REACTION OF 3H-FURAN-2-ONES WITH TETRAZONIUM SALTS

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Synthesis of novel compounds having practical application as biologically active substances or structural blocks for building of new compounds is a fundamental problem of preparative organic chemistry. From this viewpoint, of considerable interest is the azo combination reaction because it allows easy (in soft conditions) getting some compounds used as dyes either of food application or for dyeing of fabrics. Many azo dyes, depending on the medium pH, change their structure and coloring, which determines their application as indicators.

Earlier, we studied azo combination in the series of 5-aryl-3H-furan-2-ones with aryl(hetaryl)diazonium salts. These reactions have been shown to proceed easily, in soft conditions, and to form 3-aryl(hetaryl)hydrazone substituted products with a good yield [1].

O-phenylenediamine is known to produce no diazonium salts. In the diazotization reaction conditions, a cyclic diazotype compound (benzotriazol) is formed [2].

We used m- and p-phenylenediamines in the reaction of tetraazotization. To bring about the diazotization reaction, it is necessary to carefully observe the corresponding technique, the reagent mixing order, and the temperature mode, since a side reaction to form the vesuvine dye is possible. Diazonium salts without isolation from the reactionary mixture are used as the diazo components in the azo combination reaction with 5-aryl-3H-furan-2-ones. The reaction was conducted in a water-alcoholic solution at a temperature within 0–5°C.

As the used diamines are diazotized, depending on conditions, by one or both amino groups, it is possible to expect the reaction passing by Path A to form monohydrazone substituted compounds, or by Path B to form bis products.

According to our physical and chemical studies, it has been shown that bis-hydrazone-substituted 5-aryl-3H-furan-2-ones (2 a, b) are products of tetraazotization of m-phenylenediamine and the subsequent azo combination with two molecules of 5-aryl-3H-furan-2-ones.

Treatment of p-phenylenediamine with sodium nitrite in an acidic medium is known to form a tetrazonium salt.

Interaction of 5-aryl-3H-furan-2-ones with a tetrazonium salt in soft conditions leads to compounds 3a, b – bis-arylhydrazone-substituted 5-aryl-3H-furan-2-ones.

The intramolecular hydrogen bond stabilizes products 2, 3 a, b in the hydrazonic form, which is confirmed by IR spectroscopy data.

Thus, for the first time, in the series of 3H-furan-2-ones, conditions were developed and the reaction of azo combination with tetrazonium salts was brought about to form compounds of interest as potential biologically active substances and as tetradentate ligands in complex formation reactions.

EXPERIMENTAL
IR spectra were recorded on an FSM-1201 Fourier spectrometer in KBr tablets, the spectral range being 400-4000 cm⁻¹, 1H NMR spectra were obtained on a Varian-400 spectrometer within 20-25°C in CDCl₃, TMS being the internal reference. The working frequency was 400 MHz.
A solution of 1 g (6.25 mmol) of 5-phenylfuran-2(3H)-one was added dropwise under stirring to a freshly prepared solution of 0.8 g of (6.25 mmol) of fenilen-bis-tetrazonium chloride, cooled to –5 to 0°C. The precipitate was filtered off and recrystallized from hexane–chloroform.

For 2a: Yield 81%, mp 139–140°C. IR spectrum, ν, cm–1: 1756-1752(C=O), 1648-1645(C=N), 3078–3047(NH). Found, %: C 68.57; H 4.28; N 12.16. C$_{26}$H$_{18}$N$_4$O$_4$. Calc. for, %: C 69.33; H 4.00; N 12.44.

For 2b: Yield 88%, mp 151–152°C. IR spectrum, ν, cm–1: 1791-1786(C=O), 1659-1653(C=N), 3071–3065(NH). Found, %: C 69.68; H 4.76; N 11.53. C$_{28}$H$_{22}$N$_4$O$_4$. Calc. for, %: C 70.29; H 4.60; N 11.71.

For 3a: Yield 84%, mp 143–144°C. IR spectrum, ν, cm–1: 1756-1752(C=O), 1648-1645(C=N), 3078–3047(NH). Found, %: C 68.87; H 4.13; N 12.27. C$_{26}$H$_{18}$N$_4$O$_4$. Calc. for, %: C 69.33; H 4.00; N 12.44.

For 3b: Yield 85%, mp 153–154°C. IR spectrum, ν, cm–1: 1791-1786(C=O), 1659-1653(C=N), 3059–3053(NH). Found, %: C 70.15; H 4.51; N 11.84. C$_{28}$H$_{22}$N$_4$O$_4$. Calc. for, %: C 70.29; H 4.60; N 11.71.

References


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