

Oxidation of Aromatic Compounds: IX.* Stereochemistry of 1,2,3,4-Tetraaryl-2-butene-1,4-diones, Oxidation Products of Unsymmetrical Aryl(4-methoxyphenyl)acetylenes

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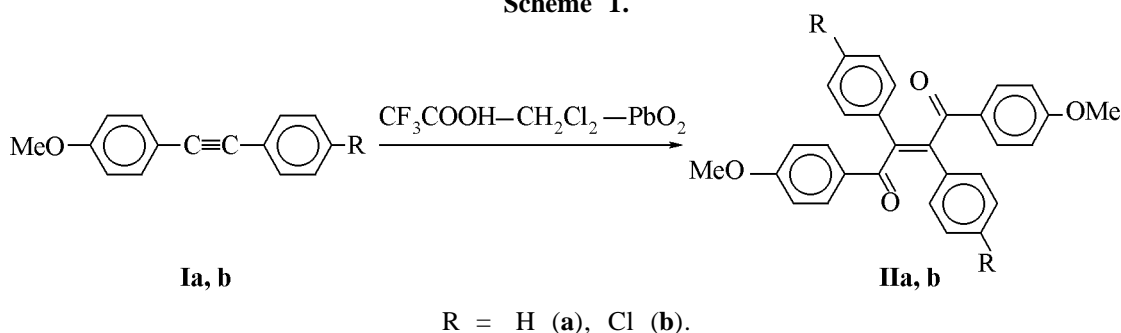
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Abstract—The identification was performed of *E*- and *Z*-isomers of 1,2,3,4-tetraaryl-2-butene-1,4-diones formed at one-electron oxidation of diarylacetylenes $p\text{-MeOC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}$ ($\text{R} = \text{H}, \text{Cl}, \text{CN}, \text{COMe}, \text{NO}_2$) in a system $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$.

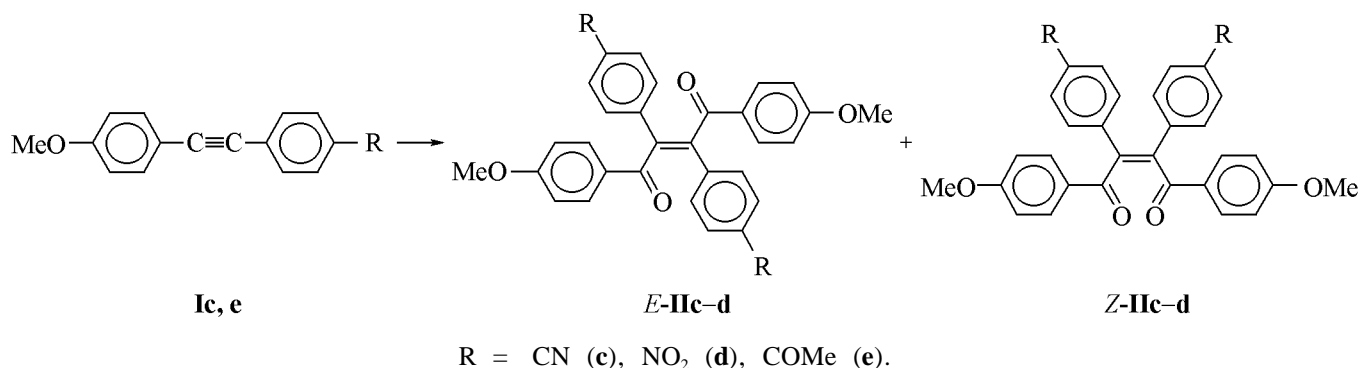
We reported formerly [2,3] that one-electron oxidation of diarylacetylenes with alkyl and electron-acceptor substituents afforded 1,2,3,4-tetraaryl-2-butene-1,4-diones (γ -diketones) with the *Z*-configuration at the double bond. Under the same conditions diarylacetylenes **Ia, b** with electron-donor methoxy group furnished regio and stereoselectively γ -diketones **IIa, b** with the *E*-configuration (Scheme 1)

[3, 4]. In its turn the reaction of aryl(4-methoxyphenyl)acetylenes **Ic-e** containing strong electron-acceptor groups resulted in pairs of *E/Z*-isomeric diketones **IIc-e** (Scheme 2) [3, 4] that were distinguished by the chromatographic and spectral characteristics but we failed to assign to each individually separated isomer **IIc-e** either *E* or *Z* configuration [3].

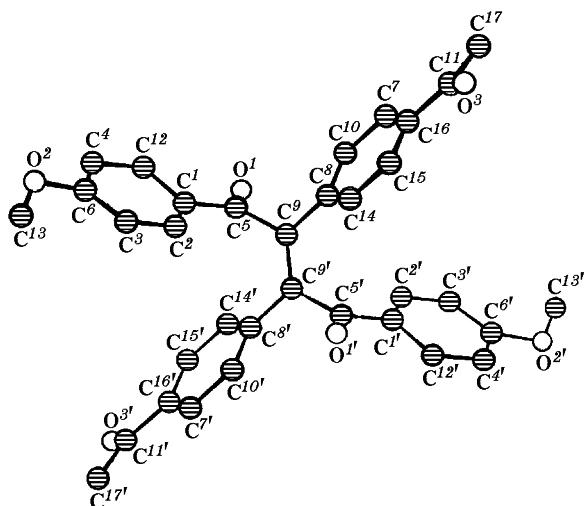
Scheme 1.



Scheme 2.

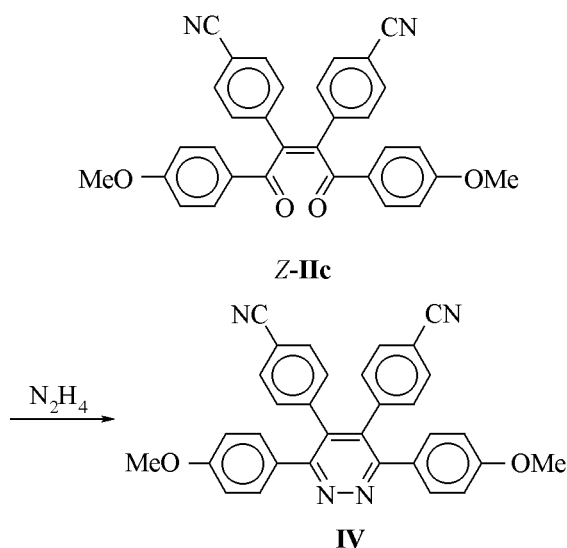


* For communication, see VIII see [1].



Molecular structure of (*E*)-2,3-bis(4-acetylphenyl)-1,4-bis(4-methoxyphenyl)-2-butene-1,4-dione (*E*-**IIe**) (hydrogen atoms not shown).

Scheme 3.



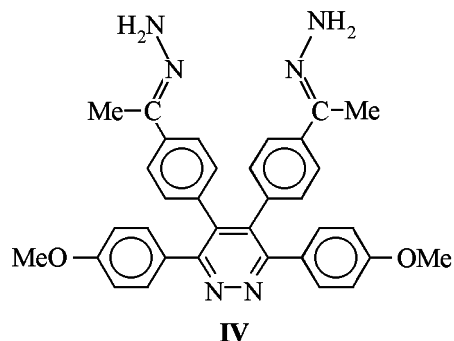
Here we report on the study of the stereochemistry of diketones **IIc–e**. We chose as criterion for assignment *E* or *Z* configuration to isomeric diketones **IIc–e** their reaction with hydrazine. We observed general trends for *E/Z* pairs of the isomeric diketones **IIc–e**. Isomers **IIc, d** with smaller chromatographic retention parameters (that are eluted from the preparative column earlier, and have larger R_f in TLC) not at all react with hydrazine and are isolated intact from the reaction mixture. Eventually these isomers were determined as having *E*-configuration at the double bond (*E*-**IIc, d**).

Since the test reaction with hydrazine for diacetyl-substituted ketones *E/Z*-**IIe** should be complicated by

polyhydrazone formation we subjected instead one of the separated stereoisomers to X-ray diffraction analysis. According to X-ray data, the isomer with smaller chromatographic retention parameter also is in *E*-configuration, (see figure, Table 1, and Experimental). Compound *E*-**IIe** is a dimer with a center of symmetry located in the middle of the $C^9-C^{9'}$ bond.

The remaining isomers in the *E/Z* pairs **IIc–e** possessing larger chromatographic retention parameters (smaller R_f) react with hydrazine indicating their *Z*-configuration. Thus diketone *Z*-**IIc** affords the corresponding pyridazine **III** (Scheme 3).

Diacetyl-substituted γ -diketone *Z*-**IIe** in reaction with hydrazine gave a complex mixture, and in the mass spectrum of the latter was observed an ion $[M]^+$ 556 corresponding to pyridazine structure **IV**.



Note that (*E*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione does not react with hydrazine not only in ethanol solution but also at boiling for 48 h in dioxane whereas its *Z*-isomer is converted into 3,4,5,6-tetraphenylpyridazine [2].

Dinitro compound *Z*-**IIId** under the reaction conditions suffers decomposition, and from the tarred reaction mixture we failed to isolate any reaction products; the stereoisomer *E*-**IIId** did not react with hydrazine (see above).

Melting points, data on ^1H NMR spectra of compounds *E*-**IIc–e** and *Z*-**IIc–e** are given in Table 2. IR, mass spectra, and elemental analyses thereof were presented in the previous publication where the configurations were not yet assigned [3].

EXPERIMENTAL

^1H NMR spectra were registered on spectrometer Bruker AM-500 (500 MHz), as internal references served the solvent signals: of acetone, δ 2.05 ppm, and chloroform, δ 7.25 ppm. IR spectra were recorded on spectrophotometer Specord 75IR from solutions in CHCl_3 . Mass spectra were measured on

MKh-1321 instrument. TLC analysis was carried out on Silufol UV-254 plates, eluent a mixture of chloroform and petroleum ether (fraction of bp 40–70°C).

X-ray diffraction analysis of diketone *E-IIe* was performed by V.S. Fundamenskii at the Chair of crystallography of geology department of St. Petersburg State University. The unit cell parameters and the intensity of reflections were measured of automatic four-circle diffractometer Syntex P2₁ (λ MoK $_{\alpha}$, graphite monochromator, θ -scanning). The structure of the compound under study was solved by the direct method and was refined in the full-matrix least-squares procedure in anisotropic approximation for nonhydrogen atoms. The location of hydrogen atoms was established from geometrical considerations and refined in isotropic approximation. All calculations were carried out on IBM PC/AT-486 along CSD software [5]. The crystals of compound *E-IIe* were obtained by slow evaporation of its diluted solution in acetone at room temperature within several days. Monoclinic crystals with the following parameters: C₃₄H₂₈O₆ (crystallographically independent is a half of the molecule) *M* 532.59; at 25°C *a* 20.307(6), *b* 5.990(2), *c* 24.17(1) Å, β 109.80(3)°, *V* 2767 Å³, *d*_C 1.279(2) g cm⁻³, *Z* 8 (for the crystallographically independent fragment, space group *C2/c*. 792 reflections were measured (at Θ_{\max} 25°). Final divergence factor *R*_F 0.0535 from 792 independent reflections with *F*(*hkl*) > 4.0sig(*F*).

Synthesis and characteristics of the initial diarylacetylenes *Ia–e* were described in [2, 3]. The procedure of oxidation of diarylacetylenes *Ia–e* in the system CF₃COOH-CH₂Cl₂-PbO₂ into 1,2,3,4-tetraaryl-2-butene-1,4-diones *IIa–e* is published in [3].

Table 1. Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic temperature of compound *E-IIe*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{equiv}
C ¹	6706 (6)	2380 (2)	3759 (5)	3.9 (4)
C ²	7001 (6)	310 (2)	3744 (5)	4.2 (5)
C ³	6925 (6)	-810 (2)	3235 (5)	3.8 (4)
C ⁴	6158 (6)	2130 (2)	2701 (5)	5.0 (5)
C ⁵	6784 (6)	3740 (2)	4289 (5)	3.3 (5)
C ⁶	6501 (6)	40 (2)	2715 (5)	4.7 (5)
C ⁷	5659 (6)	2350 (2)	5501 (5)	4.7 (5)
C ⁸	6663 (6)	1750 (2)	5174 (4)	3.3 (4)
C ⁹	7151 (5)	2560 (2)	4884 (4)	3.4 (4)
C ¹⁰	6124 (6)	3060 (2)	5208 (5)	4.2 (5)
C ¹¹	5267 (7)	-570 (3)	6052 (6)	5.0 (5)
C ¹²	6238 (6)	3210 (2)	3225 (5)	4.1 (5)
C ¹³	6801 (6)	-2830 (3)	2144 (6)	7.3 (6)
C ¹⁴	6715 (6)	-370 (2)	5409 (5)	4.1 (4)
C ¹⁵	6269 (7)	-1140 (2)	5689 (5)	4.0 (5)
C ¹⁶	5739 (6)	270 (2)	5737 (4)	4.0 (4)
C ¹⁷	4794 (7)	970 (3)	6203 (6)	7.1 (6)
O ¹	6561 (5)	5576 (15)	4279 (3)	5.0 (3)
O ²	6370 (4)	-920 (2)	2167 (3)	6.6 (3)
O ³	5264 (5)	-2550 (2)	6183 (4)	5.9 (4)

Reaction of *E*- and *Z*-isomers of 1,2,3,4-tetraaryl-2-butene-1,4-diones *IIc–e* with hydrazine.

A mixture of 0.1 mmol of *E*- or *Z*-diketone *IIc–e* and 25 mg of 85% water solution of hydrazine hydrate in 2 ml of 95% ethanol was boiled for 30 min. Then the

Table 2. Melting points and ¹H NMR spectra of *E*- and *Z*-isomers of 1,2,3,4-tetraaryl-2-butene-1,4-diones *IIc–e*

Compd. no.	mp, °C	¹ H NMR spectrum, (CD ₃) ₂ CO, δ , ppm
<i>E-IIc</i>	252–254	3.83 s (6H, 2MeO), 6.95 d (4H arom, <i>J</i> 8.8 Hz), 7.64 d (4H arom, <i>J</i> 8.7 Hz), 7.68 d (4H arom, <i>J</i> 8.7 Hz), 7.94 d (4H arom, <i>J</i> 8.8 Hz)
<i>Z-IIc</i>	210–212	3.83 s (6H, 2MeO), 6.91 d (4H arom, <i>J</i> 8.7 Hz), 7.45 d (4H arom, <i>J</i> 8.3 Hz), 7.68 d (4H arom, <i>J</i> 8.3 Hz), 7.85 d (4H arom, <i>J</i> 8.7 Hz)
<i>E-IId</i>	205–207	3.83 s (6H, 2MeO), 6.97 d (4H arom, <i>J</i> 8.9 Hz), 7.75 d (4H arom, <i>J</i> 9.0 Hz), 7.97 d (4H arom, <i>J</i> 8.9 Hz), 8.14 d (4H arom, <i>J</i> 9.0 Hz)
<i>Z-IId</i>	256–258	3.83 s (6H, 2MeO), 6.92 d (4H arom, <i>J</i> 9.0 Hz), 7.57 d (4H arom, <i>J</i> 8.9 Hz), 7.89 d (4H arom, <i>J</i> 9.0 Hz), 8.14 d (4H arom, <i>J</i> 8.9 Hz)
<i>E-IIe</i>	174–175	2.47 s (6H, 2sOMe), 3.82 s (6H, 2MeO), 6.95 d (4H arom, <i>J</i> 9.0 Hz), 7.57 d (4H arom, <i>J</i> 8.4 Hz), 7.83 d (4H arom, <i>J</i> 8.4 Hz), 7.97 d (4H arom, <i>J</i> 9.0 Hz)
<i>Z-IIe</i>	180–181	2.51 s (6H, 2sOMe), 3.82 s (6H, 2MeO), 6.90 d (4H arom, <i>J</i> 8.7 Hz), 7.36 d (4H arom, <i>J</i> 8.3 Hz), 7.84 d (4H arom, <i>J</i> 8.3 Hz), 7.85 d (4H arom, <i>J</i> 8.7 Hz)

mixture was cooled and diluted with 20 ml of water. The reaction products were extracted into chloroform (3 × 30 ml). The extract was dried with CaCl₂, and the solvent was distilled off. The residue was washed with ethyl ether (2 ± 0.5 ml) and recrystallized from 1–2 ml of acetone.

After the above workup the isomers *E*-**IIc** and *E*-**IIId** were recovered from the reaction mixture in 90% yield. Compound *Z*-**IIId** in reaction with the hydrazine hydrate underwent decomposition, and we failed to isolate the real reaction products. Diketone *Z*-**IIe** yielded a mixture of reaction products; in the mass spectra of the mixture was revealed pyridazine **IV** with $[M]^+$ 556.

3,6-Bis(4-methoxyphenyl)-4,5-bis(4-cyanophenyl)pyridazine (III) was obtained from diketone *Z*-**IIc** in 67% yield, mp 308–310°C, *R*_f 0.1 (eluent chloroform–petroleum ether, 6:1 by volume). ¹H NMR spectrum (CDCl₃, δ, ppm): 3.79 s (6H, 2MeO), 6.79 d (4H arom, *J* 8.0 Hz), 6.97 d (4H arom, *J* 8.3 Hz), 7.24 d (4H arom, *J* 8.0 Hz), 7.42 d (4H arom, *J* 8.3 Hz). IR spectrum (ν, cm⁻¹): 825, 1125, 1190, 1205, 1240, 1250, 1270, 1300, 1390, 1505, 1605,

2230 (C≡N). Mass spectrum, *m/z* (*I*_{rel}, %): 494 (100) $[M]^+$, 247 (19) $[M]^{2+}$. Found, %: C 77.89; H 4.91; N 10.96. C₃₂H₂₂N₄O₂. Calculated, %: C 77.72; H 4.48; N 11.33. *M* 494.55.

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