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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Ethyl Benzoate by Ozonolysis of Styrene in the Presence of Ethanol

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Abstract—Ozonolysis of styrene in the presence of ethanol was studied as a route to ethyl benzoate.

Thanks to the high reactivity of ozone and its selective action on C=C bonds, ozonolysis of unsaturated organic compounds shows promise for industrial synthesis of various compounds with oxygen-containing functional groups [1].

Recently the demand for benzoic acid and its derivatives increased. These compounds are widely used in various branches of the national economy. Benzoic acid esters are used in production of dyes [2], heat-resistant lubricants [3], herbicides [4], alkali-resistant polyester coatings [5], and also as plasticizers for synthetic resins, cellulose ethers and esters, rubbers, and paper, as additives for dyeing fabrics made from manmade fibers [5], as polymerization catalysts [3], drugs [6–8], active ingredients of plant growth regulators [9], and cosmetic means [10].

High selectivity of ozonolysis of unsaturated hydrocarbons gives reasons to hope that synthesis of benzoic acid esters by ozonolysis starting from styrene and alcohols would be commercially feasible.

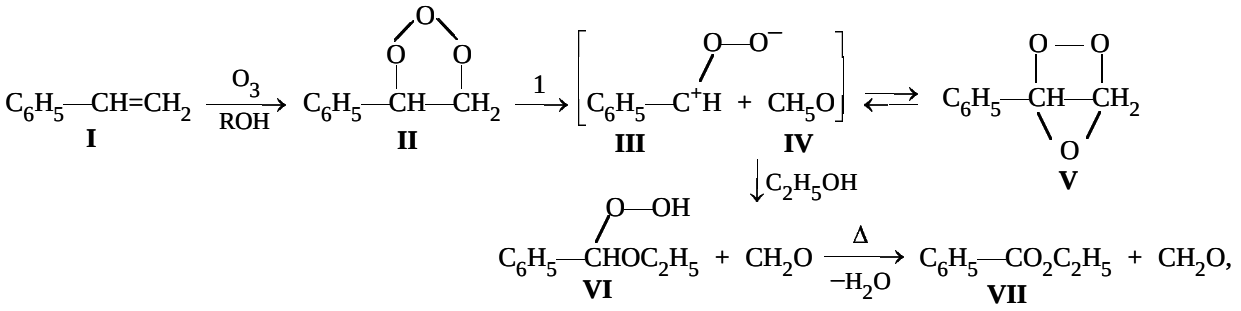
EXPERIMENTAL

Ozonolysis was performed in a glass bubbler with a porous bottom; it was charged with a styrene (**I**) solution. Ozone was generated by passing oxygen through a glow discharge at 10 kV. The ozone concentration was determined spectrophotometrically at 254 nm. Oxidation was performed to ozone breakthrough, which was detected by coloration of a 15% aqueous KI solution in a wash bottle placed at the reactor outlet (with starch as indicator). In the course of ozonolysis, we withdrew samples to determine the content of available oxygen [11] and of carboxy, carbonyl, and ester groups [12].

The thermal decomposition of ozonides was performed by heating the reaction solutions at 90–100°C for 2–4 h. In the resulting products, we determined the content of carboxy, ester, and carbonyl groups.

The IR spectra were recorded on an IFS-113V Fourier spectrometer in the range 400–4000 cm^{-1} with a resolution of 2 cm^{-1}; samples were prepared as films cast from solution on KBr plates, or as KBr pellets. The GC–MS study of ozonolysis products was performed with a Finnigan-MAT 212 device (INCOS 50 mass spectrometer, Varian 3400 gas–liquid chromatograph, capillary column with grafted SE-30, carrier gas helium, heating from 40 to 300°C at a rate of 15 deg min^{-1}, injector temperature 250°C). The ^{13}C NMR spectra of ozonolysis products were taken on a Bruker MSL 400 spectometer at 100.62 MHz; the chemical shifts were measured relative to TMS [13].

According to the experimental results, ozonolysis of styrene in the presence of ethanol can be described by the following scheme:



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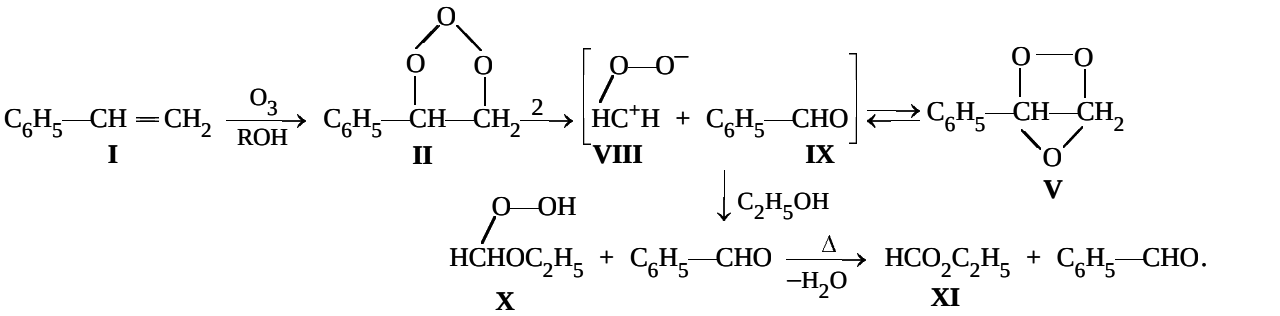

According to this scheme, addition of ozone to the double bond in styrene **I** yields unstable molozonide **II**; in the presence of a terminal double bond the aromatic system remains intact [14]. Molozonide readily decomposes into two fragments: bipolar ion **III** or **VIII** and carbonyl compound **IV** or **IX**. Presumably, owing to the positive inductive effect of the phenyl ring in styrene **I**, formation of the bipolar ion at the phenyl-substituted carbon atom [reaction (1)] is preferable [15]. The pair bipolar ion–carbonyl compound arising in decomposition of molozonide rapidly recombines in the solvent cage to form ozonide **V**. Formation of this compound is preceded by a change in the mutual orientation of fragments **III** and **IV** [reaction (1)], or **VIII** and **IX** [reaction (2)] (turn by 180°). Decomposition of ozonide **V** also yields bipolar ion **III** or **VIII** and carbonyl compound **IV** or **IX**.

Bipolar ion **III** or **VIII** is stabilized by reaction with an added active compound (ethanol) to form ethoxy hydroperoxides **VI** and **X**. In pathway (1), which is apparently preferable (see above), the second reaction product is formaldehyde **IV**. However, its content in the reaction mixture was low, probably because of easy volatilization.

We found that the content of available oxygen increases with the progress of styrene oxidation. We found that at the molar ratio styrene : ethanol = 1 : 1.5 the yield of available oxygen reaches a maximum (8.14 wt %); at the ethanol content increased further, the content of available oxygen decreases.

The IR spectra of alkoxy hydroperoxides contain the following absorption bands (cm^{-1}): 2980 [$\nu(CH_3)$]; 2950 [$\nu(CH_2)$]; 2890 [$\nu(CH_3)$]; 1310 [$\delta(C–O)$]; 1110 [$\nu(CO)$]; 990, 910, and 840 [$\nu(O–O)$] [15].

Alkoxy hydroperoxides are unstable and readily decompose even at room temperature [16]. After storage of a mixture of ethoxy hydroperoxides **VI** and **X** for 2 months at 20°C, the content of available oxygen decreased from 8.1 to 1.9%.

Thermal decomposition of alkoxy hydroperoxides **VI** and **X** was performed at 90–100°C. It is advisable to perform the reaction at elevated temperatures, because at low temperatures formation of esters is too slow. The reaction is accompanied by release of low-molecular-weight inorganic products (e.g., water, which is formed by hydrogen abstraction by the hydroxy radical).

The IR spectra of reaction products contain absorption bands at 1260 [$\nu(C–O)$] and 1715 cm^{-1} [$\nu(C=O)$], confirming the presence of ethyl benzoate. The bands at 1680 and 1690 cm^{-1} belong to benzoic acid, and the band at 1700 cm^{-1} is characteristic of aromatic aldehydes (in particular, benzaldehyde **IX**). The ^{13}C NMR spectrum of the reaction product (after vacuum distillation) confirms its identification as ethyl benzoate [δ_C, ppm: 166 (C=O), 125–135 (Ph), 61.4 (CH_2), 14.6 (CH_3)].

The major reaction products are ethyl benzoate **VII** [63.4 wt %, isolated by vacuum distillation (68°C at 15 mm Hg)] and ethyl formate **XI** (20.4 wt %); the by-products are formaldehyde (6.0 wt %), benzaldehyde (6.3 wt %), formic acid (1.8 wt %), and benzoic acid (2.1 wt %).

CONCLUSION

A procedure was suggested for preparing ethyl benzoate by ozonolysis of styrene in the presence of ethanol, followed by thermal decomposition of the intermediate ozonolysis products.

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