

Oxidative Transformation of 1,3-Cyclopentadiene in a System CuBr_2 –Ethylene Glycol

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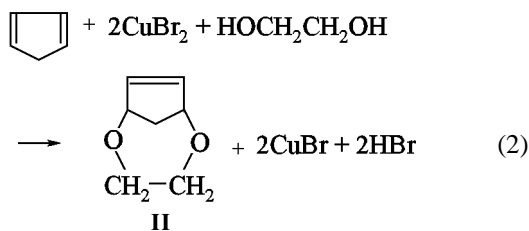
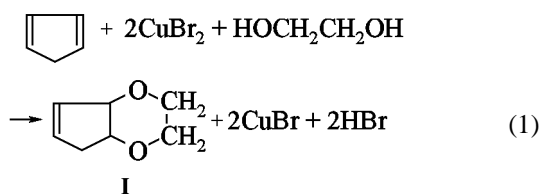
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Abstract—Oxidation of 1,3-cyclopentadiene with copper(II) bromide in dimethylformamide containing ethylene glycol resulted in 1,4-dioxabicyclo-6-nonene. The kinetic parameters of the oxidation reaction were studied. In contrast to oxidation of acyclic dienes at cyclopentadiene oxidation its interaction with one molecule of CuBr_2 is an irreversible and limiting stage.

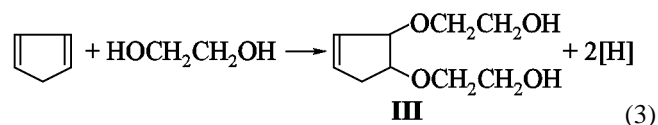
Information on conjugated dienes transformations in ethylene glycol solutions of copper(II) halides concerns an only substrate, 1,3-butadiene [1–3]. Copper(II) chlorides in the presence of Pd(II), I_2 , and I^- are capable of oxidizing conjugated dienes to alkenyldioxanes with high selectivity [4]. Therewith the main relations observed at oxidation of 1,3-butadiene and its isomers in ethylene glycol in the presence of all catalytic systems and in solutions of CuBr_2 are similar.

The similarity observed at oxidation of 1,3-cyclopentadiene and acyclic dienes with copper(II) bromide in the medium of aliphatic alcohols [5] suggested that reaction between 1,3-cyclopentadiene and CuBr_2 in ethylene glycol would provide bicyclic structures.

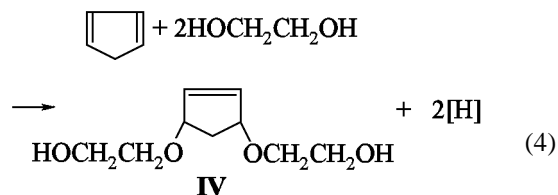
Two bicyclic compounds may presumably form in this reaction: 1,4-dioxabicyclo[4.3.0]non-6-ene (**I**), and 1,4-dioxabicyclo[4.2.1]non-6-ene (**II**) arising along equations (1) and (2) respectively.



However all attempts to obtain these compounds by oxidizing 1,3-cyclopentadiene with copper(II) bromide in ethylene glycol were unsuccessful. The interaction of cyclopentadiene with ethylene glycol solution of CuBr_2 resulted in reduction of bivalent copper, but the oxidation of diene under the applied conditions (c_{CuBr_2} 0.2–2.0 mol l^{-1} ; molar ratio diene-to-oxidant from 1 to 2, temperature 30–80°C) resulted in strong tarring. Apparently the reactions in ethylene glycol took route according to equations (3) and (4).



Compounds **III**, **IV** were not detected by chromatography due to their high boiling points. Therefore we further used DMF as solvent for it dissolved well both inorganic salts and organic compounds.



The preliminary results of the study showed that the reaction between CuBr_2 , cyclopentadiene, and ethylene glycol in DMF proceeded slower than in methanol [5] but more selectively, and that it should be carried out at higher temperature. At temperature higher than 50°C the reaction rate is too slow, and over 80°C tarring steeply grew. The effect of

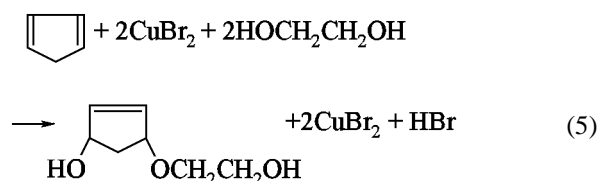
temperature on CuBr_2 conversion is shown on Fig. 1.

The reaction products were isolated from the solution containing copper bromides by extraction with ethyl ether. The extracts obtained were analyzed by GLC. By analysis of different phases of the extracts three substances were detected, one among them was dicyclopentadiene, and two others were oxidation products.

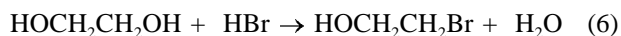
In the mass spectrum of compound **I** appeared the molecular ion of mass 126 at 100% relative abundance. Ions with masses 98, 82, and 66 arise on cleavage of groups CH_2CH_2 , $\text{CH}_2\text{CH}_2\text{O}$, and $\text{OCH}_2\text{CH}_2\text{O}$ respectively. These ions can suggest that the compound is a bicyclic diether **I** or **II**. Since at the use of different stationary phases appeared only one chromatographic peak corresponding to the compound with molecular weight 126 it is presumable that forms predominantly one of the isomeric diethers.

In the IR spectrum of oxidation product **I** was revealed a band at 1139 cm^{-1} corresponding to C–O vibrations in alkyl ether. In the course of reaction disappears the band in the UV spectrum at 240 nm corresponding to the conjugated double bonds of the cyclopentadiene, and arises a band at 215 nm from a single double bond. Taking into account greater possibility of 6-membered rings formation as compared to 7- or 8-membered [6], and also the total lack of 8-membered rings in the oxidation products of acyclic dienes [1–3] the obtained compound of molecular weight 126 should be regarded as diether **I**.

The second product of cyclopentadiene oxidation was a substance of molecular weight 146 that basing on its mass spectrum was assigned a structure of monoether **V** originating from reaction (5).



Water required for reaction (5) is presumably supplied by reaction (6).



The conditions of experiments and their results are listed in table. The quantitative study of cyclopenta-

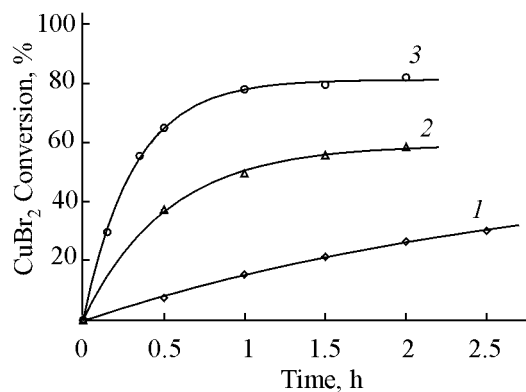


Fig. 1. Degree of CuBr_2 conversion as a function of temperature ($c_{\text{CuBr}_2}^0$ 2.0 mol l^{-1} ; $c_{\text{diene}}^0 = c_{\text{glycol}}^0$ 0.1 mol l^{-1} ; solvent DMF). (1) 50; (2) 70; (3) 90°C.

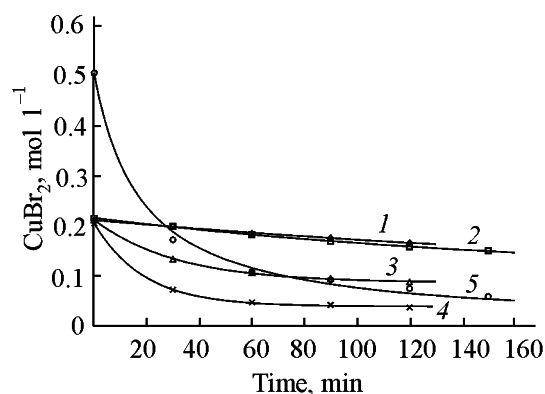


Fig. 2. Variation of CuBr_2 concentration at oxidation of cyclopentadiene in the presence of ethylene glycol (solvent DMF). (1) 35; (2) 50; (3) 70; (4) 80; (5) 90°C.

diene oxidation by copper(II) bromide in the presence of ethylene glycol in DMF was performed at the temperature 35–90°C and molar ratio diene– CuBr_2 –ethylene glycol 1:2:1. The change in oxidant concentration at various temperatures and initial concentrations is shown on Fig. 2.

To obtain the primary information on the mechanism of the process we studied the kinetic parameters of cyclopentadiene oxidation in the presence of ethylene glycol at a large and constant excess of bromide ions (5 mol l^{-1}) at 30°C. The reaction rate was followed by variation in the CuBr_2 concentration. The kinetic data were treated by differential procedure using the initial rates. The dependence of the initial rate [$v_0 = -0.5 (dc_{\text{CuBr}_2}/d\tau)$] on the starting concentration of CuBr_2 under the chosen conditions is described by equation (7) which is of the first order both with respect to $c_{\text{CuBr}_2}^0$ and c_{diene}^0 ($k = 0.031 \pm 0.0016\text{ l-mol}^{-1}\text{-min}^{-1}$).

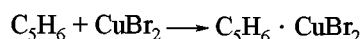
$$v_0 = (0.031 + 0.0016)c_{\text{diene}}^0 c_{\text{CuBr}_2}^0 \quad (7)$$

Results of experiments on cyclopentadiene oxidation with copper(II) bromide in the presence of ethylene glycol (solvent DMF)

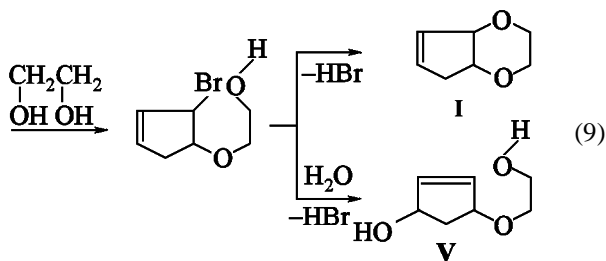
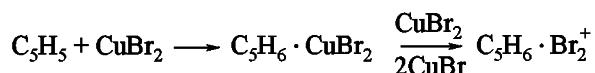
Run no.	$c_{\text{CuBr}_2}^0$, mol l ⁻¹	c_{diene}^0 , mol l ⁻¹	c_{glycol}^0 , mol l ⁻¹	T, °C	Time, min	Conversion CuBr ₂ , %	Yield ether (I), ^a %	Yield of oxidation products (I + V), ^a %
1	0.211	0.100	0.105	50	60	15	23	91
2	0.215	0.121	0.113	70	60	49	40	87
3	0.608	0.302	0.300	80	60	88	59	86
4	0.608	0.302	0.300	80	90	91	55	83
5	0.205	0.100	0.110	90	60	77	41	62

^aCalculated with respect to consumed CuBr₂.

In the presence of excess LiBr and assuming that under these conditions no polynuclear copper(II) complexes are formed in ethylene glycol the kinetic equation (7) corresponds to a simple scheme (8) of reaction mechanism where the first stage is irreversible and limiting.



No data suggest that cyclopentadiene would be completely bound in an adduct with copper(II) bromide, C₅H₆-CuBr₂. Apparently unlike the acyclic dienes [3] the cyclopentadiene adduct with CuBr₂ reacts with the second CuBr₂ molecule fast, and the first stage becomes irreversible. In aliphatic alcohols without LiBr the reaction order with respect to $c_{\text{CuBr}_2}^0$ reaches 4 apparently due to formation and involvement into the reaction of associates [CuBr₂]_n [5]. The sequence of transformations resulting in compounds I and V is represented by scheme (9) (see [5]).



Kinetic curves for $c_{\text{CuBr}_2}^0$ - in the system CuBr₂-DMF-ethylene glycol where reaction occurred

with high selectivity (86–91%) with respect to the sum of oxidation products we succeeded to describe with empirical equation (10).

$$v = -0.5 \frac{dc_{\text{CuBr}_2}}{dt} = kc_{\text{diene}}^n c_{\text{CuBr}_2}^n \quad (10)$$

Here $n = 0.2$ in the range 35–90°C, and the order of the process with respect to c_{glycol} is zero. Low order of reaction with respect to $c_{\text{CuBr}_2}^0$ in this system is caused by growing in time concentrations of CuBr and HBr.

EXPERIMENTAL

IR spectra of compounds obtained were recorded on spectrometer Specord M80 (Carl Zeiss) in the range 400–4000 cm⁻¹ from thin films. MS-GS measurements were carried out on Hewlett Packard 5071 instrument. GLC analyses were performed on chromatograph Sigma 2000 (Perkin Elmer), flame-ionization detector, carrier gas nitrogen, flow rate 1 ml min⁻¹, column 50000×0.32 mm, stationary phase Carbowax 20M; column 30000×0.25 mm, stationary phase SPB1, oven temperature 180°C, vaporizer temperature 250°C. Concentration of CuBr₂ was determined by titration.

Dicyclopentadiene was subjected to depolymerization just before the experiment. The temperature in the flask was maintained at 180–200°C. The cyclopentadiene was distilled off as it formed boiling at 40–42°C with the purity of 95–97%.

1,4-Dioxabicyclo[4.3.0]non-6-ene (I). To a solution of copper(II) bromide (80.4 g, 0.36 mol) in DMF (700 ml) was added ethylene glycol (10 ml, 0.18 mol), and to a stirred mixture within 30 min at 80°C was added freshly distilled 1,3-cyclopentadiene (14.9 ml, 0.18 mol). The stirring was continued for another

15 min. The mixture obtained was diluted with equal volume of water, the reaction product were thrice extracted into cyclohexane at the ratio solution to extractant 10:1. The precipitated copper(I) bromide was filtered off, the extract was washed with water and dried with magnesium sulfate. On removing the solvent the residue was distilled in a vacuum. The fraction boiling at 29.7–30.0°C (1 hPa) was collected. Yield 13.4 g (59% with respect to used cyclopentadiene), purity 98%. UV spectrum, λ , nm: 215 (C=C). IR spectrum, ν , cm^{-1} : 1139 (C-O), 1544 (C=C_{cycle}), 3074 (=CH). Mass spectrum, m/z (I_{rel} , %): 126 M^+ (100), 98 $[M-C_2H_4]^+$ (10), 82 $[M-C_2H_4O]^+$ (10), 66 $[M-C_2H_4O_2]^+$ (33).

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