Effect of Temperature on the Reaction of 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic Acid with Oxygen in an Alkaline Condition

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Abstract

Results of oxidation 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid oxygen depend on temperature. At 55°C - 60°C, 2,4-di-tert-butylbicyclo(4,3,1)deca-4,6-dien-8-(N-acetylamine)-3,9-dion-1-oxa is formed. The constitution is based on dates of spectrums ¹H and ¹³C NMR. At 95°C - 97°C, mixtures of 2,4-di-tert-butylbicyclo(4,3,1)deca-4,6-dien-8-(N-acetylamine)-3,9-dion-1-oxa and of 6,8-di-tert-butyl-3-(N-acetylamine)spiro(4,5)deca-1-oxa-5,8-dien-2,7-dione are produced. Structures are calculated by the method of Hartrii-Foka. Values of enthalpies and of entropies allow to assume dynamic isomerism.

Keywords
2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic Acid, 6,8-di-tert-butyl-3-(N-acetylamine)spiro(4,5)deca-1-oxa-5,8-dien-2,7-dione Oxidation by Oxygen, 2,4-Di-tert-butylbicyclo(4,3,1)deca-4,6-dien-8-(N-acetylamine)-3,9-dion-1-oxa, NMR-Spectroscopy

1. Introduction

The oxidation by oxygen 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid (analogue ty-
NMR spectrums registered on the device “Avance-500 Bruker” rather TMS.

Example 1. Oxidation 2-(N-acetylamino)-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid at 55°C - 60°C. In solution of 3.35 g (0.01 mol) 2-(N-acetylamino)-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid 1.2 g (0.04 mol) NaOH in 60 ml of ethanol at 55 °C passed oxygen within 6 h. In a day to solution added HCl prior to the beginning of breaking (pH ≈ 6). Organic part have separated and after crystallization in the course of solvent evaporation received 0.6 g (=18%) 2,4-di-t-butylbicyclo(4,3,1)-deca-4,6-dien-8-(N-acetylamino)-3,9-dion-1-oxa and 6,8-di-t-butyl-3-(N-acetylamino)-spiro(4,5)deca-1-oxa-5,8-diene-2,7-dione. The interrelarion of results of oxidation by oxygen depends on temperature.

2. Experimental Part

2-(N-acetylamino)-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid it is synthesis on a method [7], m.p. 204°C - 206°C according to [8]; m.p. 204°C - 206°C.

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3. Results and Discussions

In conditions of interaction 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid (1) with NaOH in air atmosphere at ambient temperature 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate sodium is formed, solvable in aqueous-alcoholic solutions. However at temperature of 55°C - 60°C oxidation process proceeds, which speed above in oxygen atmosphere. For 6 h reactions ≈18 % 2,4-di-tert-butyl-bicyclo(4,3,1)deca-4,6-dien-8-(N-acetylamine)-3,9-dion-1-oxa (2) is formed (Scheme 1) At ambient temperature on air salt 3 does not react with oxygen. The composition analysis of reactionary masses and a yield of compound 2 are resulted from the data of the spectrum $^1$H NMR (Figure 1).

From the data of the spectrum $^1$H NMR follows that signals of 6.69 and 6.95 ppm ($J = 2.9$ Hz) to belong to two various protons in a hexatomic cycle of structure 2. In the spectrum $^{13}$C NMR signals of 138.92 and 139.59 ppm from atoms of carboneum correspond to the data, which analysis in a format debi (Figure 2) specifies in communication of these atoms with hydrogen.

Signal of 185.4 ppm in spectrum $^{13}$C NMR (Figure 3) confirms presence of a carbonyl group at a hexatomic cycle of structure 2.

![Scheme 1. Structures of compounds 2 and 3.](image1)

![Figure 1. Spectrum $^1$H NMR of reactionary mass of reaction compound 1 with oxygen in an alkaline condition at 55°C - 60°C for 6 h.](image2)
Figure 2. Fragment of the spectrum $^{13}$C NMR compound 2 in a format $\textit{dept}$.

Figure 3. Spectrum $^{13}$C NMR from reactionary mass of compound 1 with oxygen in an alkaline condition at 55°C - 60°C for 6 h.
At last, a signal of 76.28 ppm belongs to tetrahedral atom of carboneum, forming communications with cycle carboneums atom, tert-butyl group and atom of oxygen (Figure 4).

According to [9], a position of a signal from tetrahedral atom of carboneum in spiran to system with atom of nitrogen is in area of 75 ppm.

Data of spectrums NMR is sufficient for conclusions about structure of compound, producing by a interaction of 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid wih O₂ at temperature of 50°C - 60°C in solution of ethanol. This fact confirms bonding between atom of oxygen of a carboxyl group and of carboneum atom from hexatomic cycle.

In reaction 1 at temperature 95°C - 97°C (thermostatic control) 6,8-di-tert-butyl-3-(N-acetylamine)spi-ro(4,5) deca-1-oxa-5,8-dien-2,7-dione (4) is formed, along with compound 2 (Scheme 2).

The interrelation of resultants of reaction (2 and 4) are found from comparison there of integrals signals in spectrum ^1H NMR reactionary mass (Figure 5 and Figure 6).

The analysis of dates of a spectrum specifies in presence at reactionary mass of three compounds are identified: one of them is with structure 2 and two compounds are with structure 4 which, apparently, are structure of isomers (Figure 6).

Signals “doublet of doublets” belong to one of structure 4a, the signal “triplet” belongs to 4b (Scheme 3).

Figure 4. Correlation of data spectrums ^1H and ^13C NMR in co-ordinates C-H.

Scheme 2. Structures of compounds isolating in reaction compound 1 with oxygen.
Figure 5. Spectrum $^1$H NMR reactionary mass after oxidation of compound 1 by oxygen at 95°C - 97°C for 6 h.

Figure 6. Fragment of the spectrum $^1$H NMR (2.9 - 2.7 ppm) from a signal from group CH$_2$ of structure 4.
One of the possible factors influencing allocation of frequencies in spectrums $^1$H and $^{13}$C NMR can be asymmetry because of influence tert-butyl groups on geometrical parameters.

Path comparison of structures 2 and 4 by method of Hartree-Foka (UHF) on energy formations the result is received: (Hf$^\circ$) for 2 Hf$^\circ$ = -179.3 for 4 = -144.4 kcal$\cdot$mol$^{-1}$, values of charges on atoms of oxygen [2, O (15) $q$ = -0.58; 4, O (15) $q$ = -0.59].

Distinctions in charges on atoms of carboneum in a hexatomic cycle [2, C (1) $q$ = -0.02, 4, C (1) $q$ = +0.3].

Angle between a plane of hexatomic cycle and communication С=О (15), for 2 [C (2)-C (1)-(O)-(16)] $\omega'$ hailstones = 27.6°, for 4 [C (2) - C (1)-O (15)] $\omega'$ hailstones = 26°.

A calculates of enthalpies (H$^\circ$) and of entropies (S$^\circ$) for structures 2 and 4 have appeared comparable (2, Hf$^\circ$ = 17.5 kcal$\cdot$mol$^{-1}$, Sf$^\circ$ = 182.3 unite$\cdot$cal$\cdot$K$^{-1}$mol$^{-1}$; 4, Hf$^\circ$ = 17.1 kcal$\cdot$mol$^{-1}$, Sf$^\circ$ = 174.9 unite, cal$\cdot$K$^{-1}$mol$^{-1}$). These results in of set with calculation of geometry of structures 2 and 4 specifies in dynamic isomerism possibility.

4. Conclusion

At oxidative ring, the formation is produced in process interaction of 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with oxygen in the presence of alkali and 2,4-di-tert-butylbicyclo(4,3,1)deca-4,6-dien-8-(N-acetylamine)-3,9-dion-1-oxa and 6,8-di-tert-butyl-3-(N-acetylamine)-spiro(4,5)deca-1-oxa-5,8-di-en-2,7-dione are formed. The interrelation of results by oxygen depends on temperature. These results may by important for investigation of components during reactions 2-(N-acetylamine)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid in the conditions of biological researches.
References


