

Oxidation of Aromatic Compounds: XI.* Oxidation of Methyl 3-(4-Methoxyphenyl)propynoate in the System $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$

A. V. Vasilyev¹, V. S. Fundamenskii², P. Yu. Savchenkov¹,
and A. P. Rudenko¹

¹St. Petersburg State Academy of Forestry Engineering, St. Petersburg, Russia

²St. Petersburg State University, St. Petersburg, Russia

Received May 17, 2002

Abstract—Oxidation of methyl 3-(4-methoxyphenyl)propynoate in the system $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ at 0–2°C within 2 h affords in a preparative yield of 55% a product of oxidative dimerization, dimethyl 2,3-bis(4-methoxyphenylcarbonyl)but-2-ene-1,4-dicarboxylate (**II**) whose double bond is in *E*-configuration according to X-ray diffraction data.

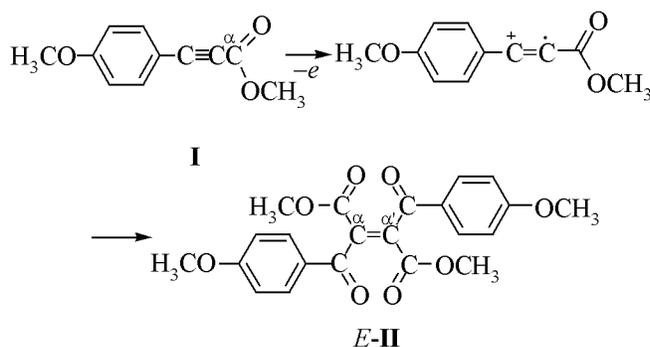
3-Arylpropynoic acids and their derivatives are extensively used in organic synthesis in preparation of versatile heterocyclic compounds [2], in Diels–Alder reactions [3], in the synthesis of substituted naphthalenes [4].

Oxidative reactions of arylpropynoic acids esters commonly result in monomeric products of the triple bond oxidation [5]. The one-electron reactions of arylacetylene compounds that we are investigating take basically another route at oxidation and afford dimeric products. For instance, the oxidative dimerization of diarylacetylenes in the systems $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ and $\text{HSO}_3\text{F}-\text{PbO}_2$ proceeded through intermediate formation of cation-radicals and furnished unsaturated γ -diketones, 1,2,3,4-tetraaryl-2-butene-1,4-diones [6], and 1,3-diarylpropynones yielded tetraketones, 1,1,2,2-tetraaroyl ethenes [7]. Similar reaction of 3-phenylpropynoic acid derivatives also should lead to polyfunctional structures.

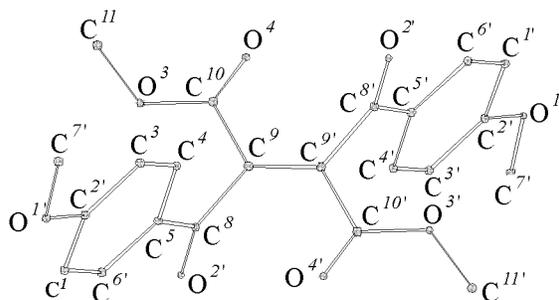
We report here on the study of methyl 3-(4-methoxyphenyl)propynoate (**I**) transformations in the system $\text{CF}_3\text{COOH}-\text{CH}_2\text{Cl}_2-\text{PbO}_2$ and on the structure determination of the product obtained. The oxidation of ester **I** in this system gave rise to diketoester (**E-II**) originating from stereo- and regiospecific oxidative dimerization of two initial molecules occurring at acetylene C^α atoms.

Exact *E-trans*-stereochemical structure of compound **II** was established by X-ray diffraction study (see figure, table, and EXPERIMENTAL). The oxid-

ation product (**E-II**) is a dimer possessing a center of symmetry in the middle of the $\text{C}^9-\text{C}^{9'}$ bond (see figure).



The synthesis of diketoester (**E-II**) from ester **I** is the first example of one-stage preparation of a representative from a class of such difficultly accessible [9] promising polycarbonyl synthons.



Molecular structure of dimethyl *E*-2,3-bis(4-methoxyphenylcarbonyl)but-2-ene-1,4-dicarboxylate (**E-II**) (hydrogen atoms are not shown).

* For communication X see [1].

EXPERIMENTAL

^1H and ^{13}C NMR spectra (the latter with and without decoupling from protons) were registered on spectrometer Bruker AM-500 at operating frequencies 500 and 125.76 MHz respectively from solutions in CDCl_3 . As internal references were used the signals of solvent (δ of residual protons at 7.25 and δ_{C} at 77.0 ppm). Mass spectra were measured on MKh-1321 instrument. IR spectra were recorded on spectrophotometer Specord 75 IR from solutions in CHCl_3 .

Methyl 3-(4-methoxyphenyl)propynoate (I) was obtained by methylation with dimethyl sulfate of 3-(4-methoxyphenyl)propynoic acid along procedures [3, 12]. Yield 70%, mp 44–46°C (from hexane) (publ.: 45–47°C [3]). IR spectrum, ν , cm^{-1} : 1710 (C=O), 2220 (C \equiv C). ^1H NMR spectrum, δ , ppm: 3.80 s (3H, OCH_3), 3.81 s (3H, OCH_3), 6.86 d (2H arom, J 8.7 Hz), 7.51 d (2H arom, J 8.7 Hz). ^{13}C NMR spectrum, δ , ppm: 52.7 q (CH_3 from COOCH_3 , J 148 Hz), 55.4 q (OCH_3 , J 144 Hz), 79.8 s (C_{sp} [α q C=O]), 87.4 t (C_{sp} [β q C=O], J 5.1 Hz), 111.3 t [C arom, *ipso*- (*ipso*- q C \equiv C)], J 8.3 Hz), 114.4 d.d (C arom, *meta*-, J 162, 4.8 Hz), 135.0 d.d (C arom, *ortho*-, J 163, 7.0 Hz), 154.8 m (C arom, *para*-), 161.6 q (C=O, J 5.0 Hz).

Preparation procedure for dimethyl 2,3-bis-(4-methoxyphenylcarbonyl)but-2-ene-1,4-dicarboxylate (E-II). In a cooled to 0–2°C mixture of 4 ml of CH_2Cl_2 and 0.76 ml (10 mmol) of CF_3COOH was dissolved at stirring 0.4 g (2.1 mmol) of ester I. To this solution was added 0.5 g (2.1 mmol) of PbO_2 , and the dispersion obtained was stirred at 0–2°C for 2 h. Then the reaction mixture was poured into 200 ml of CHCl_3 . The chloroform solution was washed with water (2 \times 30 ml), with saturated water solution of NaHCO_3 (2 \times 30 ml), with water (3 \times 30 ml), dried with sodium sulfate, and the solvent was distilled off. The solid residue was first washed on glass frit filter with ethyl ether (2 \times 1 ml), and then recrystallized from 1 ml of acetone. Yield of product II 0.22 g (55%), mp 175–177°C. IR spectrum, ν , cm^{-1} : 1715 (C=O from COOCH_3), 1670 (C=O). ^1H NMR spectrum, δ , ppm: 3.56 s (6H, 2COOCH_3), 3.88 s (6H, 2OCH_3), 6.98 d (4H arom, J 8.8 Hz), 7.95 d (4H arom, J 8.8 Hz). ^{13}C NMR spectrum, δ , ppm: 53.2 q (CH_3 from COOCH_3 , J 148 Hz), 55.6 q (OCH_3 , J 145 Hz), 114.2 d.d (C arom, *meta*-, J 162, 4.6 Hz), 128.7 t [C arom, *ipso*- (*ipso*- q C=O), J 7.2 Hz], 131.2 d.d (C arom, *ortho*-, J 161, 7.0 Hz), 142.0 s (C=C), 163.1 q (C=O from

Coordinates of nonhydrogen atoms and factors of equivalent isotropic displacement for compound (E-II)

Atom	x	y	z	B_{eq}
C ¹	0.6724(8)	0.170(2)	0.5758(6)	3.7(2)
C ²	0.6253(7)	0.020(2)	0.6250(6)	3.1(2)
C ³	0.6807(8)	-0.190(2)	0.6623(7)	3.5(2)
C ⁴	0.7837(7)	-0.249(2)	0.6483(6)	3.1(2)
C ⁵	0.8315(7)	-0.102(2)	0.5983(6)	2.8(2)
C ⁶	0.7787(7)	0.109(2)	0.5642(6)	3.2(2)
C ⁷	0.4635(8)	0.279(2)	0.6121(8)	4.9(3)
C ⁸	0.9403(8)	-0.175(2)	0.5858(6)	3.2(2)
C ⁹	1.0071(8)	-0.008(2)	0.5455(6)	3.5(2)
C ¹⁰	1.0989(7)	0.141(2)	0.6202(6)	3.5(2)
C ¹¹	1.1626(8)	0.268(2)	0.7815(6)	4.8(3)
O ¹	0.5232(5)	0.0606(13)	0.6410(4)	4.5(2)
O ²	0.9869(6)	-0.3585(13)	0.6137(5)	4.7(2)
O ³	1.0828(5)	0.1333(11)	0.7026(4)	4.3(2)
O ⁴	1.1751(5)	0.2471(13)	0.6056(4)	4.5(2)

COOCH_3 , J 4.2 Hz), 164.3 m (C arom, *para*-), 189.6 t [C=O (ketone), J 4.2 Hz]. Mass spectrum, m/z (I_{rel} , %): 412 (12) M^+ , 381 (5) [$M - \text{OCH}_3$]⁺, 353 (6) [$M - \text{COOCH}_3$]⁺, 289 (4), 261 (3), 159 (4), 135 (100) [$\text{CH}_3\text{OC}_6\text{H}_4\text{CO}$]⁺, 107 (15) [$\text{CH}_3\text{OC}_6\text{H}_4$]⁺, 92 (20). Found, %: C 63.84; H 5.02. $\text{C}_{22}\text{H}_{20}\text{O}_8$. Calculated, %: C 64.07; H 4.89. M 412.39.

X-ray diffraction study of compound (E-II). Parameters of unit cell and reflections intensities were measured on an automatic four-circle diffractometer Syntex P21 ($\lambda\text{MoK}\alpha$, graphite monochromator, ω -scanning). The structure of compound under study was solved by the direct method and refined by full-matrix least-squares method in anisotropic approximation for nonhydrogen atoms. The hydrogen atoms positions were determined geometrically and were refined in isotropic approximation. All calculations were carried out on IBM PC/AT along CSD software [9]. The crystals of compound (E-II) fit for X-ray study were obtained by slow evaporation of acetone solution within several days at room temperature. The main crystallographic data are as follows: $\text{C}_{22}\text{H}_{20}\text{O}_8$ (crystallographically independent is a half of the molecule), M 412.39; at 25°C a 12.198(5), b 5.838(4), c 14.944(6) Å, β 111.75(3)°, V 988(2) Å³, d_{C} 1.386(2) g cm⁻³, Z 4 (for the crystallographically independent fragment), space group P21/ n . In total 1119 reflections were measured (at θ_{max} 30°). The final divergence factor R_{F} 0.0456 for 1083 independent reflections with $F(\text{hkl}) > 4.0\text{sig}(F)$. The (E-II) molecule is shown on the figure, the atomic coordinates are given in the table.

The 3-(4-methoxyphenyl)propynoic acid required for preparation of the initial ester **I** was preliminarily synthesized from a 3-(4-methoxyphenyl)propenoic acid by procedure similar to described in [10]. The melting point of acid obtained was 139–141°C [11].

REFERENCES

1. Yuzikhin, O.S. and Rudenko, A.P., *Zh. Org. Khim.*, 2002, vol. 38, p. 1332.
2. Jia, C., Piao, D., Kitamura, T., and Fujiwara, Y., *J. Org. Chem.*, 2000, vol. 65, p. 7516; Levon, V.F., Zborovskii, Yu.L., and Staninets, V.I., *Zh. Obshch. Khim.*, 1998, vol. 68, p. 288; Zborovskii, Yu.L., Levon, V.F., and Staninets, V.I., *Zh. Obshch. Khim.*, 1996, vol. 66, p. 1847.
3. Benghiat, I. and Becker, E.J., *J. Org. Chem.*, 1958, vol. 23, p. 885.
4. Brown, D. and Stevenson, R., *Tetrahedron Lett.*, 1964, vol. 43, p. 3213.
5. Dayan, S., Ben-David, I., and Rozen, S., *J. Org. Chem.*, 2000, vol. 65, no. 25, p. 8816.
6. Rudenko, A.P. and Vasil'ev, A.V., *Zh. Org. Khim.*, 1995, vol. 31, p. 1502; Vasil'ev, A.V., and Rudenko, A.P., *Zh. Org. Khim.*, 1997, vol. 33, p. 1639; Rudenko, A.P., Vasil'ev A.V., *Zh. Org. Khim.*, 2000, vol. 36, p. 1583; Vasil'ev, A.V., Rudenko, A.P., and Fundamenskii, V.S., *Zh. Org. Khim.*, 2001, vol. 37, p. 558.
7. Vasil'ev, A.V., Rudenko, A.P., and Grinenko, E.V., *Zh. Org. Khim.*, 2000, vol. 36, p. 1193.
8. Graziano, M.L., Iesce, M.R., Carli, B., and Scarpati, R., *Synthesis*, 1983, p. 125.
9. Axelrud, L.G., Grin, U.N., Zavali, P.U., Pecharsky, V.K., and Fundamensky, V.S., *12th Eur. Crystallogr. Meeting., Moscow. Collect. Abstr.*, 1989, vol. 3, p. 155.
10. Walker, G.N., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 309.
11. Noyce, D.S., Matesich, M.A., and Peterson, P.E., *J. Am. Chem. Soc.*, 1967, vol. 89, p. 6225.
12. Freudenberg, K. and Wilke, G., *Chem. Ber.*, 1952, vol. 85, p. 78.