

Synthesis of Polyfunctional Substance by Condensation of Acetoacetic Ether with Acrylamide

Abstract

The purposeful synthesis of polyfunctional substances are an important task in organic and bioorganic chemistry. Here is presented the result for obtaining of organic compound with acetyl-carbethoxy-carbamoyl groups in one molecule. The synthesis based on the Michael type reaction between ethyl ether of acetoacetic acid and acrylamide for formation of adduct with the mentioned groups. To achieve this aim there is used a method previously developed in our research group for acrylamide condensation with organic C-H acids in phase transfer catalysis conditions for synthesis of such compounds through the reaction of Michael acrylamide with ethyl ether of acetoacetic acid. It's known, that when in organic molecule exist more atoms and atomic groups with function as electron pair donors can make possible coordination complex with metal ion as polydentate ligand. It has been investigated in quality level the possibility of coordination of the received substance in relation to iron (III) ions.

Keywords: Polyfunctional substances; Ligand; Polydentate; Ethyl ether of acetoacetic acid; Acrylamide; Phase transfer catalysis; Electron pair donors; Coordination complex; Iron ion.

Mini Review

The purposeful synthesis of polyfunctional organic substances is an important task in organic chemistry, as well as for solving practical problems in technologies of fine organic chemistry and biochemistry. This type compounds can used also as ligands, which is an important task in organometallic chemistry. Ligands from a number of organic compounds include two or more separate parts capable of forming coordinate bonds with a metal or with a metallic ion. The ethyl acetate enolate has a similar behavior, which as a bidentate ligand forms the purple coordination complexes with iron (III) salts. In this article presents the results of studies on the synthesis of a polyfunctional substances as possible ligand based on ethyl ether of acetoacetic acid, where three atomic groups can functioned as donor atoms in the coordination complex. To achieve this, we used a method previously developed in our laboratory for the synthesis of such compounds by the reaction of Michael for acrylamide with ethyl ether of acetoacetic acid.

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Mini Review Article

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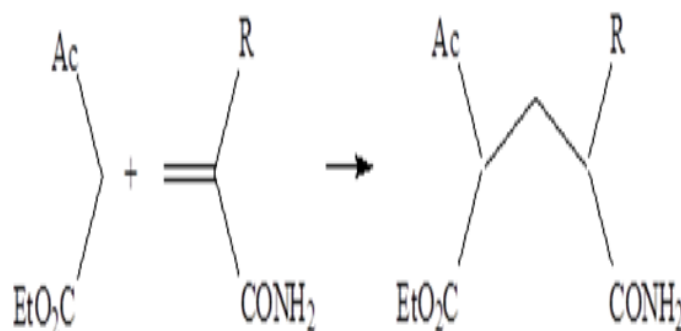
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Michael condensation between acrylamide and ethyl ether of acetoacetic acid

The condensation of acetoacetic acid ethyl ether with acrylamide in phase transfer catalysis conditions leads to new derivative-1-acetyl-1-carbethoxy-3-carbamoylpropane. It has been investigated the kinetics of 1-acetyl-1-carbethoxy-3-carbamoylpropane formation by the method of UV spectrometry [2,3].



The interaction of acetoacetic ester with acrylamide is carried out at room temperature (25-30° C). As a quaternary ammonium salt, trimethylcetyl ammonium chloride (TMCACH) is used which contributes to the yield of the product [2]. The chelating ability of the obtained compound was studied for one of the most common metal as iron in the field of human nutrition and in plants. The resulting chelate was investigated by high performance liquid chromatography with electrospray ionization / mass spectrometry. It was conducted the preliminary qualitative studies for complexation possibilities of the obtained compound. It has been investigated the coordination of the received substance in relation iron ions. The resulting complex compound is stable in organic solvent and water [3]. The received complex differs by intensive colour, which saturation changes depending on concentration of an organic solution.

Experimental Part

Equipment and Chemicals

Acetoacetic acid ethyl ester and acrylamide was supplied by the National Polytechnic University of Armenia supplier. The structure of the obtained compounds is confirmed by PMR spectroscopy, IR and mass spectrometry. IR spectra were recorded on a SPECORD M-80 IR spectrometer. The reaction progress and purity of the compounds were monitored by TLC on SilufolUV-254 plates in a the eluent was benzene-ethanol (2:1), and the display was performed using iodine vapor. The maximum absorption of acetoacetic ester in water without KOH is observed at $\delta_{\max}=250$ nm, and in the presence of KOH after 20 minutes stirring at 200C-270 nm. This can be explained by the formation of the keto-enol form of diketone with KOH, in the absorption spectrum of which the maximum corresponds to this region. ¹H NMR spectra were recorded on a Varian MERCURY-300 NMR spectrometer (300 MHz), in DMSO-d₆, internal standard-HMDS. The working frequency on protons is 300.077 MHz, on the ¹³C nucleus-75.46 MHz, chemical shifts are given in ppm regarding TMS. The study of 1-acetyl-1-carbethoxy-3-carbamoylpropanes presence in aqueous solution was carried out using Sciex Triple Quad™ 4500 Quadruple Mass Spectrometer. The sample dilution was carried out using HPLC Grade Methanol and Deionized water supplied by Carl Roth, Germany. Formic Acid (98% ACS grade) Carl Roth (Germany). The instrument and chemicals were supplied by Darmantest Laboratories, Armenia.

The synthesis of 1-acetyl-1-carbethoxy-3-carbamoylpropane

In a flask equipped with a stirrer, reflux condenser and a dropping funnel at 200° C, a mixture of 7.48 ml (57.6 mmol) of acetoacetic acid ethyl ester, 4.8 ml of a 10 N aqueous solution of KOH (57.6 mmol) and 2.4 mol of TMCACH were stirred. Within 20 minutes a solution of 3.4 g AA in 25 ml of water (57.6 mmol) was added drop wise to the mixture. The reaction mixture was stirred for 2 hours, extracted with benzene, then the aqueous layer was acidified with 5.9 ml of 30% HCl and extracted again with benzene. The benzene extracts were combined and dried over MgSO₄ overnight, after which benzene was distilled off. It had received 6.4 g of compound, yield 95%. Rf 0.82. Found, %: C 53.43; H 7.81; N 7.12. C₉H₁₅NO₄. Calculated, %: C 53.71; H 7.46; N 6.96. IR spectrum, cm⁻¹: 3200, 3450, 1740, 1700, 1680, 1620, 1290, 1140, 1030. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.25t (, J 5.2 Hz), 2.05 s, 2.12-2.32 m, 3.13 t, J 6.3 Hz), 4.05 m, 7.06 s. ¹³C

NMR (CDCl₃), δ , ppm: 203.231, 177.613, 170.054, 61.342, 54.925, 38.219, 31.446, 28.151, 16.932, 14.1. In the mass spectra of 1-acetyl-1-carbethoxy-3-carbamoylpropanethere are quite intense peak of molecular ion, the most common and consistent ions were observed at m/e 201.54.

Iron Ion Extraction

10 ml of a 0.01 M benzene solution of 1-acetyl-1-carbethoxy-3-carbamoylpropane and 1 ml of a 0.001 M aqueous solution of FeCl₃ were placed in a separatory funnel, 5 ml of a 1 M KNO₃ solution, 4 ml of H₂O were added. The mixture was stirred for 30 minutes, sedimented for 15 minutes. When moving, there was a color of the aqueous solution changed from light yellow to light lilac. The isolated aqueous layer was treated with ammonium rhodanite and a solution of amyl alcohol with ether, it was stained with a blood red color, which was compared with the color of the alcohol-ether extract obtained with treating the initial solution (1 ml of 0.001 M FeCl₃ and 9 ml of H₂O) under similar conditions [3].

Conclusion

The developed method was proved to be efficient way for 1-acetyl-1-carbethoxy-3-carbamoylpropane as poly functional organic compound synthesis. The obtained compound is characterized by modern methods of physicochemical analysis.

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