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LETTERS
TO THE EDITOR

Epoxidation of Cyclohexa-1,4-dienylphosphonates

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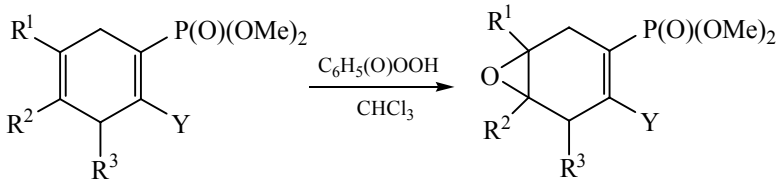
The interest to the oxirane-containing compounds is caused by their availability and high reactivity, which allows using them for the synthesis of a variety of polyfunctional compounds.

The development of the synthetic approaches to the phosphorylated oxiranes is important both in theoretical and practical aspects. In continuation of the research aimed at developing the methods for the synthesis and studying the reactions of the functionalized carbocyclic organophosphorus compounds [1, 2] in the present work we carried out the epoxidation of cyclohexa-1,4-dienylphosphonates. As the epoxidizing reagents in the reaction with the phosphorus-containing cyclodienes peracetic, perbenzoic, monoperphthalic acids and a mixture of ammonium tungstate and hydrogen peroxide were tested. However, only the epoxidation with perbenzoic acid resulted in the target carbocyclic oxiranes. In the other cases the aromatization of the starting compounds occurred to form the corresponding benzene phosphonate, while the desired product was detected only in the trace amounts. Therefore, we chose perbenzoic acid as the epoxidizing agent for various cyclohexa-1,4-dienephosphonates.



Ia–If **IIa–IIf**

$R^1 = R^2 = Me$, $R^3 = H$, Y = PO(OMe) (**a**); $R^1 = R^2 = H$, $R^3 = Me$, Y = PO(OMe) (**b**); $R^1 = Me$, $R^2 = R^3 = H$, Y = PO(OMe) (**c**); $R^1 = R^2 = Me$, $R^3 = H$, Y = Cl (**d**); $R^1 = R^2 = H$, $R^3 = Me$, Y = Cl (**e**); $R^{1(2)} = Me$, $R^{2(1)} = R^3 = H$, Y=Cl (**f**).

The epoxidation of cyclohexa-1,4-dienephosphonates **Ia**–**If** proceeds in a chloroform by stirring equimolar amounts of the starting reagents while cooling. Only the double bond distant from the phosphonate group was epoxidized to give the corresponding substituted 7-oxabicyclo[4.1.0]hept-3-ene phosphonates **IIa**–**IIf**.

The structure of the obtained oxiranes **IIa**–**IIf** was confirmed by the ^1H, ^{13}C, and ^{31}P NMR spectroscopy. In the ^{13}C NMR spectrum the carbon atoms of the C=CP fragment resonate as the doublet signals at δ_C 117–139 ppm ($^1J_{CP}$ ~ 190 Hz). The carbon atoms of the oxirane ring are represented by the singlets at δ_C ~55–60 ppm. The methyl groups are registered in the strong field (δ_C 15–22 ppm). The resonance of methoxy carbon atoms at the phosphorus atoms is recorded as a broad signal δ_C ~ 52 ppm; the constant of spin-spin coupling with the phosphorus nucleus $^2J_{CP}$ could not be determined due to insufficient resolution.

In the ^1H NMR spectra of the substituted 7-oxabicyclo[4.1.0]hept-3-enephosphonates **IIa**–**IIf** there are the signals of methylene protons of the cyclohexene ring as two doublet signals of an *AB*-system in the range of 2.5–3.0 ppm with the spin–spin coupling constant $^2J_{HH}$ ~18–19 Hz. The methoxy protons resonate at 3.7 ppm ($^3J_{HP}$ 12 Hz). Strong singlet signals at 1.3 ppm belong to protons of the methyl groups attached to the cyclohexene ring.

The ^{31}P NMR spectra of the obtained phosphorus-containing carbocyclic oxiranes **IIa**–**IIf** contain a single signal at δ_P 15-–16 ppm.

In some cases in the ^{1}H and ^{13}C NMR spectra of the reaction mixtures the signals of aromatic ring were observed, which indicated the negligible formation of the aromatization products. In the case of tetramethyl-(2-dimethyl-7-oxabicyclo[4.1.0]hept-3-ene-3,4-diyl)bis-phosphonate **IIb** only aromatic product was obtained.

Epoxidation of a mixture of the isomeric methyl-substituted 2-chloro-1,4-hexadienephosphonate **Ie** produces also two regioisomers, 1-methyl- and 6-methyl-substituted (4-chloro-7-oxabicyclo[4.1.0]hept-3-en-3-yl)phosphonates in a ratio of 2:1, respectively.

The initial cyclohexa-1,4-dienediphosphonates **Ia**–**If** were obtained by the Diels–Alder reaction of acetylenediphosphonates with the classical donor 1,3-alkadienes: 1,3-butadiene, isoprene, piperylene, and 2,3-dimethylbuta-1,3-diene [3, 4].

General procedure for the synthesis of compounds IIa–IIf. To a solution of the corresponding cyclohexa-1,4-diene-phosphonate **I** in chloroform was added dropwise a solution of an equimolar amount of perbenzoic acid in chloroform under cooling and stirring. After completing the addition the reaction mixture was allowed to stand for 1 day at room temperature, and then it was washed with sodium hydrogen carbonate, water, dried over sodium sulfate, and concentrated. The residue, yellowish oil, is the target 7-oxabicyclo[4.1.0]hept-3-enephosphonates **IIa**–**IIf**.

Tetramethyl (1,6-dimethyl-7-oxabicyclo[4.1.0]-hept-3-ene-3,4-diyl)bisphosphonate (IIa). ^{1}H NMR spectrum, δ_H, ppm: 1.33 s (6H, CH_3), 2.58 d (2H, CH^AH^B, J_{AB} 18 Hz), 3.01 d.d (2H, CH^AH^B, J_{AB} 18, $^{3}J_{BP}$ = $^{4}J_{BP}$ 4.2 Hz), 3.73 d (10H, CH_3OP, $^{3}J_{HP}$ 10.4 Hz), 3.75 d (2H, CH_3OP, $^{3}J_{HP}$ 9.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.56 (CH_3), 36.13 t (CH_2, $^{2}J_{CP}$ 13.33 Hz), 52.81 (CH_3OP), 59.86 (COC), 137.24 d (=CP, $^{1}J_{CP}$ 189.99 Hz). ^{31}P NMR spectrum: δ_P 15.37 ppm.

Tetramethyl (1-methyl-7-oxabicyclo[4.1.0]hept-3-ene-3,4-diyl)bisphosphonate (IIc). ^{1}H NMR spectrum, δ_H, ppm: 1.35 s (3H, CH_3), 2.59 d (1H, CH^AH^B, J_{AB} 19.6 Hz), 2.72 d. d (1H, CH^AH^B, J_{AB} 19.6 Hz), 2.96–3.09 m (3H, CH^AH^B+CH), 3.73 d (12H, CH_3OP, $^{3}J_{HP}$ 10.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.04 (CH_3), 30.53 t (CH_2, $^{2}J_{CP}$ 12.68 Hz), 34.40 t (CH_2, $^{2}J_{CP}$ 13.84 Hz), 52.88 (CH_3OP), 55.45 d ($CH_3\underline{C}O$, $^{3}J_{CP}$ 6.1 Hz), 56.37 d (OCH, $^{3}J_{CP}$ 7.9 Hz), 135.93 d (=CP, $^{1}J_{CP}$ 191.4 Hz), 136.00 d (=CP, $^{1}J_{CP}$ 190.3 Hz). ^{31}P NMR spectrum: δ_P 15.41 ppm.

Dimethyl (4-chloro-1,6-dimethyl-7-oxabicyclo-[4.1.0]hept-3-en-3-yl)phosphonate (IId). ^{1}H NMR spectrum, δ_H, ppm: 1.27 s (3H, CH_3), 1.28 s (3H, CH_3), 2.49–2.89 m (4H, CH_2), 3.63 br.d (3H, CH_3OP), 3.66 br.d (3H, CH_3OP). ^{13}C NMR spectrum, δ_C, ppm: 18.23 (CH_3), 18.42 (CH_3), 35.22 d (CH_2, $^{2}J_{CP}$ 7.1 Hz), 41.91 d (CH_2, $^{3}J_{CP}$ 12.9 Hz), 52.21 d (CH_3OP, $^{3}J_{CP}$ 6.6 Hz), 52.24 d (CH_3OP, $^{3}J_{CP}$ 6.6 Hz), 59.51 d ($CH_3\underline{C}$, $^{3}J_{CP}$ 10.6 Hz), 60.88 ($CH_3\underline{C}$), 119.37 d (=CP, $^{1}J_{CP}$ 188.9 Hz), 139.81 (=CCl). ^{31}P NMR spectrum: δ_P 16.12 ppm.

Dimethyl (4-chloro-5-methyl-7-oxabicyclo[4.1.0]-hept-3-en-3-yl)phosphonate (IIe). The first isomer (75%). ^{1}H NMR spectrum, δ_H, ppm: 1.19 d (3H, CH_3, $^{3}J_{HH}$ 7.2 Hz), 2.90–3.30 m (5H, CH, CH_2), 3.70 d (3H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.67 (CH_3), 30.75 d ($\underline{CH}CH_3$, $^{2}J_{CP}$ 8.8 Hz), 40.41 d (CH_2, $^{3}J_{CP}$ 12.2 Hz), 49.30 d (CH, $^{3}J_{CP}$ 10.8 Hz), 52.46 (CH_3OP), 55.00 (CH), 125.09 d (=CP, $^{1}J_{CP}$ 184.9 Hz), 142.63 (=CCl). ^{31}P NMR spectrum: δ_P 17.17 ppm. The second isomer (25%). ^{1}H NMR spectrum, δ_H, ppm: 1.20 d (3H, CH_3, $^{3}J_{HH}$ 7.2 Hz), 2.90–3.30 m (5H, CH, CH_2), 3.74 d (3H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.36 (CH_3), 34.80 d (CH_2, $^{2}J_{CP}$ 7.8 Hz), 39.14 d ($\underline{CH}CH_3$, $^{3}J_{CP}$ 10.2 Hz), 50.41 (CH), 52.46 (CH_3OP), 54.96 d (CH, $^{3}J_{CP}$ 8.8 Hz), 123.11 d (=CP, $^{1}J_{CP}$ 179.9 Hz), 139.73 (=CCl). ^{31}P NMR spectrum: δ_P 16.51 ppm.

Dimethyl (4-chloro-1-methyl-7-oxabicyclo[4.1.0]-hept-3-en-3-yl)phosphonate (IIf). Content is 65%. ^{1}H NMR spectrum, δ_H, ppm: 1.35 s (3H, CH_3), 2.56–3.10 m (5H, CH, CH_2), 3.71 d (3H, CH_3OP, $^{3}J_{HP}$ 11.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.63 (CH_3), 29.73 d (CH_2, $^{2}J_{CP}$ 8.5 Hz), 40.51 d (CH_2, $^{3}J_{CP}$ 14.6 Hz), 52.44 (CH_3OP), 56.27 d (CH, $^{3}J_{CP}$ 11.1 Hz), 57.10 (OCH), 118.35 d (=CP, $^{1}J_{CP}$ 188.9 Hz), 140.00 (=CCl). ^{31}P NMR spectrum: δ_P 16.50 ppm.

Dimethyl (4-chloro-6-methyl-7-oxabicyclo[4.1.0]-hept-3-en-3-yl)phosphonate (IIf'). Content is 35%. ^{1}H NMR spectrum, δ_H, ppm: 1.36 s (3H, CH_3), 2.56–3.10 m (5H, CH, CH_2), 3.76 d (3H, CH_3OP, $^{3}J_{HP}$ 11.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.04 (CH_3), 33.76 d (CH_2, $^{2}J_{CP}$ 8.0 Hz), 36.65 d (CH_2, $^{3}J_{CP}$ 12.8 Hz), 52.44 (CH_3OP), 55.33 d (OCH, $^{3}J_{CP}$ 9.3 Hz), 57.66 ($\underline{CH}CH_3$), 119.28 d (=CP, $^{1}J_{CP}$ 188.1 Hz), 139.68 (=CCl). ^{31}P NMR spectrum: δ_P 16.32 ppm.

The NMR spectra were recorded on spectrometers Bruker AC-200 [200.132 (^{1}H), 50.328 (^{13}C), 81.014 MHz (^{31}P)] and Bruker AC-400 [400.133 (^{1}H)]. Hexamethyldisiloxane (HMDS) was used as an internal reference for the ^{1}H NMR spectra. The phosphorus chemical shifts were determined relative to external 85% phosphoric acid. The ^{13}C spectra were taken relative to internal $CDCl_3$.

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