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SHORT COMMUNICATIONS

Oxidation of Bis(4-acetylphenyl)acetylene in the System HSO_3F–PbO_2

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We showed formerly that one-electron oxidation of diarylacetylenes with lead(IV) oxide in strong acids CF_3CO_2H [1, 2] or HF [3] provided a possibility to obtain difficultly accessible unsaturated 1,4-dicarbonyl compounds or fluorinated derivatives of 1,3-butadiene respectively.

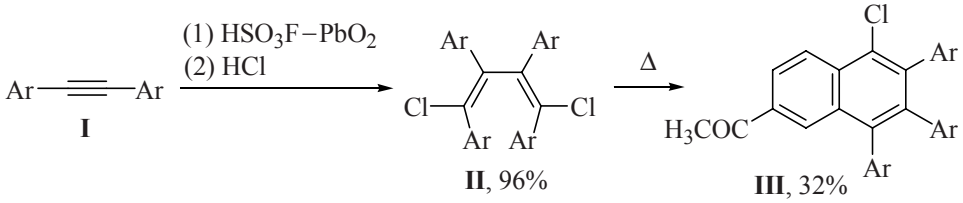
We report here on conversion of bis-(4-acetylphenyl)-acetylene (**I**) under the action of PbO_2 in the superacid HSO_3F and on further electrocyclic reactions of the oxidation product.

The oxidation of compound **I** in the system HSO_3F–PbO_2 at –50°C followed by quenching the reaction mixture in concn. hydrochloric acid cooled to –60°C led to the formation of (*E,E*)-1,2,3,4-tetrakis(4-acetylphenyl)-1,4-dichloro1,3-butadiene (**II**) in quantitative yield (Scheme 1). At storage in air at room temperature within 60 days the crystalline butadiene **II** spontaneously transformed into 6-acetyl-2,3,4-tris(4-acetylphenyl)-1-chloronaphthalene (**III**) whose structure was established by X-ray diffraction analysis (see the Figure).

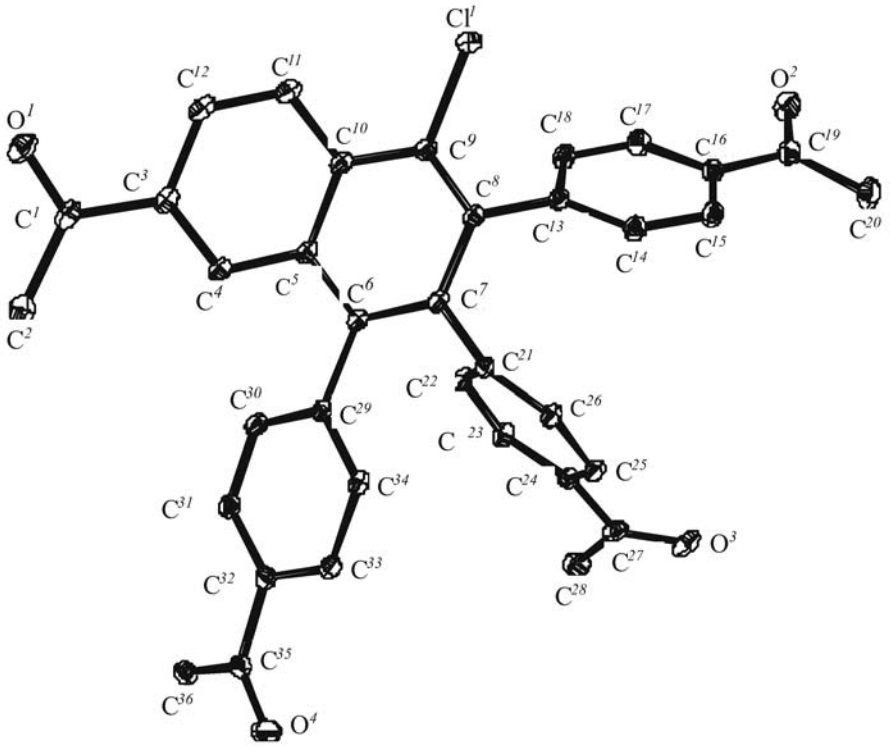
The most probable mechanism of compounds **II** and **III** formation is presented in Scheme 2. The key intermediate on the transformation path of diarylacetylene **I** to butadiene **II** is a cyclobutadiene dication **B** formed either by dimerization of cation radicals **A**, or by reaction of species **A** with initial compound **I** involving a one-electron transfer. Versatile cyclobutadiene dications that are aromatic 2π-electron systems are thoroughly investigated, and their stable existence in superacids at low temperature has been established [4]. The formation of a stable butadiene intermediate **C** is impossible even in the low-nucleophilic syperacidic media due to the extreme instability of vinyl type cations [5], especially in the case of substrates with electron-withdrawing groups [6, 7].

The reaction of dication **B** (or the corresponding mono- or difluorosulfonates forming from it in HSO_3F) with HCl molecules leads to cyclobutadiene **IV** with the *trans*-location of substituents (Scheme 2). Under the temperature of quenching the reaction mixture (–60...20°C) the conrotatory opening of the cyclobutene ring occurred very easily [8, 9] and resulted in butadiene **II** of *E,E*-configuration of the double bonds (cf. with analogous difluorobutadiene systems in [3]). Only in *E,E*-isomer **II** exists the *s-cis*-conformation (as shown in Schemes 1 and 2), the single one favoring further disrotatory [8, 9] six-electron electrocyclic transformation into compound **V**. The involvement of the π-bond

Scheme 1.



Ar = 4-$CH_3COC_6H_4$.



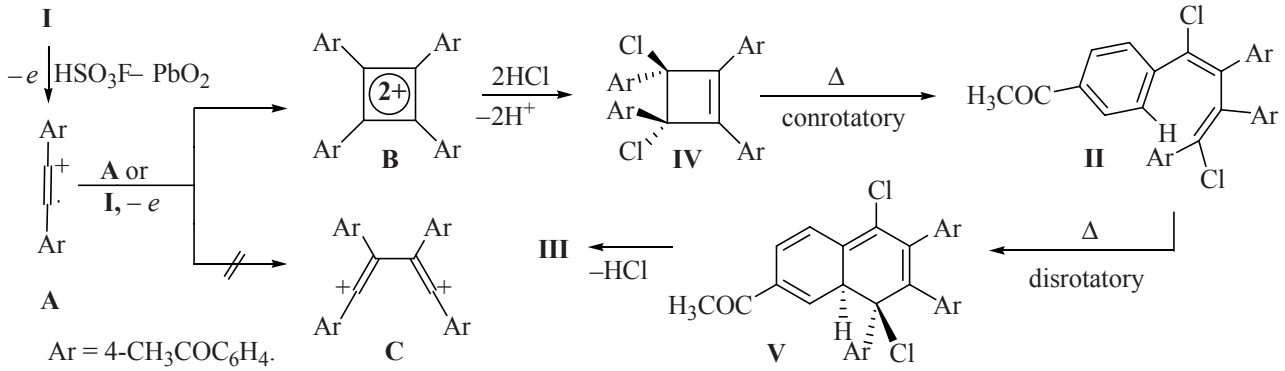
Molecular structure of 6-acetyl-2,3,4-tris(4-acetylphenyl)-1-chloronaphthalene (**III**) according to X-ray diffraction analysis.

of the aromatic ring into this electrocyclic reaction attracted our attention (see similar examples in books [8, 9]). The favorable *trans*-elimination of HCl molecule from compound **V** gave finally substituted naphthalene **III**. The driving force of this stage is the formation of an aromatic naphthalene system.

The alternative intermediate formation of cyclobutene **IV** with the *cis*-location of substituents is excluded for in this event the conrotatory opening of the cyclobutene system would provide *E,Z*-isomer **II** [8–10] where all four aromatic rings would be magnetically nonequivalent and therefore would give rise to separate signals in the ^{1}H and ^{13}C NMR spectra. Actually in the ^{1}H and ^{13}C NMR spectra of butadiene **II** the aromatic rings are equivalent in pairs (see the spectra below) in conformity to *E,E*- or *Z,Z*-isomers **II**. The latter can also form at the conrotatory opening of cyclobutene **IV** but does not really form since it has no conformation fit for cyclization into compound **V**.

It should be stressed that the ^{13}C NMR data unambiguously confirmed that after the workup of the oxidative reaction mixture just butadiene **II** and not cyclobutene **IV** was isolated, since in the ^{13}C NMR spectrum of compound obtained all the signals (save

Scheme 2.



those of the acetyl groups) were observed in the range δ 127.9–143.0 ppm (see the spectrum below) corresponding to the range of sp^2-hybridized carbon atoms, whereas in 1,2,3,4-tetraaryl-substituted cyclobutenes sp^3-hybridized atoms C^3 and C^4 of the cyclobutene ring should give rise to signals at δ 52–57 ppm [11]. The calculation by an additive scheme of the chemical shifts of atoms C^3 and C^4 in dichlorobutadiene **IV** taking into account the increment of the chlorine gave a value no more than δ 98 ppm [12] that did not exist in the spectrum.

(*E,E*)-1,2,3,4-Tetrakis(4-acetylphenyl)-1,4-dichloro1,3-butadiene (II) was obtained by oxidizing 178 mg (0.68 mmol) of diarylacetylene **I** with 162 mg (0.68 mmol) of PbO_2 in 4 ml of HSO_3F at –50°C for 2.5 h. On completion of the oxidation the reaction mixture was quenched by hydrochloric acid (30 ml) cooled to –60°C. The reaction product was filtered off, washed with water, and dried in air. Yield 202 mg (96%), mp 150–153°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.55 s (6H, 2COMe), 2.59 s (6H, 2COMe), 7.21 d ($4H_{arom}$, *J* 8.3 Hz), 7.55 d ($4H_{arom}$, *J* 8.1 Hz), 7.72 d ($4H_{arom}$, *J* 8.3 Hz), 7.81 d ($4H_{arom}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 26.5, 26.7, 127.9, 128.0, 128.5, 130.1, 135.2, 136.3, 136.8, 137.9, 142.8, 143.0, 197.1, 197.2. Mass spectrum, *m/z* (I_{rel}, %): 594 (23) M^+, 559 (26), 558 (15), 540 (100), 525 (17), 517 (49), 475 (20). Found, %: C 72.55; H 4.80. $C_{36}H_{28}Cl_2O_4$. Calculated, %: C 72.61; H 4.74. *M* 594.14.

6-Acetyl-2,3,4-tris(4-acetylphenyl)-1-chloronaphthalene (III) was obtained from 100 mg of butadiene **II**. Yield 30 mg (32%), mp 274–276°C (hexane–ethyl acetate). ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H, COMε), 2.52 s (3H, COMe), 2.55 s (3H, COMe), 2.58 s (3H, COMe), 6.90 d ($2H_{arom}$, *J* 8.3 Hz), 7.22 d ($2H_{arom}$, *J* 8.3 Hz), 7.24 d ($2H_{arom}$, *J* 8.3 Hz), 7.49 d ($2H_{arom}$, *J* 8.3 Hz), 7.81 d ($2H_{arom}$, *J* 8.3 Hz), 7.86 d ($2H_{arom}$, *J* 8.3 Hz), 8.11 d ($1H_{arom}$, *J* 1.6 Hz), 8.21 d.d ($1H_{arom}$, *J* 8.9, 1.6 Hz), 8.55 d ($1H_{arom}$, *J* 8.9 Hz). Mass spectrum: *m/z* 558 M^+. Found, %: C 77.39; H 4.86. $C_{36}H_{27}ClO_4$. Calculated, %: C 77.34; H 4.87. *M* 558.16.

X-ray diffraction analysis was performed on a single crystal of compound **III** of a size 0.60 × 0.50 × 0.40 mm ($C_{36}H_{27}ClO_4$) at temperature 100(2) K: crystals triclinic, *a* 10.1231(5), *b* 10.2137(5), *c* 14.3998(7) E, α 94.8760(10)°, β 109.9210(10)°, γ 96.3710(10), *V* 1379.06(12) E^3, *Z* 2, space group *P*-1, d_{calc} 1.346 g/cm^3, μ 0.180 mm^{-1}, 2.02 ≤ θ ≤ 29.18°. 10286 reflections were measured, 7159 (R_{int} 0.0118) among them independent, R_1 0.0504 [$I > 2\sigma(I)$], wR_2 0.1238 (for all data). The structure was solved by the direct method and refined by least-squares method for F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were found from the difference Fourier synthesis and refined in the isotropic approximation. All the calculations were carried out using software SHELXTL v. 6.10 [13].

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-500 (at operating frequencies 500 and 125.76 MHz respectively) in $CDCl_3$. As internal references served the residual signals of $CHCl_3$ (δ 7.25 ppm) in the ^{1}H NMR spectra and the signal of solvent $CDCl_3$ (δ 77.0 ppm) in the ^{13}C NMR spectra. Mass spectra were measured on MKh-1321 instrument. The X-ray diffraction study was performed using automatic diffractometer Smart APEX (graphite monochromator, MoK_α radiation, ω-θ scanning).

The synthesis and properties of bis(4-acetylphenyl)-acetylene (**I**) were described before [2].

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