Study of the synthesis of biaryls on homoionic forms of bentonite or montmorillonite

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Dedicated to Professor RNDr. V. Sutoris, CSc., in honour of his 60th birthday

It was found that the product yields of oxidative coupling of anisole producing 4,4'-dimethoxybiphenyl on homoionic forms of montmorillonite decrease in the same order as reduction potential of metallic ions, *i.e.* Fe^{3+}, Cu^{2+}, Co^{2+}, Al^{3+}, and Ca^{2+}. No expressive difference has been observed between bentonite and montmorillonite during their application. The course of oxidative coupling of a benzene derivative is significantly influenced by the substituents on the benzene ring.

Обнаружено, что величины выходов продуктов окислительной димеризации анизола в 4,4'-диметоксибифенил на гомоионных формах монтмориллонита понижаются в такой же последовательности, в какой уменьшается восстановительный потенциал металлических ионов: Fe^{3+}, Cu^{2+}, Co^{2+}, Al^{3+} и Ca^{2+}. Существенного различия между использованием бентонита или монтмориллонита не наблюдалось. Ход окислительной димеризации производных бензола в значительной степени зависит от заместителей в бензольном кольце.

Synthesis of biaryls and polyaryls from aromatic hydrocarbons using a mixture of copper(II) chloride and aluminium chloride (Kovacic reaction) was described long ago [1—4]. It has been proved [4] that this reaction as well as the Scholl reaction [5], which is a dimerization of alkyl aryl ethers by the action of Friedel—Crafts catalysts, proceeds through cation radicals. During the Scholl reaction, dealkylation of ethers can also proceed, giving rise to 1,4-biphenoquinones. Biphenoquinones are formed beside polyaryl ethers and biaryls also by the action of transition metals on 2,6-dialkylphenols [6]. Cu^{2+} salts catalyze oxidation of phenols by the air oxygen to 1,4-biphenoquinones and polyphenyl ethers [7, 8].

At present, the number of papers dealing with the use of inorganic carriers, including montmorillonite [9, 10], in organic synthesis increases. The presence of 4,4'-dimethoxybiphenyl was detected at the reaction of anisole with Cu^{2+}-montmorillonite [11], and the presence of quinones was spectrally proved after heating montmorillonite on which phenol [12] was adsorbed, up to the temperature of 180 °C.

This paper is aimed to examine the influence of exchangeable ion in homoionic forms of montmorillonite upon the yields of oxidative coupling of anisole and the influence of substitution in the benzene ring upon the yields and composition of the products of oxidative coupling on Cu^{2+}-montmorillonite.

Experimental

Roentgenographic measurements were performed on a vertical goniometer Philips. The used voltage was 15 kV and current intensity 20 mA. Emitted radiation had the wavelength $\lambda = 0.154037$ nm. The results are presented in Table 1. The ^1H NMR spectra of C^2HCl_3 (99 % of ^2H isotope) solutions of the prepared compounds were measured with a Tesla BS 487 instrument operating at 80 MHz. Tetramethylsilane was used as internal standard. Infrared spectra (in CCl_4) were recorded using a Perkin—Elmer 598 apparatus. Gas chromatography was performed on a CHROM-4 instrument, column length 140 cm, column fitted with Carbowax 20M with 2 % of KOH. Melting points were determined on a Kofler micro-hot-stage and are uncorrected.

Table 1

Characteristic of some types of M^{n+}-montmorillonite

Type of montmorillonite	Natural	Ca^{2+}	Co^{2+}	Cu^{2+}	Fe^{3+}
d_{001}/nm	1.51	1.5	1.5	1.27	1.52
Content of M^{n+} ions/(mg g^{-1})	94.5 (Ca); 7.3 (Mg)	92.2	51.8	100.3	16.8
Content of M^{n+} ions/(mmol g^{-1})	2.36 (Ca); 0.3 (Mg)	2.3	0.88	1.58	0.3

1,2-Dimethoxybenzene was prepared according to [13] and 1,2,4-trimethoxybenzene according to [13, 14]. The used bentonite, supplied in the form of filter cake, n.e. Ore Mines Banská Bystrica, from locality Jelšový Potok, according to [15], contained approximately 80 % of montmorillonite. Silica gel L 100/250 (Lachema, Brno) was used for chromatography.

Isolation of natural montmorillonite

Bentonite (760 g), which was dried at 105—110 °C for 24 h, was stirred up in 38 dm³ of distilled water. Thoroughly stirred up mixture was left to sedimentate for 5 h and then, 20 dm³ of suspension (upper layer) was taken into separate vessel. To this suspension, coagulator — $CaCl_2$ solution (100 cm³) having concentration 1 mol dm^{-3} was added. Precipitated montmorillonite was sucked off and dried at 105—110 °C for 24 h.

Preparation of homoionic forms of montmorillonite, resp. bentonite

Into a solution (50 cm³) of selected inorganic salt having concentration $0.1 \ mol \ dm^{-3}$, 10 g of natural montmorillonite (Ca—Mg form) was added. Suspension was shaken thoroughly for 2 h and then allowed to sedimentate for 24 h. Solution was decanted from deposited montmorillonite and a new solution of salt (50 cm³) was again added to the solid phase. This procedure was repeated six times. Homoionic montmorillonite was sucked off and washed with distilled water until total removal of free ions. Finally, washing with 50 % ethanol (20 cm³) and drying followed. For the preparation of homoionic forms of montmorillonite, solutions of the following salts were used: $CaCl_2$, $CuCl_2$, $Co(NO_3)_2$, $Fe_2(SO_4)_3$. The content of ions in individual forms of montmorillonite was determined after their liberating by usual analytical procedures. For liberation, a solution (50 cm³ per 1 g of montmorillonite) of anilinium chloride ($c = 1 \ mol \ dm^{-3}$), which was allowed to affect montmorillonite for 24 h, was used. The results are presented in Table 1. The same procedure was applied for preparation of homoionic forms of bentonite.

Preparation of 4,4′-dimethoxybiphenyl (I) on homoionic forms of M^{n+}-bentonite (M^{n+} = exchangeable cation)

To a solution (5 cm³; 4.6 mmol) of anisole in 45 cm³ of n-heptane, 4 g of M^{n+}-bentonite were added. The reaction mixture was stirred under reflux for 6 h. At the temperature of 60—70 °C, colour change of bentonite was observed. After cooling, bentonite was filtered off and the product was continuously extracted into methanol using a Soxhlet apparatus. Methanol was evaporated and the residue (brown-yellow crystalline material) was purified by sublimation at 140 °C (2.399 Pa). Resulting 4,4′-dimethoxybiphenyl (I) was characterized on the basis of m.p. = 170—172 °C (in accordance with Ref. [16]) and ¹H NMR spectrum (δ/ppm): 3.85 (s, 6H, CH_3), 6.95 (d, 4H, C_6H_4), 7.45 (d, 4H, C_6H_4). No 4,4′-dimethoxybiphenyl was found in n-heptane solution (GLC). The results are presented in Table 2.

Note: Experiments employing Cu^{2+}-montmorillonite instead of Cu^{2+}-bentonite were carried out at the same conditions.

Oxidative coupling of substituted benzenes on Cu^{2+}-bentonite

To a stirred solution of 0.04 mol of benzene derivative in 35 cm³ of n-heptane, 3 g of Cu^{2+}-bentonite were added and the reaction mixture was stirred under reflux for 3 h. After cooling, Cu^{2+}-bentonite was filtered off and the products were extracted into methanol using a Soxhlet apparatus. Methanol was evaporated and the residue was chromatographed on a column of SiO_2 (V(benzene) : V(ethyl acetate) = 9 : 1). From n-heptane solution, after evaporation of solvent under vacuum, starting material was isolated. In the case of dimethoxy derivatives of benzene and 2,6-dimethoxyphenol, a portion of starting material was obtained also from the methanolic extract. The results are presented in Discussion.

Table 2

Conversion of anisole to 4,4'-dimethoxybiphenyl in dependence on exchangeable ion in M^{n+}-bentonite

Experiment No.	M^{n+}	Colour of bentonite after reaction	Conversion %	Standard redox potential V	[21]
1	Cu^{2+}	Dark blue	5		
2	Cu^{2+a}	Dark blue	6.2		
3	Cu^{2+b}	Dark blue	0	Cu^{2+}/Cu^{+} 0.158	
4	Cu^{2+c}	Dark blue	22.8		
5	Cu^{2+d}	Dark blue	3.1		
6	Fe^{3+}	Dark blue	8.1	Fe^{3+}/Fe^{2+} 0.770	
7	Cr^{3+}	Pink-violet	1.1	Cr^{3+}/Cr^{2+} − 0.41	
8	Al^{3+}	Violet	0.4	Al^{3+}/Al^{0} − 1.706	
9	Co^{2+}	Dark green	0.4	Co^{2+}/Co^{0} − 0.280	
10	Ca^{2+}	Grey-blue	0.4	Ca^{2+}/Ca^{0} − 2.76	

a) Reaction performed with Cu^{2+}-montmorillonite; *b*) reaction performed with Cu^{2+}-montmoril-lonite dried at 200 °C for 2 h; *c*) reaction performed with Cu^{2+}-bentonite where the mass ratio anisole : Cu^{2+}-bentonite = 1 : 5; *d*) reaction performed with Cu^{2+}-bentonite under simultaneous bubbling of air.

Results and discussion

The used bentonite contains up to 80 % of mineral montmorillonite [15, 17] and upon oxidation of acetophenones with thallium(III) nitrate coated on H^{+}-benton-ite, resp. upon synthesis of acetals under catalysis by H^{+}-bentonite, the same results were obtained as in the analogical reactions using H^{+}-montmorillonite [18].

The reaction under study — synthesis of biaryls — is a reaction of oxidative coupling and the course of this reaction ought to depend on oxidizing ability of exchangeable ion, its concentration and, in the case that the reaction proceeds in an interlayer of clay mineral, also on interlayer distance. For the given reasons, we decided to characterize individual forms of the used homoionic montmorillonite. In this way, the results can be applied with a considerable approximation also to the homoionic forms of bentonite.

As it is apparent from the results of X-ray analysis (Table 1), in majority of cases, the value of interlayer distance d_{001} is about 1.5 nm, indicating that two layers of water are present in their interlamellar space. Cu^{2+} form is an exception, where d_{001} is 1.27 nm and so only one layer of water is present [19]. In the case of Ca^{2+} form, the highest molar concentration of exchangeable ion in montmorillonite is attained, as seen from Table 1.

It is obvious from the results presented in Table 2 that the conversion of anisole into 4,4'-dimethoxybiphenyl depends only a little on that fact, whether the reaction is done with bentonite or montmorillonite (experiment No. *1* or No. *2*) and therefore, all further experiments we performed using M^{n+}-bentonite only. Conversion of anisole depends markedly on the quality of exchangeable ion and roughly correlates with the standard redox potential of these ions, *i.e.* $\alpha(Fe^{3+}) > \alpha(Cu^{2+}) \gg \alpha(Cr^{3+}) > \alpha(Al^{3+}) > \alpha(Co^{2+}) > \alpha(Ca^{2+})$ (Table 2). In the case of Fe^{3+}-bentonite, the reaction proceeds already at 25 °C, however essentially lower yields of 4,4'-dimethoxybiphenyl are obtained.

All experiments, excepting experiment No. 4, we performed using an excess of anisole because we assumed that the reaction will be catalytic and the formed product will diffuse back into solution. However, the results indicate that exchangeable ions operate as a reagent and the reaction proceeds in interlayers of montmorillonite. This hypothesis is supported by the fact that no adsorption of anisole on Cu^{2+}-bentonite has been observed at room temperature and no product has been found (GLC) in n-heptane solution, but only in methanolic extracts from bentonite. In effort to verify this hypothesis, we performed an experiment where the ratio Cu^{2+}-bentonite/anisole (experiment No. 4) was significantly increased. Essential, fourfold increase of yields of product was achieved, in accord with our hypothesis. Indirectly, this hypothesis is also supported by such a fact that bubbling of the air through the reaction mixture (experiment No. *5*) did not result in an increase of yields and that traces of 4,4'-dimethoxybiphenyl were also observed in those cases when the corresponding ions (Al^{3+}, Co^{2+}, Ca^{2+}) do not possess oxidative character. There are unexchangeable ions of Fe^{3+} [19, 20] incorporated in the structure of montmorillonite, where the reaction can proceed. Since the original Kovacic reaction [1—4] is carried out using a mixture of anhydrous $CuCl_2$ and $AlCl_3$, we performed an experiment (experiment No. 3) where Cu^{2+}-montmorillonite devoid of water by drying at 200 °C for 2 h was used, but no reaction took place. An attempt for further simulation of the Kovacic reaction, *i.e.* application of a mixture of Cu^{2+}- and Al^{3+}-bentonite in the ratio 1 : 1, also failed. The reaction gave low conversion and yielded a mixture of four compounds, which we were not able to separate (Scheme 1).

In additional part of the work, we have studied the influence of substitution in benzene ring on the course of oxidative coupling of aromatic compounds. All experiments were carried out using Cu^{2+}-bentonite. In accordance with mechanism of the reaction, no product of reaction was observed in the case of toluene and ethylbenzene. In the case of anisole, conversion was 5 %, giving 4,4'-dimethoxybiphenyl as a product. From 1,2-dimethoxybenzene, where all positions are at the same time activated by $+M$ effect of one and deactivated by $-I$ effect of the second methoxy group, only 0.3 % of undefined compound resulted. In the case of 1,3-dimethoxybenzene, conversion increased to 15 % and four oily compounds (in

CH₃O—⟨○⟩—⟨○⟩—OCH₃

I

II

III

IV
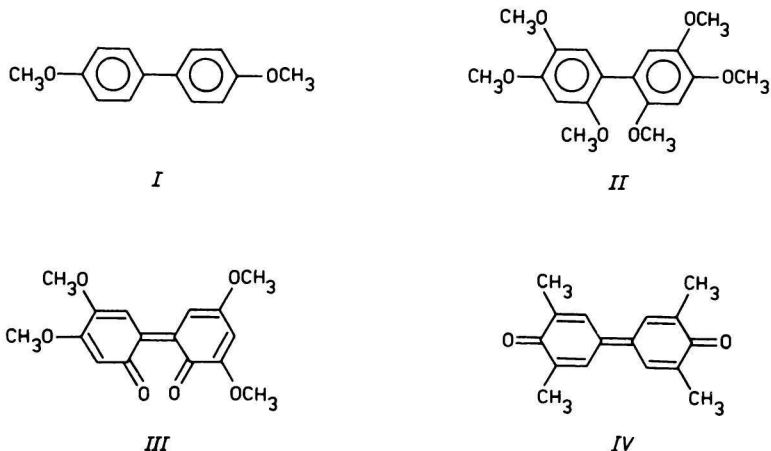
Scheme 1

the ratio 1 : 1 : 1 : 1, according to TLC) originated, but we were unable to purify and characterize them. In the infrared spectra of these compounds, $\tilde{v}(CO)$ bands are observed at about 1750 cm^{-1}, indicating the quinone structure. Starting from 1,2,4-trimethoxybenzene, conversion increased to 43 % and three compounds were formed in the ratio 6.5 : 3 : 1. Using chromatography on SiO$_2$ column, we succeeded to separate them and the first two of them also characterize. 2,4,5,2′,4′,5′-Hexamethoxybiphenyl (*II*), having m. p. = 177 °C, which is in accordance with [21], was predominant (26.5 %). ^{1}H NMR spectrum (δ/ppm): 3.76 (s, 6H, CH$_3$), 3.85 (s, 6H, CH$_3$), 3.92 (s, 6H, CH$_3$), 6.63 (s, 2H, CH), and 6.85 (s, 2H, CH). Further, metallo-grey 3,5,4′,5′-tetramethoxy-2,2′-biphenoquinone (*III*) (12.3 %) having m. p. = 173—176 °C was formed. For C$_{16}$H$_{16}$O$_6$ (M_r = 304.3) w_i(calc.): 63.15 % C, 5.30 % H; w_i(found): 64.15 % C, 5.50 % H. In the IR spectrum, following bands were observed: $\tilde{v}_s$(CH$_3$) = 2880 cm^{-1}, $\tilde{v}$(C=O) = 1670 cm^{-1}, $\tilde{v}$(C=C) = 1600 cm^{-1}, $\tilde{v}$(CH$_3$) = 1470 cm^{-1}, and $\tilde{v}$(C—O—C) = 1010 cm^{-1}. On the basis of following ^{1}H NMR spectral data (δ/ppm): 3.77 (s, 3H, CH$_3$), 3.85 (s, 6H, CH$_3$), 3.92 (s, 3H, CH$_3$), 6.00 (s, 1H, C$_6$H$_2$), 6.57 (s, 1H, C$_6$H$_2$), 6.75 (s, 1H, C$_6$H$_2$), and 6.82 (s, 1H, C$_6$H$_2$), we suggest unsymmetrical structure of this biphenoquinone.

In the case of 2,6-dimethylphenol, conversion was 25 % and three compounds were formed in the ratio 1 : 2 : 2. By chromatographic separation, right after starting material, a compound having (after purification) m. p. = 221—223 °C was isolated. For C$_{16}$H$_{16}$O$_2$ (M_r = 240.3) w_i(calc.): 79.97 % C, 6.71 % H; w_i(found): 79.10 % C, 7.59 % H. In the IR spectra, the band at $\tilde{v}$(CO) = 1730 cm^{-1} was observed and so, we attribute the structure of 3,5,3′,5′-tetramethyl-4,4′-biphenoquinone (*IV*) to this compound. Further compounds were isolated in the form of yellow oils and we were unable to characterize them fully. The presence

of bands at 1740 cm^{-1} and 1700 cm^{-1}, respectively, with a shoulder at 1750 cm^{-1}, belonging to $\tilde{v}(CO)$ indicates a quinone structure of these oily compounds. A decrease of carbon content down to 63.40 % C indicates a deeper oxidation. By the bubbling of oxygen through the reaction mixture, only compound *IV* was obtained (yield = 8 %).

Attempted oxidative coupling of *N,N*-dimethylaniline afforded 3 % of conversion. A mixture of five compounds was formed, which we were unable to purify and characterize. The presence of bands $\tilde{v}(C=O) = 1700—1750$ cm^{-1} in their IR spectra, indicates a quinone structure.

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