, %: C 80.41; H 4.79. M^+ 238. $C_{16}H_{11}FO$. Calculated, %: C 80.66; H 4.65. *M* 238.08.

3-(4-Methoxyphenyl)-1-(4-nitrophenyl)propynone (Ig). Yield 34%, mp 196–198°C. IR spectrum, ν, cm^{-1}:1650 (C=O), 2190 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 s (3H, OMe), 6.96 d (2$\mathrm{H_{arom}}$, *J* 8.6 Hz), 7.66 d (2$\mathrm{H_{arom}}$, *J* 8.6 Hz), 8.36 s (4$\mathrm{H_{arom}}$). Found, %: C 67.93; H 4.11; N 5.08. M^+ 281. $C_{16}H_{11}NO_4$. Calculated, %: C 68.32; H 3.94; N 4.98. *M* 281.07.

1-(4-Methylphenyl)-3-phenylpropynone (Ih). Yield 56%, mp 68–69°C (publ.: mp 67–68°C [11]). IR spectrum, ν, cm^{-1}:1625 (C=O), 2195 (C≡C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.44 s (3H, Me), 7.41 d (2$\mathrm{H_{arom}}$, *J* 8.0 Hz), 7.50–7.60 m (3$\mathrm{H_{arom}}$), 7.76–7.78 m (2$\mathrm{H_{arom}}$), 8.13 d (2$\mathrm{H_{arom}}$, *J* 8.0 Hz).

1-(4-Methoxyphenyl)-3-phenylpropynone (Ii). Yield 58%, mp 97–99°C (publ.: mp 98–99 [11], 100°C [12]). IR spectrum, ν, cm^{-1}:1610 (C=O), 2200 (C≡C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.93 s (3H, OMε), 7.11 d (2$\mathrm{H_{arom}}$, *J* 8.9 Hz), 7.50–7.60 m (3$\mathrm{H_{arom}}$), 7.75–7.86 m (2$\mathrm{H_{arom}}$), 8.21 d (2$\mathrm{H_{arom}}$, *J* 8.9 Hz).

Oxidation of 1,3-diarylpropynones Ia–Ij into 1,1,2,2-tetraaroylethenes IIIa–IIIg. To a solution of 0.2–0.8 ml of CF_3CO_2H in 2–5 ml of CH_2Cl_2 was added at 18–20°C while vigorous stirring 0.4–2.0 mmol of substrates for oxidation **Ia–Ij**, then 0.4–2.0 mmol of PbO_2 was added, and the reaction mixture was stirred for 1–20 h. On completion of the reaction the mixture was poured into 50–250 ml of chloroform. The solution in $CHCl_3$ was washed with water, with saturated water solution of $NaHCO_3$, and again with water, and then it was dried over Na_2SO_4. The solvents were distilled off, and the residue was subjected to column chromatography on silica gel, eluent petroleum ether (bp 40–70°C)–chloroform. Yield of tetraketones **IIIa–IIIg** was determined from the weight of the fractions obtained by chromatography.

***E*-1,2-Bis(4-methylphenylcarbonyl)-1,2-bis(phenylcarbonyl)ethene (IIIa),** mp 200–202°C. IR spectrum, ν, cm^{-1}:1650 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (6H, 2Me), 7.16 d (4$\mathrm{H_{arom}}$, *J* 8.0 Hz), 7.37 t (4$\mathrm{H_{arom}}$, *J* 7.5 Hz), 7.50 t (2$\mathrm{H_{arom}}$, *J* 7.5 Hz), 7.81 d (4$\mathrm{H_{arom}}$, *J* 8.0 Hz), 7.92 d (4$\mathrm{H_{arom}}$, *J* 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.82 q (*J* 126.9 Hz), 128.73 d.d (*J* 163.5, 7.6 Hz), 129.52 d.t (*J* 159.8, 4.9 Hz), 129.74 d.t (*J* 161.7, 6.8 Hz), 129.89 d.d (*J* 161.2, 6.3 Hz), 133.59 t (*J* 7.5 Hz), 134.14 d.t (*J* 162.1, 7.4 Hz), 136.01 t (*J* 7.2 Hz), 145.4 m (*J* 6.0 Hz), 150.42 s, 191.81 t (*J* 3.9 Hz), 192.42 t (*J* 5.0 Hz). Found, %: C 80.97; H 5.30. M^+ 472. $C_{32}H_{24}O_4$. Calculated, %: C 81.34; H 5.12. *M* 472.17.

***E*-1,2-Bis(3,4-dimethylphenylcarbonyl)-1,2-bis(phenylcarbonyl)ethene (IIIb),** mp 196–198°C. IR spectrum, ν, cm^{-1}:1640 (C=O). ^{1}H NMR spectrum

($CDCl_3$), δ, ppm: 2.19 s (6H, 2Me), 2.23 s (6H, 2Me), 7.12 d ($2H_{arom}$, *J* 7.9 Hz), 7.36 t ($4H_{arom}$, *J* 7.5 Hz), 7.49 t ($2H_{arom}$, *J* 7.5 Hz), 7.65 C ($2H_{arom}$), 7.68 d ($2H_{arom}$, *J* 7.9 Hz), 7.92 d ($4H_{arom}$, *J* 7.5 Hz). Found, %: C 81.65; H 5.62. M^+ 500. $C_{34}H_{28}O_4$. Calculated, %: C 81.58; H 5.64. *M* 500.20.

***E*-1,2-Bis(2,4,6-trimethylphenylcarbonyl)-1,2-bis(phenylcarbonyl)ethene (IIIc),** mp 257–260°C. IR spectrum, ν, cm^{-1}:1660 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.08 s (6H, 2Me), 2.13 s (12H, 4Me), 6.48 s ($2H_{arom}$), 7.40 t ($4H_{arom}$, *J* 7.4 Hz), 7.53 t ($2H_{arom}$, *J* 7.4 Hz), 7.71 d ($4H_{arom}$, *J* 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.73 q.d (*J* 127.2, 4.9 Hz), 21.02 q.t (*J* 127.2, 4.9 Hz), 128.25 d.d (*J* 162.2, 7.0 Hz), 28.51 d.m (*J* 156.6, 4.9 Hz), 128.80 d.t (*J* 160.3, 6.9 Hz), 133.56 d.t (*J* 161.5, 7.7 Hz), 134.86 m (*J* 4.0 Hz), 135.92 q (*J* 5.6 Hz), 136.51 t (*J* 7.7 Hz), 140.56 q (*J* 5.9 Hz), 149.36 s, 193.03 t (*J* 5.3 Hz), 197.77 C. Found, %: C 81.53; H 6.19. M^+ 528. $C_{36}H_{32}O_4$. Calculated, %: C 81.79; H 6.10. *M* 528.23.

A single crystal of compound **IIIc** of size 0.3×0.3×0.08 mm for X-ray diffraction study (Fig. 1) was obtained by slow evaporation of the solution of the compound in acetone at room temperature within several days. Crystals $C_{36}H_{32}O_4$ monoclinic, at 100 K *a* 21.487(4), *b* 8.1517(15), *c* 16.310(3) Å, β 99.297(4)°, *V* 2819.3(9) Å^3, *Z* 4, space group *C2/c*, d_{calc} 1.245 g/cm^3, μ 0.080 mm^{-1}, $1.92 \leq \theta \leq 24.99°$, 7123 reflectrions were measured, among them 2433 independent reflections (R_{int} 0.0258). The final divergence factors for all data are *R* 0.0456 and R_w 0.1181, for $I > 2\sigma(I)$ *R* 0.0391 and R_w 0.1137, *S*(*F*2) 1.064.

***E*-1,2-Bis(2,3,5,6-tetramethylphenylcarbonyl)-1,2-bis(phenylcarbonyl)ethene (IIId),** mp 258–261°C (decomp.). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.17 s (12H, 4Me), 2.24 s (12H, 4Me), 6.48 s ($2H_{arom}$), 7.37 t ($4H_{arom}$, *J* 7.5 Hz), 7.49 t ($2H_{arom}$, *J* 7.5 Hz), 7.92 d ($4H_{arom}$, *J* 7.5 Hz). Found, %: C 81.53; H 6.61. M^+ 556. $C_{38}H_{36}O_4$. Calculated, %: C 81.99; H 6.52. *M* 556.26.

***E*-1,2-Bis(4-methoxyphenylcarbonyl)-1,2-bis-(phenylcarbonyl)ethene (IIIe),** mp 150–152°C. IR spectrum, ν, cm^{-1}:1660 (C=O). ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.85 s (6H, 2MeO), 6.97 d ($4H_{arom}$, *J* 8.7 Hz), 7.47 t ($4H_{arom}$, *J* 7.4 Hz), 7.61 t ($2H_{arom}$, *J* 7.4 Hz), 7.88 d ($4H_{arom}$, *J* 8.7 Hz), 7.93 d ($4H_{arom}$, *J* 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.56 q (*J* 144.9 Hz), 114.09 d.d (*J* 162.4, 4.6 Hz), 128.73 d.d (*J* 162.9, 7.3 Hz), 129.22 d (*J* 6.5 Hz), 129.80 d.t (*J* 161.6, 6.7 Hz), 132.32 d.d (*J* 162.4, 7.0 Hz), 134.14 d.t (*J* 162.1, 7.6 Hz), 136.03 t (*J* 7.2 Hz), 150.23 s, 164.47 s, 190.48 t (*J* 3.5 Hz), 192.66 t (*J* 4.4 Hz). Found, %: C 75.88; H 4.90. M^+ 504. $C_{32}H_{24}O_6$. Calculated, %: C 76.18; H 4.79. *M* 504.16.

***E*-1,2-Bis(4-methylphenylcarbonyl)-1,2-bis(4-fluorophenylcarbonyl)ethene (IIIf),** mp 246–248°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (6H, 2Me), 7.05 t ($4H_{arom}$, *J* 8.4 Hz), 7.19 d ($4H_{arom}$, *J* 7.9 Hz), 7.81 d ($4H_{arom}$, *J* 7.9 Hz), 7.95 d.d ($4H_{arom}$, *J* 8.4, 5.3 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –99.00 m. Found, %: C 75.32; H 4.65. M^+ 508. $C_{32}H_{22}F_2O_4$. Calculated, %: C 75.58; H 4.36. *M* 508.15.

***E*-1,2-Bis(4-methoxyphenylcarbonyl)-1,2-bis-(4-nitrophenylcarbonyl)ethene (IIIg),** mp 230–232°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.83 s (6H, 2MeO), 7.05 t ($4H_{arom}$, *J* 8.4 Hz), 6.87 d ($4H_{arom}$, *J* 8.8 Hz), 7.85 d ($4H_{arom}$, *J* 8.8 Hz), 8.09 d ($4H_{arom}$, *J* 8.5 Hz), 8.24 d.d ($4H_{arom}$, *J* 8.5 Hz). Found, %: C 64.65; H 3.79; N 4.82. M^+ 594. $C_{33}H_{22}N_2O_{10}$. Calculated, %: C 64.65; H 3.73; N 4.71. *M* 594.13.

Reaction of tetraaroylethenes IIIa and IIIe with hydrazine was carried out as described in [4].

3-(4-Methoxyphenyl)-5-(4-methoxyphenylcarbonyl)-6-phenyl-4-(phenylcarbonyl)pyridazine (IVe). Yield 14%, mp 252–255°C. ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.80 s (3H, MeO), 3.83 s (3H, MeO), 6.85 d ($2H_{arom}$, *J* 8.7 Hz), 6.95 d ($2H_{arom}$, *J* 8.6 Hz), 7.23–7.27 m ($5H_{arom}$), 7.39–7.41 m ($3H_{arom}$), 7.55 d ($2H_{arom}$, *J* 8.7 Hz), 7.51–7.54 m ($2H_{arom}$), 7.68 d ($2H_{arom}$, *J* 8.6 Hz). Found, %: C 76.22; H 5.08; N 5.93. M^+ 500. $C_{32}H_{24}N_2O_4$. Calculated, %: C 76.78; H 4.83; N 5.60. *M* 500.17.

1,5-Bis(4-methylphenyl)-4,8-bisphenyl-2,3,6,7-tetraazanaphthalene (Va). Yield 35%, mp >300°C. ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 2.27 s (6H, 2Me), 7.02 d ($4H_{arom}$, *J* 7.8 Hz), 7.22 d ($4H_{arom}$, *J* 7.8 Hz), 7.24–7.27 m ($2H_{arom}$), 7.43–7.45 m ($4H_{arom}$), 7.54–7.56 m ($4H_{arom}$). Found, %: C 83.00; H 5.39; N 11.87. M^+ 464. $C_{32}H_{24}N_4$. Calculated, %: C 82.73; H 5.21; N 12.06. *M* 464.20.

1,5-Bis(4-methoxyphenyl)-4,8-bisphenyl-2,3,6,7-tetraazanaphthalene (Ve). Yield 28%, mp >300°C. ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.79 s (6H, 2MeO), 6.77 d ($4H_{arom}$, *J* 8.6 Hz), 7.35–7.38 m ($2H_{arom}$), 7.51 d ($4H_{arom}$, J 8.6 Hz), 7.54–7.56 m ($4H_{arom}$), 7.64–7.66 m ($4H_{arom}$). Found, %: C 77.92; H 5.06; N 11.03. M^+ 496. $C_{32}H_{24}N_4O_2$. Calculated, %: C 77.40; H 4.87; N 11.28. M 496.19.

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