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New approaches to syntheses of diethers and haloethers from cyclopentadiene

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Cyclopentadiene (CPD) is oxidized by copper(II) bromide and chloride in alcohol solutions to form dialkoxy- and haloethers and exhibits a higher reactivity than butadiene. Dialkoxy-, chloroalkoxy-, and dichlorocyclopentenes are formed from CPD and $CuCl_2$ without catalysts. The reaction selectivity (yield of ethers calculated per consumed $CuBr_2$) reaches 98%. The characteristic feature of the oxidation mechanism is the parallel formation of all reaction products through a common intermediate (presumably, the bromonium cation) and bromine-containing carbocationic intermediates.

Key words: cyclopentadiene, copper(II) halides, oxidation, dialkoxycyclopentenes, mechanism, kinetics.

Cyclopentadiene (CPD) is a by-product in the pyrolysis of gasoline fractions in ethylene production and exhibits a high reactivity. CPD can be used as a raw material for the preparation of valuable products: synthetic fragrants, medicines, chlorine-containing pesticides, special polymers, plasticizers, thermo- and photostabilizers, *etc.*

One of the promising ways for CPD processing is the preparation of oxygen-containing substances (*viz.*, alcohols, esters, and carbonyl compounds) used in the pharmaceutical[1—24] and perfumery[25,26] industries.

The five-membered carbon cycle in the CPD derivatives is a convenient initial structure for the synthesis of cyclopentane-derived naturally occurring substances.[3,5,17,24] The operation sequence includes, as a rule, the preparation of cyclopentene-derived ethers and esters followed by their partial hydrolysis to hydroxyethers and -esters.[3—20,27] Enzymes are often used as catalysts at the hydrolysis stage.[3—5,8,12—20] Synthons thus obtained possess a high optical purity necessary for the creation of molecules with a specific biological activity.

The known methods for the synthesis of the oxygen-containing CPD derivatives are multistage and produce the target products in low yields. The interaction of acyclic conjugated dienes with solutions of $CuBr_2$ in alcohols and acids results in the formation of diethers and diesters or bromoethers and bromoesters.[28—30] The oxidation of conjugated and nonconjugated cyclic dienes by copper(II) halides in alcoholic solutions was not studied earlier. However, we can expect that they will be oxidants in the case of CPD. Rather simple technology of oxidation processes make them very promising for the production of the CPD-based oxygen-containing substances.

This work was aimed at studying the products of CPD oxidative alkoxylation in the presence of metal complex oxidants and catalysts and the kinetics of CPD oxidation.

Experimental

The concentration of copper(II) in reaction mixtures was determined titrimetrically. GLC analyses were carried out on a Sigma 2000 instrument (Perkin Elmer) with a flame-ionization detector using nitrogen as the carrier gas and capilalry columns with lengths of 100 m (OV-101) and 50 m (Carbowax-20000). The internal standard method (1,2,3-triethyl- and 1,2-dichlorobenzene) was used for the quantitative analysis of products. IR spectra were recorded using a UR-20 spectrometer in solutions of CCl_4. The spectra of all analyzed compounds contain intense bands of C—O stretching vibration in a region of 1060—1150 cm^{-1}. ^1H NMR spectra were recorded on a Bruker AM-250 instrument (250 MHz) in $CDCl_3$ solutions using Me_4Si as the internal standard. The ^1H NMR spectra of the synthesized compounds are presented in Table 1. Cyclopentadiene (content of the main substance is 95—97%) was prepared by the monomerization of dicyclopentadiene **13** (180—200 °C) prior to syntheses.

CPD oxidation with alcoholic solutions of copper(II) halides (general procedure). A solution of CPD in the corresponding alcohol was added with stirring to a solution of copper(II) halide in the same alcohol (in particular cases, together with a

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catalyst) heated to a specified temperature. Alcohol excess with respect to CPD was 23—35 vol.%. The moment of CPD addition was taken as the beginning of reaction. After the cessation of reaction, the mixture was diluted with equal volume of water and triply extracted with equal volume of the solvent (usually cyclohexane, after double extraction, the degree of extraction of the reaction products was 93%), at the solution to extragent ratio equal to 10 : 1. The copper(I) halide that precipitated was filtered off, and the extract was washed with water and dried with $MgSO_4$. Then the extragent was distilled off at an atmospheric pressure, and the residue was distilled *in vacuo*. In some cases, a DMF —alcohol mixture (1 : 1) was used as a solvent. A suspension of copper salts in alcohols was also used.

The catalytic oxidation of CPD with dioxygen in the presence of copper(II) halides was conducted in a flask with a stirrer equipped with a bubbler for O_2 supply. The oxidation rate of CuBr was preliminarily measured at $P^0_{O_2}$ = 96 kPa, $[HBr]_0$ = 0.6 mol L^{-1}, $[CuBr]_0$ = 0.4 mol L^{-1}, and 25 °C in a shaken "catalytic necked flask." Under these conditions, the oxidation rate of CuBr was proportional to P_{O2} and [CuBr]. Experiments on the oxidation of CPD with copper bromide and regeneration of the oxidant with dioxygen were conducted in a reactor with a volume of a solution of 250 mL at $[CuBr_2]_0$ = 1.18 mol L^{-1} and $[HBr]_0$ = 1.1 mol L^{-1}. To the reaction mixture CPD (6.1 mL, the amount corresponding to the 50% conversion of the oxidant) was added at 35 °C. After 1.5 h, the reaction ceased when a 48% degree of conversion with respect to $CuBr_2$ was reached. Then air was passed through the reactor with a flow rate of 3 L h^{-1}. The concentration of $CuBr_2$, close to the initial concentration, was reached in 1.5 h at the same temperature. Six oxidation—regeneration cycles were carried out.

Results and Discussion

CPD oxidation in alcoholic solutions of $CuBr_2$. By analogy to buta-1,3-diene, the formation of diethers ($C_5H_6(OR)_2$), bromoethers ($C_6H_5(Br)OR$), and dibromides ($C_5H_6Br_2$) is possible in the reactions of CPD with alcohols.

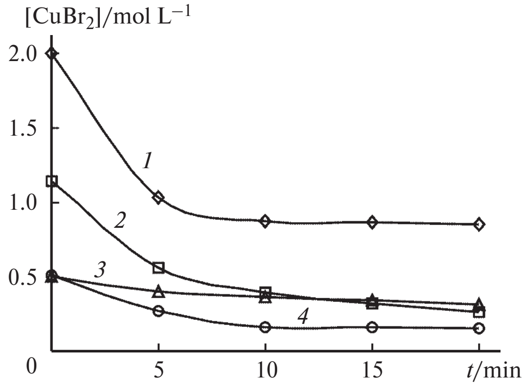
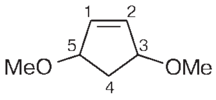


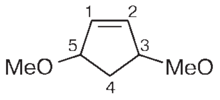
Fig. 1. Kinetic curves for the reaction of $CuBr_2$ with CPD in methanol.

	$[CuBr_2]_0$	$[CPD]_0$	T/°C
	mol L^{-1}		
1	2.010	0.500	30
2	1.141	0.571	37
3	0.519	0.200	30
4	0.512	0.200	50

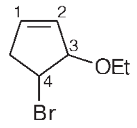
Table 1. Chemical shifts in the ^1H NMR spectra of ethers **2**, **3**, and **5—9** obtained by CPD oxidation with copper(II) bromide in MeOH and EtOH (Me_4Si, $CDCl_3$)



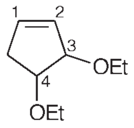
trans-**2**



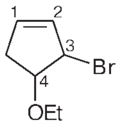
cis-**3**



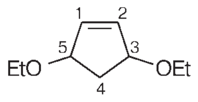
trans-**5**



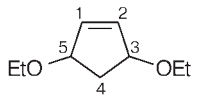
trans-**6**



trans-**7**



trans-**8**



cis-**9**

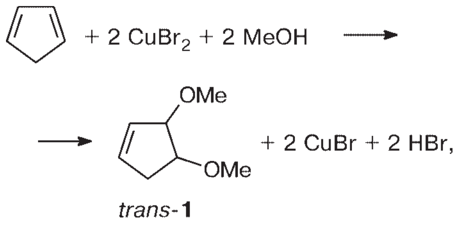
Compound	δ						
	H(1)	H(2)	H(3)	H(4)	H(4´)	H(5)	H(5´)
2	6.10	6.10	4.55	2.00	2.00	4.55	—
3	5.95	5.95	4.15	2.50	1.50	—	4.15
5	5.87	5.78	4.41	3.96	—	2.25	2.76
6	5.77	5.88	4.41	3.98	—	2.49	2.23
7	5.80	5.91	4.70	4.21	—	2.68	3.16
8	6.09	6.09	4.87	2.04	2.04	4.87	—
9	6.02	6.02	4.32	2.62	1.58	—	4.32

Table 2. Properties of ethers **2**, **3**, and **5—9** obtained by the oxidation of CPD with copper(II) bromide in MeOH and EtOH

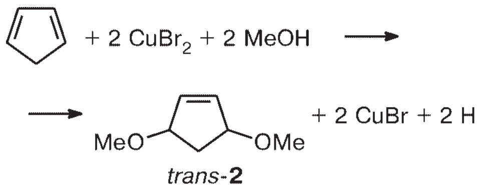
Compound	B.p.[a]/°C	n_D	Compound	B.p.[a]/°C	n_D
2	45.2	1.4442[b]	**7**	62.8	1.4510[c]
3	48.7	1.4508[b]	**8**	67.8	1.4440[c]
5	55.8	1.4405[c]	**9**	69.9	1.4452[c]
6	59.3	1.4405[c]			

[a] The b.p. values were determined at 11 hPa.
[b] The n_D index was determined at 22 °C;
[c] n_D was determined at 20 °C.

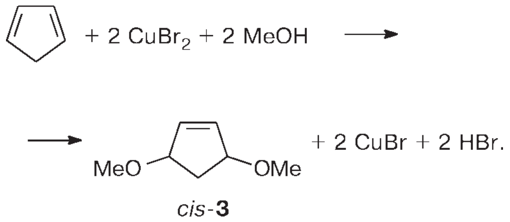
It turned out that copper(II) bromide in methanol in the reaction with CPD is reduced already at ~20 °C (Fig. 1). Four organic products of CPD oxidation with 95—98% purity were isolated on a preparative chromatograph. According to the ^1H NMR spectra (Table 1) and characteristics of the CPD oxidation products (Table 2), oxidation in the $CuBr_2$—MeOH system can be described by the following equations:



(1)

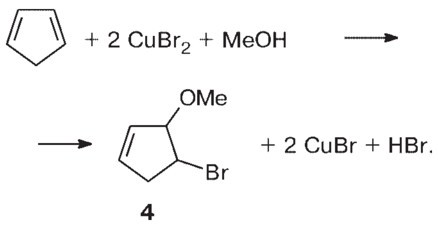


(2)



(3)

Bromomethoxycyclopentene is formed along with dimethoxycyclopentenes



(4)

Cyclic ethers are the main (87—98%) products of CPD oxidation with copper(II) bromide in methanol. The experimental conditions and results are presented in Table 3.

The initial $CuBr_2$ to CPD molar ratio correspond to stoichiometry of reactions (1)—(3). The complete conversion of the oxidant X_{CuBr_2} in a methanolic solution is reached at 37 °C and a reaction time of 87 min. The degree of conversion of $CuBr_2$ remained almost unchanged when $CaCO_3$ was added to neutralize HBr.

The oxidation of CPD in ethanol was conducted using a general procedure (see Experimental). Five fractions with a content of the main substance of 95—99% (see Tables 1 and 2, compounds **5—9**) were obtained using the preparative chromatography. The degree of copper(II) conversion is 90% already at 20 °C and increases to 97% at 80 °C. In further preparation runs, we used the reaction time of 70 min at 50 °C, which provided the 95% copper(II) conversion.

Table 3. Conditions for synthesis of methyl ethers of cyclopentene, yields of ethers, and conversion of $CuBr_2$ (X_{CuBr_2})

Entry	$[CuBr_2]_0$	$[CPD]_0$	T/°C	t /min	Yield of ethers* (%)	X_{CuBr_2}
	mol L^{-1}					
1	0.443	0.405	30	20	87	25
2	0.443	0.405	30	60	90	28
3	0.519	0.200	30	20	94	26
4	1.436	0.358	30	20	92	56
5	1.337	0.632	37	70	98	95
6	0.512	0.211	50	20	95	65

* Calculated per reacted Cu^{II}.

The temperature plots of the degree of conversion of $CuBr_2$ were studied for the reactions in PrOH, BuOH, and methyl cellosolve (Fig. 2).

An increase in the concentration of Br^- when LiBr is added to the reaction mixture somewhat decreases the yield of cyclopentene diethers. For example, in a methanol solution containing 5 mol L^{-1} LiBr, the yields of the target compounds decrease by 10—15% ($[CuBr_2]_0$ = 0.221 mol L^{-1}, 30 °C) due to the selectivity decrease.

Kinetics of CPD oxidation in alcohol solutions of $CuBr_2$. Typical plots for the concentrations of diethers and bromoethers formed by CPD oxidation in methanol and time changes in the copper(II) concentration at different initial concentrations of CPD and $CuBr_2$ are presented in Fig. 3. The error of measuring the concentrations of the products and reactants found by repeated experiments in the middle of the studied concentration region for $CuBr_2$ is 5—7%.

An important feature of CPD oxidation in alcoholic solutions of $CuBr_2$ is the absence of the S-like character of the curves for diether accumulation and a maximum

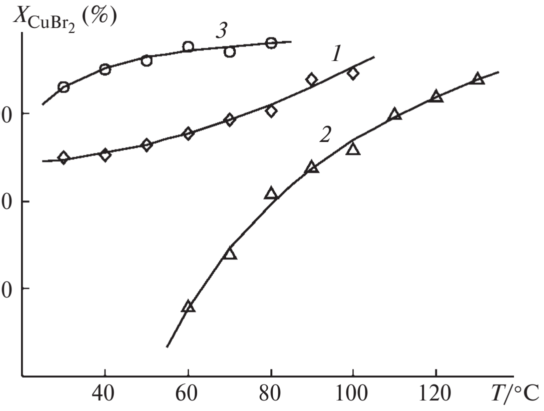


Fig. 2. Temperature effect on the degree of $CuBr_2$ conversion (X) (t = 180 min) in PrOH (*1*), BuOH (*2*), and methyl cellosolve (*3*).

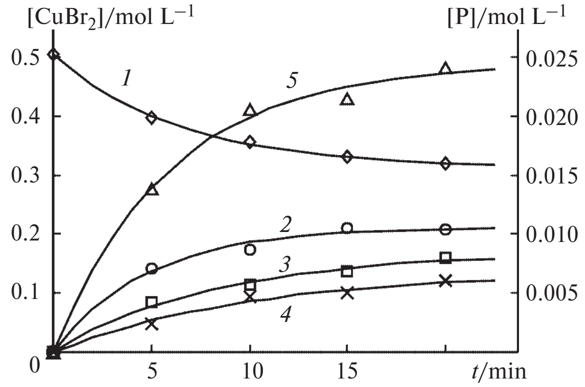


Fig. 3. Concentrations of $CuBr_2$ ($[CuBr_2]$) and the products of CPD oxidation ([P]) as functions of time ($[CuBr_2]_0$ = 0.505 mol L^{-1}, $[CPD]_0$ = 0.250 mol L^{-1}, 30 °C): *1*, $CuBr_2$; *2*, *trans*-3,4-dimethoxy-1-cyclopentene (**1**); *3*, *trans*-3,5-dimethoxy-1-cyclopentene (**2**); *4*, *cis*-3,5-dimethoxy-1-cyclopentene (**3**); and *5*, 3-methoxy-4-bromo-1-cyclopentene (**4**).

in the curve for bromoether accumulation (see Fig. 3). This indicates a low concentration of the products preceding diether formation and a low rate of further transformations of the bromoether. The latter fact can be explained under the assumption that the bromine atom in the bromoether is not allylic and the observed bromoether has structure **4** or **5**.

The ratios of the concentrations of isomeric diethers and bromoether remain unchanged during the reaction (beginning from the third minute of the reaction). This can be treated as a proof for the formation of all detected ethers through one common intermediate (Scheme 1).

Good convergence of the material balance of the process (92—98%) suggests that in the whole studied temperature and concentration interval the following equality is fulfilled:

$$-0.5\mathrm{d}[CuBr_2]/\mathrm{d}t = \mathrm{d}[\mathbf{1}]/\mathrm{d}t + \mathrm{d}[\mathbf{2}]/\mathrm{d}t + \mathrm{d}[\mathbf{3}]/\mathrm{d}t + \mathrm{d}[\mathbf{4}]/\mathrm{d}t, \quad (5)$$

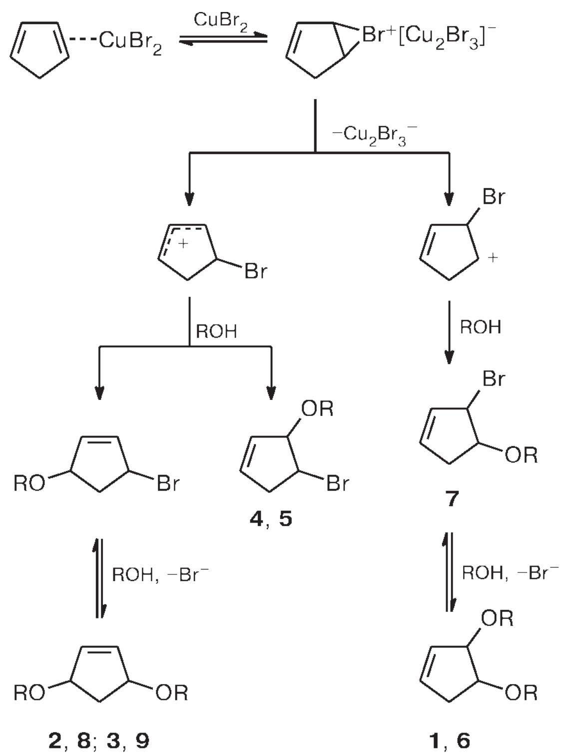
where [**1**]—[**4**] are the concentrations of compounds shown in Fig. 3 and in Eqs. (1)—(4). The constancy of the ratios of product concentrations when the initial concentrations of the reactants and time are varied

$$[\mathbf{1}] : [\mathbf{2}] : [\mathbf{3}] : [\mathbf{4}] = 0.38 : 0.26 : 0.33 : 1 \quad (6)$$

allows us to restrict the kinetic model by the equation describing the change in the overall rate of copper(II) bromide consumption during CPD oxidation because the rates of formation of all oxidation products are proportional to the overall reaction rate.

Taking into account a complicated dependence of the concentration of free $CuBr_2$ on the overall concentration of copper bromide in solutions with the changing concentrations $[Br]^-$ and [CuBr], the reaction rate was considered as a function of the overall concentration of $CuBr_2$. The following variants were analyzed.

Scheme 1



1. Power equation with a constant order with respect to $[CuBr_2]$

$$r = -\mathrm{d}[CuBr_2]/2\mathrm{d}t = k[CPD][CuBr_2]^n. \quad (7)$$

2. Power equation with a variable order with respect to $[CuBr_2]$ depending on $[CuBr_2]$,

$$r = -\mathrm{d}[CuBr_2]/2\mathrm{d}t = k[CPD][CuBr_2]^n, \quad n = f([CuBr_2]). \quad (8)$$

3. Fraction-rational equation with constant orders n_1 and n_2 with respect to $[CuBr_2]$

$$r = -\mathrm{d}[CuBr_2]/2\mathrm{d}t = k_1[CPD][CuBr_2]^{n_1}/(1 + k_2[CuBr_2]^{n_2}). \quad (9)$$

The reaction order with respect to CPD was taken equal to 1 by analogy to the data obtained for the kinetics of butadiene oxidation in solutions of copper(II) halides.[30]

The constants in the kinetic equation were estimated using the nonlinear least-squares method by the minimization of the adequacy criterion Φ,[31] which is the sum of squares of relative deviations of the calculated $CuBr_2$

Table 4. Results of calculation of the kinetic parameters for CPD oxidation by copper(II) bromide in methanol at 30 °C in different kinetic models

Number of model	Form of equation	*Φ* (%)^2	Δ (%)	k_1[a]	k_2[b]	k_3[c]
1	$r = k_1[\mathrm{CPD}][\mathrm{CuBr_2}]^{k_2}$	1833	5.6	0.29 (±0.03)	3.4 (±0.3)	—
2	$r = k_1[\mathrm{CPD}][\mathrm{CuBr_2}]^{k_2+k_3[\mathrm{CuBr_2}]}$	1605	5.2	0.29 (±0.03)	3.8 (±0.4)	−0.84 (±0.42)
3	$r = k_1[\mathrm{CPD}][\mathrm{CuBr_2}]^4/(1 + k_2[\mathrm{CuBr_2}]^3)$	1580	5.2	0.47 (±0.05)	0.59 (±0.15)	—

[a] The dimensionality of k_1 in model 1 is $\mathrm{L^{3.4}\ mol^{-3.4}\ min^{-1}}$, and that in model 3 is $\mathrm{L^4\ mol^{-4}\ min^{-1}}$; the dimensionality of k_1 in model 2 depends on the concentration of $CuBr_2$ in the exponent.

[b] In models 1 and 2, k_2 is dimensionless; in model 3, the dimensionality is $\mathrm{L^3\ mol^{-3}}$.

[c] The dimensionality of k_3 is $\mathrm{L\ mol^{-1}}$.

concentrations ($C^{\,\mathrm{calc}}$) from those measured experimentally ($C^{\,\mathrm{exp}}$)

$$\Phi = \sum_i \sum_j [(C_{i,j}^{\mathrm{calc}} - C_{i,j}^{\mathrm{exp}})100 / C_{i,j}^{\mathrm{exp}}]^2 \qquad (10)$$

where *i* is the run number, and *j* is the number of the measurement time.

The root-mean-square deviation (Δ) is the following:

$$\Delta = (\Phi/n)^{0.5}, \qquad (11)$$

where *n* is the number of measurements.

The results of estimation of the constants are presented in Table 4. Analysis of the found values of the constants and orders showed that all three kinetic models are adequate to the experimental data. The distinctions in accuracy of description between the models are much lower than the experimental error. Therefore, the discrimination of the models using objective criteria is impossible.

The calculated curves and experimental values for the time plots of the $CuBr_2$ concentration obtained using model 1 are presented in Fig. 4.

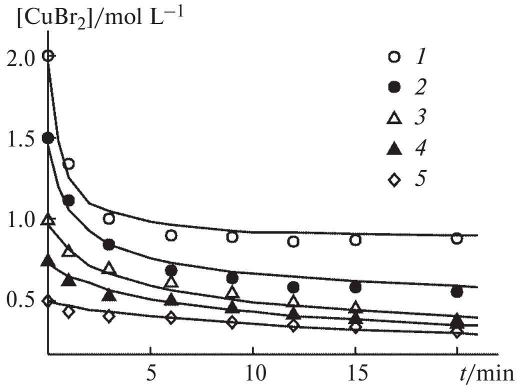


Fig. 4. Concentrations of $CuBr_2$ ([$CuBr_2$]) as functions of time calculated using model 1. [CPD] = 0.5 mol L^{-1}, 30 °C. Points are experiment, and solid lines are calculation; $[\mathrm{CuBr_2}]_0$/mol L^{-1}: *1*, 2.0; *2*, 1.5; *3*, 1.0; *4*, 0.75; and *5*, 0.5.

Based on the values of the k_2 constants in Eqs. (1) and (2) and the k_2 constant in Eq. (3) (see Table 4), we can conclude that the reaction order with respect to [$CuBr_2$] ranges from 3 to 4. The high orders with respect to [$CuBr_2$] (exceeding the stoichiometric coefficient with respect to copper(II) bromide in Eqs. (1)—(3)) are associated with a possible participation of the $(CuBr_2)_n$ polynuclear neutral associates or the $Cu_mBr_n^{(n-m-2)-}$ anionic complexes in the reaction and with the influence of CuBr on the concentration of free Br$^-$, which slows down the reaction (see above). Note that according to the thermodynamic concepts, at least two CuX_2 molecules must participate in the limiting step of the two-electron substrate oxidation by copper(II) chloride or bromide.[32,33] Two $CuBr_2$ molecules can be involved in the formation of the cyclopentenebromonium cation and bromine-containing carbocations (see Scheme 1). The formation of the polynuclear Cu$^{\mathrm{II}}$ chloride and bromide complexes has been repeatedly described in the literature. We present only some examples: $(MeCN)_2Cu_3Cl_6$,[34] $(MeCH_2CH_2OH)_2Cu_5Cl_{10}$,[35] $(Me_4N)_2Cu_4Cl_{10}$,[36] $(Et_4N)_4Cu_4Cl_{12}$,[37] and $(Me_3NH)_2Cu_4Br_{10}$.[38]

For each model (Table 5), we determined the rate constants for the formation of all ethers taking into account that correlation (6) between the concentrations of the ethers depends only on the temperature and is valid in the whole concentration interval studied.

Table 5. Rate constants for $CuBr_2$ consumption (k_1) and formation of ethers **1—4** (k_1(**1**)—k_1(**4**)) at 30 °C

Number of model	k_1	k_1(**1**)	k_1(**2**)	k_1(**3**)	k_1(**4**)
1	0.29	0.056	0.038	0.049	0.15
2	0.29	0.056	0.038	0.049	0.15
3	0.47	0.091	0.062	0.079	0.24

Note. For dimensionalities of the k_1 constants, see Table 4.

Table 6. Rate constants for CPD oxidation by copper(II) bromide (k_1) in a DMF solution in the presence of various alcohols at 30 °C

Alcohol	k_1	Alcohol	k_1
MeOH	0.32	BuOH	0.37
EtOH	0.34	Bu^{i}OH	0.32
PrOH	0.32	Bu^{s}OH	0.33
Pr^{i}OH	0.35	Bu^{t}OH	0.36

Note. The k_1 constants were calculated using model 1 ($L^{3.4}$ $mol^{-3.4}$ min^{-1}). Volume ratio alcohol : DMF = 1 : 1; molar ratio $[CuBr_2]_0 : [CPD]_0 = 2$.

The influence of the alcohol nature on the formation of cyclopentene ethers was quantitatively estimated by the comparison of the rate constants of CPD oxidation by copper(II) bromide (at the stoichiometric molar ratio) in a DMF—alcohol solution (2 : 1 v/v). The experimental data were processed using model 1 (see Table 4) assuming that the presence of the solvent (DMF) and variation of the alcohol nature have no effect on the form of the kinetic equation. The found values of the constants (Table 6) confirmed these assumptions in agreement with the scheme of product formation through common carbocationic intermediates.

CPD oxidation in a methanolic solution of $CuCl_2$. In alcoholic solutions of $CuCl_2$, the oxidation of conjugated dienes in the presence of diiodine or iodine-containing compounds, which act as catalysts,[39,40] produces mainly diethers. In this connection, it was of interest to study the interaction of CPD with alcoholic solutions of $CuCl_2$ and the influence of additives of KI or I_2 on oxidation. It was found that, unlike acyclic dienes, CPD is oxidized by $CuCl_2$ even when a catalyst is absent. Changes in the copper(II) concentration depending on the conditions are shown in Fig. 5.

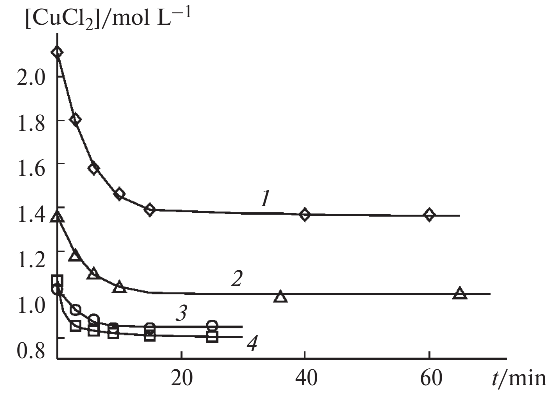
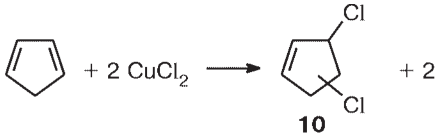
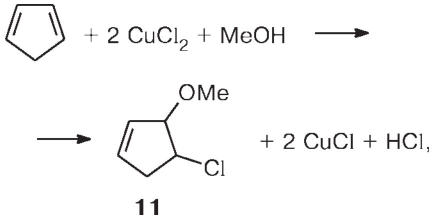


Fig. 5. Curves for $CuCl_2$ consumption in MeOH (T = 24—26 °C, molar ratio $CuCl_2$: CPD = 2 : 1), $[CuCl_2]_0$/mol L^{-1}: *1*, 2.109; *2*, 1.360; *3*, 1.067; and *4*, 1.027.

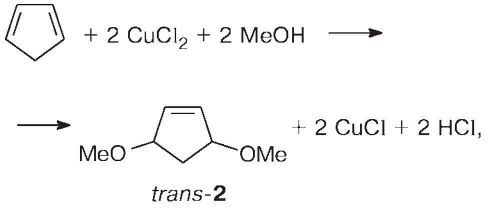
Based on the results of analysis of the reaction products of CPD oxidation by copper(II) chloride in methanol, we can describe oxidation by the following reactions:



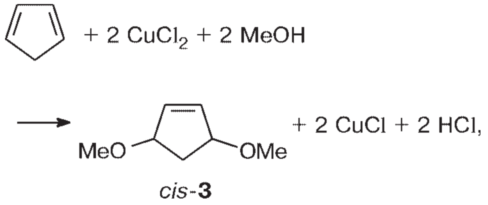
(12)



(13)



(14)



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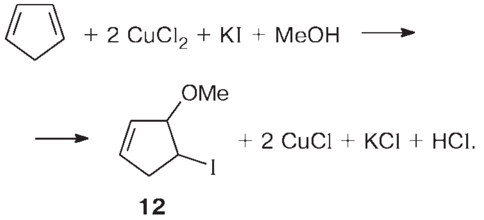
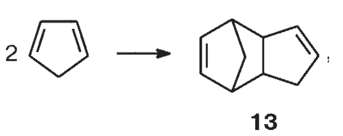
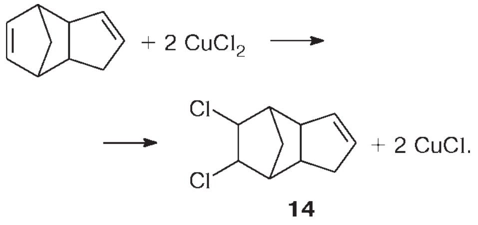


(16)

The reaction of CPD with copper(II) chloride always affords dicyclopentadiene (**13**) and the products of its chlorination along with the products of CPD oxidation.[14]



(17)



(18)

Table 7. Results of studying CPD oxidation by copper(II) chloride in methanol

Entry	$[CuCl_2]_0$	$[KI]_0$	T	t	Conversion	Overall yield[a] (%)		Yield of[b] (%))		
	mol L^{-1}		/°C	/min	X_{CuCl_2} (%)	I	II	ethers	chlorides	oxidation products
1	1.027	0	25	30	19	22	14	9	81	90
2	1.027	0	25	60	22	24	15	9	83	92
3	2.109	0	24	30	33	31	22	21	61	82
4	2.109	0	24	60	34	39	24	33	60	93
5	3.313	0	26	60	49	43	27	45	39	84
6	1.067	0.0213	23	60	24	26	11	62	35	97
7	1.067	0.0213	23	140	26	30	15	60	14	74
8	0.982	0.0107	26	30	20	—	20	—	76	—
9	1.098	0.0211	50	60	36	36	14	32	58	90
10[c]	1.075	0.0108	23	60	23	27	13	59	39	98
11[d]	1.059	0.0210	25	60	22	27	21	14	83	97

[a] The yield calculated per taken CPD using Eqs. (19) and (20) for the oxidation products (I) and dimerization (II), respectively.

[b] The yield calculated per change in the concentration of $CuCl_2$.

[c] The experiment was carried out in the presence of I_2.

[d] The experiment was carried out in the presence of KBr.

The main quantitative findings for the reaction under different conditions are presented in Table 7.

The yield of ethers calculated per converted copper(II) is at most 62% (see Table 7, entry *6*). Unlike butadiene oxidation,[41] the KI additives to a solution of $CuCl_2$ do not virtually increase the oxidation rate but substantially change the ratio of the products: the yield of diethers increases and the yield of dichlorides decreases. The chloroether : dichloride ratio decreases simultaneously. In the presence of KI, one more compound, which was preliminarily identified as iodoether, appeared in the products. The KBr additive to a solution of $CuCl_2$ has no effect on the products composition and copper(II) conversion (see Table 7, entry *11*). The kinetic regularities of oxidation in the $CuCl_2$—MeOH and $CuCl_2$—KI—MeOH systems are presented in Figs. 6 and 7. The characteristic feature of the curves in these figures (similarly to the reactions with $CuBr_2$) is the absence of the S-like shape, which is pronounced for butadiene oxidation under similar conditions.[41] It is most likely that in the chloride system chloroether **11** is not a precursor of diethers and does not contain the chlorine atom in the allyl position. Chloroethers with such a chlorine atom are much more reactive and rapidly transform into diethers (Scheme 2).

Synthesis of cyclopentene diethers using CPD oxidation by dioxygen in the presence of $CuBr_2$ as a catalyst.

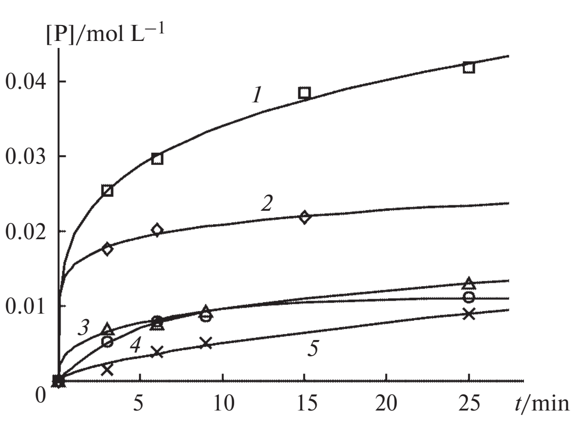


Fig. 6. Change in the concentration of the products ([P]) of CPD oxidation by copper(II) chloride ($[CuCl_2]_0$ = 1.027 mol L^{-1}, $[CPD]_0$ = 0.493 mol L^{-1}, 25 °C): *1*, 3,5-dichlorocyclopentene (**10**); *2*, *3*, 3,4-dichlorocyclopentene (**10**); *4*, **13**; and *5*, **11**.

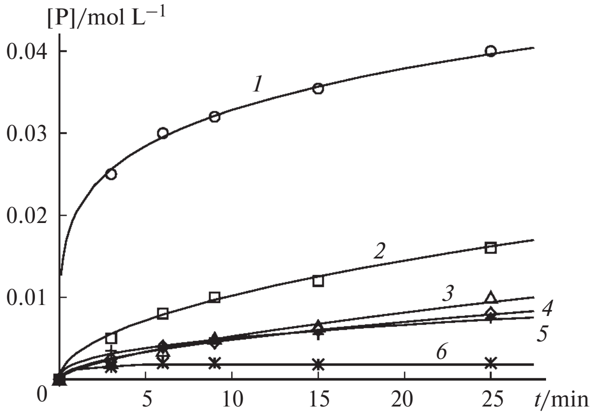
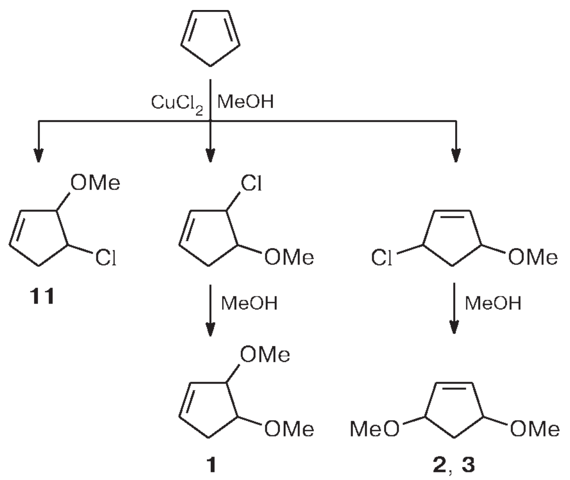


Fig. 7. Change in the concentration of the products ([P]) of CPD oxidation by copper(II) chloride in the presence of KI ($[CuCl_2]_0$ = 1.067 mol L^{-1}, $[CPD]_0$ = 0.505 mol L^{-1}, $[KI]_0$ = 0.0213 mol L^{-1}, T = 23 °C): *1*, **12**; *2*, **10**; *3*, **14**; *4*, curves for **2** and **3** coincide; *5*, **13**; and *6*, **11**.

Scheme 2



To check the possibility of the formation of cyclopentene diethers according to the stoichiometric equation

$$C_5H_6 + 2\ MeOH + 0.5\ O_2 \xrightarrow{CuBr_2} C_5H_6(OMe)_2 + H_2O \qquad (19)$$

and the estimations of stability of the products under the conditions of copper(I) oxidation, we carried out experiments in which the stages of formation of diethers according to the equation

$$C_5H_6 + 2\ CuBr_2 + 2\ MeOH \longrightarrow C_5H_6(OMe)_2 + 2\ CuBr + 2\ HBr \qquad (20)$$

and regeneration of CuBr

$$2\ CuBr + 2\ HBr + 0.5\ O_2 \longrightarrow 2\ CuBr_2 + H_2O \qquad (21)$$

were separated in time but occurred in the same reactor.

We conducted six cycles, whose durations were nearly the same. In each cycle (CPD oxidation for 1.5 h and $CuBr_2$ regeneration for 1.5 h), 50% conversion of $CuBr_2$ in the oxidation cycle was reached. The constant duration of each cycle indicates that the reaction products and water accumulated in the solution do not affect the oxidation and regeneration rates. During the whole experiment, the material balance did not substantially change, *i.e.*, the oxidation products did not enter into further transformations. New substances were not found in the cyclohexane extract of the reaction sample. A comparatively high stability of dimethoxycyclopentenes allow one to maintain high concentrations of $CuBr_2$ in the reaction solution without loss in selectivity and regenerate copper(II) before the extraction of diethers (or to conduct their isolation and regeneration in the same apparatus).

It is inconvenient to isolate diethers by distillation from the reaction solution because of a great difference in the boiling temperatures of diethers and methanol. In addition, the complete removal of methanol would be accompanied by the formation of a precipitate containing inorganic salts and the products of CPD oxidation. Therefore, we developed the variant of isolation of the target products by extraction with saturated hydrocarbons. When this method was used to separate dimethoxycyclopentenes, the concentration of the extragent (cyclohexane) in the catalytic solution containing 1.5 mol L^{-1} $CuBr_2$ in methanol was at most 2.7%. The practice showed that this amount of cyclohexane has no effect on the solubility of $CuBr_2$.

Thus, CPD oxidation by copper(II) chloride and bromide in alcoholic solutions, similarly to acyclic conjugated dienes, produces isomeric dialkoxyethers and halogen ethers containing no halogen in the allyl position. Cyclopentadiene exhibits a higher reactivity in these reactions than butadiene and, in the case of $CuCl_2$, does not require catalysts. The selectivity of ether formation reaches 98%. In the case of $CuCl_2$, oxidation begins only at high concentrations of the oxidant, at least 2.5 mol L^{-1}. The oxidation is characterized by the parallel formation of all products through the common intermediate, presumably the bromonium cation, and bromine-containing carbocationic intermediates.

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