

## **Study of (all-rac)- $\alpha$ -tocopherol synthesis from trimethylhydroquinone and isophytol at the presence of solid catalysts**

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### **Abstract**

The cyclocondensation of trimethylhydroquinone and isophytol to (all rac)- $\alpha$ -tocopherol was studied at the presence of solid catalyst and  $\text{ZnCl}_2$ . The obtained results confirm that the catalytic activity of alumina and silica base catalysts is satisfactory only at the presence of  $\text{ZnCl}_2$ . The strongly acidic aluminosilicates catalyze not only the cyclocondensation of trimethylhydroquinone and isophytol to (all rac)- $\alpha$ -tocopherol but also the formation of unacceptable side products.

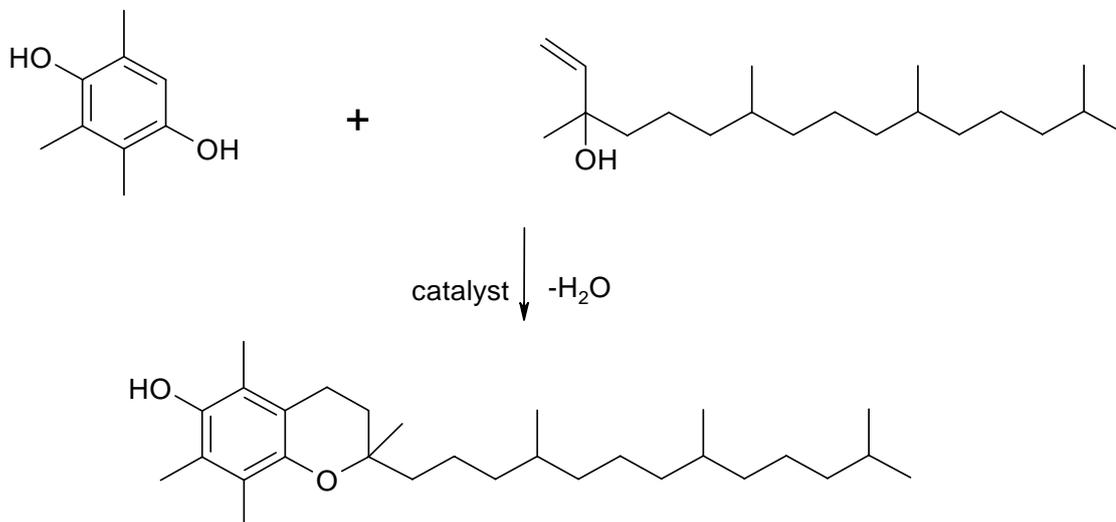
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### **Introduction**

(All-rac)- $\alpha$ -tocopherol (synthetic vitamin E) is the most important industrial fat-soluble antioxidant. A majority of its production (74%, over 30 000 t/y) is used in the production of animal fodder (Bonrath, 2007b; Baldenius, 1996). Other application includes production of cosmetics (3%), pharmaceuticals and food. Thus, the production of animal feed represents the most valuable demand for vitamin E (Bonrath, 2007a). Tocopherol as a vitamin is used mainly in the form of acetate (98%) (Bonrath, 2007b; Baldenius, 1996), which is chemically significantly more stable as the free form of tocopherol.

The last step in the industrial synthesis of (all-rac)- $\alpha$ -tocopherol is the reaction of isophytol, phytol, or the reaction of phytyl halide and trimethylhydroquinone (Bonrath, 2007a; Baldenius, 1996), i.e. the acid-catalyzed Friedel-Crafts alkylation of trimethylhydroquinone by (all-rac)-isophytol or by its  $\text{C}_{20}$  equivalent. Traditionally the latter

reaction is catalyzed by a combination of a Lewis acid, e.g. Zinc(II) dichloride, and a Brønsted acid, such as hydrochloric acid (Bonrath, 2005, 2007a, 2007b; Baldenius, 1996).



Recent reports (Bonrath, 2007b) mention triflates (tris-trifluoromethanesulfonates) of rare earths, e.g. (Me<sup>III</sup>(OTf)<sub>3</sub>), such as Gd(OTf)<sub>3</sub> as suitable catalysts for the reaction between trimethylhydroquinone (hereinafter only TMHQ) and isophytol (IPh) monoacetate. The reaction can be carried out at temperatures 80-150 °C in several solvent systems, e.g. two-phase systems based on ethylene or propylene carbonate, and hexane, heptane or octane, respectively. In contrast to zinc dichloride the same conversion and selectivity of tocopherol (TPh) formation can be achieved with much less catalyst.

Similar activity is exhibited by microencapsulated catalysts (MC) (Schager, 2000), e.g. MC-imides (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NH and triflates MC-Sc(OTf)<sub>3</sub> with maximal yields of tocopherol 87.5 % and 86.8 %, respectively. However, these catalysts have leaching problem, and the activity of MC-catalysts cannot be restored.

The nanocomposite catalysts Nafion/SiO<sub>2</sub> (Nafion content between 5 and 20%) or Nafion NR50 alone (an ion-exchanging resin) in toluene as a solvent under nitrogen atmosphere produce tocopherol from trimethylhydroquinone and isophytol in yields over 90 % (Wang, 2004). However, attempts of reusing the above nanocomposite catalysts have not succeeded due to a significant decrease in activity. The more general use of composite Nafion/silica catalyst for the synthesis of pure chemicals, including tocopherol, has been described in the recent paper of Hinze et. al (2009). The highest tocopherol yield (88 %) was

achieved at 40 % wt. of Nafion. Reused catalysts displayed significantly lower activity. Kemnitz and coworkers in their European patent (2009) describe the reaction of IPh and TMHQ catalyzed by a heterogeneous fluoride catalyst of the general formula  $MgF_{2-x}(OH)_x$  or  $AlF_{3-x}(OH)_x$  in a two-phase solvent system (propylene carbonate and heptane). The reaction is carried out at a solvent reflux or in a closed system. A quantitative yield of tocopherol, relative to IPh, has been achieved at a molar ratio of TMHQ : IPh exceeding 2 : 1, at catalyst content of about 7 % wt. However, the examples in this patent do not mention any reuse of catalysts. The same authors (Coman, 2008) also describe preparation of a nanocomposite catalyst based on aluminium fluoride made from aluminium isopropylate by a “sol-gel” fluorination with hydrofluoric acid. The reaction conditions, reactants, as well as the results are similar to the above mentioned patent. Huabin Xing et al. (2009) describe a continuous process of the synthesis of d,l-tocopherol catalyzed by an ionic solution of tetrafluoroborate. The propylene carbonate solution of TMHQ and the solution of IPh in supercritical  $CO_2$  were continuously fed into a reactor. During the reaction the product was continually separated from the reaction mixture by extraction with supercritical  $CO_2$ . Decompression of a supercritical mixture affords a product to be divided from catalyst. The adjusted temperature/pressure regimen affects the continuous reaction as well as product separation. d,l-Tocopherol was prepared with 90.4% yield at 100 °C, 20 MPa, at IPh/TMHQ/propylene carbonate / $CO_2$  molar ratio of 1/1.5/35/3358 at a retention time of 12.6 min. From the so far published data it appears that catalysts containing fluorine in organic or inorganic form have been intensely studied, albeit their use is hampered by high price and problematic reuse. For the selection of environmentally acceptable and recyclable catalysts as well as reaction medium multiphase solvent systems were used as alternative medium, including supercritical liquids (Wang, 2000; Bonrath, 2005, 2009). The use of polar aprotic and above all two-phase solvent system containing e.g. ethylene or propylene carbonate as the polar and heptane as the non-polar component gave good results even with “traditional” catalysts such as  $ZnCl_2/HCl$ . Nevertheless bulk production has led to the discharge of waste water contaminated with zinc and halide ions, an environmental problem that has to be dealt with by e.g. effective recycling of catalysts and solvents. Recently we studied recycling of the classic catalysts – zinc dichloride (Gömöry 2010a) and the influence of lowered pressure designed to shift the reaction equilibrium by releasing the side product of the cyclocondensation reaction in the form of water vapor (Gömöry 2010b).

In this work we studied the effect of catalytic system in the reaction of IPh with TMHQ and compared the effect of zinc dichloride with other types of available acidic heterogeneous catalysts – natural and synthetic aluminosilicates, alumina as well as some other catalyst, e.g. Envirocat EPZ 10, utilized as a very good, ecological catalyst for various acid-catalyzed reactions.

## Experimental

### Chemicals used

isophytol (Hoffmann La Roche), > 96 %, trimethylhydroquinone (Hoffmann La Roche) > 98.5 %, butyl acetate (Zentiva, jsc.) > 99%, sodium hydroxide (mikroCHEM) > 98%, hydrochloric acid (mikroCHEM) > 35%.

### Catalysts

ZnCl<sub>2</sub> - (mikroCHEM) >98,5 %.

EPZ 10- acidic heterogeneous catalyst Envirocat, supplied by Contract Chemicals Ltd. (England), natural montmorillonit purified by mineral acid and impregnated with ZnCl<sub>2</sub>.

KSF – modified montmorillonit in acidic form supplied by Fluka.

HY - zeolite in H<sup>+</sup> form was prepared by calcination of NH<sub>4</sub>Y at 500 °C for 6 h.

Rudex – natural aluminosilicate purified by solution of hydrochloric acid. A sample was obtained by courtesy of Rudex (Istrochem jsc), Bratislava.

Alumina – sample obtained from Alfa Aesar.

The total acidity of the above mentioned catalysts was determined by potentiometric titration with 0,1 M ethylamine solution in acetonitrile (Rakottyay, 2010). The results are given in Table 1.

Table 1 Acidities of the tested catalysts

Catalyst	mmol H <sup>+</sup> .g <sup>-1</sup>
KSF	1,12
HY	1,05
RUDEX	1,02
ALUMINA	0,67

### **Method of analysis**

**(All-rac)- $\alpha$ -tocopherol (TPh)** – was determined by gas chromatography (GLC), gas chromatograph Hewlett Packard with autoinjector, computer-controlled chemical station ChemStation, column – ULTRA 2, quartz, 50 m x 0,32 mm x 0,52  $\mu$ m, temperature program: at 245 °C 2 min., ramp 30 °C/min. up to 300 °C, isothermally 22 min, detector – FID, detector temperature 300 °C, injector temperature 260 °C, carrier gas was nitrogen, flow rate 1.4 ml/min, injection volume 2.5  $\mu$ l of samples in hexane, split 1:18. The content of compounds was determined by the internal normalization method. The difference between two parallel runs not exceeded 1.6%.

### **Liquid chromatography (HPLC)**

Liquid chromatography equipment ISCO, using external standard TPh from Fluka: Column – metallic, 30 cm length, 4 mm ID, packing – octadecyl-silanized silica gel, Particle size 5 to 10  $\mu$ m, mobile phase methanol : water (49 : 1), UV detector, tocopherol detected at 292 nm, preparation of standards and samples: 0.05 g of tocopherol or sample was dissolved in 50 ml of anhydrous ethanol, injection volume 20  $\mu$ l.

### **Apparatus and general procedure**

The used equipment, consisted of a reaction vessel (500 ml three-necked flask with flat bottom), was placed in a silicone oil bath with temperature control (accuracy  $\pm 0.5^\circ$  C). The reaction mixture was stirred by magnetic stirrer. The superstructure of the reaction vessel consisted of a short (20 cm) bump vacuum column, silver-coated jacket, distillation head with attached phase separator with upper layer overflowing back to the reactor, whereas the lower layer (reaction water) was collected and its volume measured.

The experimental procedure involved charging the reactor with 21 g (0.138 mole) of TMHQ, different amount and type of catalysts (Table 1) and 50 ml of butyl acetate. The reaction mixture was stirred, flushed with nitrogen and heated up to about 130 °C, so that the azeotropic mixture of butyl acetate and water was distilled off. Next 41.4 g (0.139 mole) of IPh was added drop by drop. The reaction mixture was left in the reactor another hour after adding whole IPh. The generated reaction water was taken at regular intervals to ascertain its total volume, indicating the end of the reaction. After cooling down the reaction mixture, the

catalyst was separated by filtration or in experiments with  $\text{ZnCl}_2$  it was washed 3 times by water to remove the zinc dichloride. After separation of catalyst the mixture was 3 times extracted by aqueous NaOH (8 % wt.), then by aqueous HCl (5 % wt.) and finally by water again. After the last washing organic layer was carefully separated and under aspirator vacuum concentrated under inert nitrogen atmosphere. After removal of butyl acetate by distillation the raw tocopherol was weighed and analyzed to determine its tocopherol content (by HPLC or GLC). All aqueous extracts were mixed and acidified by hydrochloric acid to weakly acidic reaction from which unreacted TMHQ was precipitated, filtered off, dried and weighed. Its amount was used to calculate TMHQ conversion.

## Results and Discussion

Since both, industrial experience and literature references (Bonrath 2005, Gömöry 2010a, 2010b) indicate that  $\text{ZnCl}_2$  is a selective and effective catalyst,  $\text{ZnCl}_2$  was chosen as catalyst for the basic, comparative experiment. This experiment was made at reaction conditions used in our recent work (molar ratio of TMHQ : IPh :  $\text{ZnCl}_2$  = 1 : 1 : 0.2, reaction at the presence of supplementary solvent, butyl acetate, at the temperature of refluxing reaction mixture at atmospheric pressure). Under the above mentioned conditions the reaction was over after 3 hours, i.e. the reaction mixture no longer contained either TMHQ or IPh. The yield of TPh, based on determination of its content in the raw product was 83.8% (relative to IPh). As can be seen in Table 2, no TMHQ could be isolated from the aqueous extracts of reaction products. With lower amount of catalysts (1.3g of  $\text{ZnCl}_2$ ), i.e. at molar ratio of TMHQ : IPh :  $\text{ZnCl}_2$  = 1 : 1 : 0.07, the yield of TPh decreased to 75.5% and the content of impurities in the raw TPh increased from 12.6% wt. to 16.9% wt.; in addition 4.7% of TMHQ could be isolated from the aqueous extract of reaction mixture.

The used heterogeneous acidic catalysts were chosen considering their acidity and tested in a series of experiments. Gamma-alumina has been known to possess at its surface only weakly acidic centers of the Lewis and Brønsted type. In the presence of  $\gamma$ -alumina only insignificant amount of TPh was formed and nearly all TMHQ could be recovered from the reaction mixture (Table 2). At the presence of this catalyst with weak acidity mainly side reactions, accompanied by degradation of IPh took place.

Table 2 Effect of catalyst on the preparation of  $\alpha$ -tocopherol by the reaction of isophytol (41.4g) with 2,3,5-trimethylhydroquinone (21 g) in 50 ml of butyl acetate.

Catalyst / amount [ g ]	water <sup>b</sup> [g]	TMHQ <sup>a</sup> [g]	Weight of raw TPh [g]	TPh content [wt. %]	TPh yield [%]
<b>ZnCl<sub>2</sub> /3,9<sup>d</sup></b>	<b>2.4</b>	<b>0</b>	<b>57</b>	<b>87.4</b>	<b>83.8</b>
ZnCl <sub>2</sub> /1,3	2.4	1.0	54	83.1	75.5
EPZ10 /2,1	2.1	1.0	55	43.2	40.2
KSF /1,05	2.5	4.4	52	7.4	6.4
HY/2,1	1.8	9.0	41.5	34.2	23.8
Rudex /2,1	2.2	2.0	54.5	67.3	61.7
Al <sub>2</sub> O <sub>3</sub> /2,1	0.1	21.0	40	2.2	1.5
EPZ10 /2,1+ HCOOH/0,5	2.6	1.0	58	23.6	23
EPZ10/2,1+ H <sub>3</sub> PO <sub>4</sub> /0,84	2.8	2.0	48	68.3	55.2
EPZ10 <sup>c</sup> /2,1	1.0	7.0	51.5	39.2	33.9

a- Amount of TMHQ, isolated after the reaction

b- Amount of azeotropically separated water, maximum theoretical amount 2.5 g.

c- Activated at 260° C

d- Basic comparative experiment

Only 4% of the expected reaction water could be isolated. As can be seen from the measured data (Table 2), weakly acidic centers are practically unable to catalyze the condensation reaction between TMHQ and IPh. The spatial arrangement of reactants of adsorbed reactants is also unpleasant. In the coordination sphere of zinc TMHQ and IPh are brought close to each other and activated, while on the surface of alumina the adsorbed reactants remain farther apart. Moreover the adsorption of TMHQ on the acidic centre does not activate TMHQ molecule for nucleophilic attack, rather its electrons are withdrawn from the aromatic ring. As far as the studied condensation reaction is concerned, molecules of TMHQ can „poison“ active acidic sites of alumina. Thus the molecule of IPh, activated by adsorption would more prone to react with a free rather than with TMHQ molecules adsorbed on acidic centers.

The very weakly acidic silica (containing silanol groups) was also inactive in the condensation reaction of TMHQ and IPh. Conversely, some aluminosilicates possessing strong acidic Brønsted type centers show catalytic activity. However, the well-known zeolites with relatively narrow pores, such as e.g. zeolite ZSM5 are unsuitable to catalyze this reaction, because contain too narrow pores, which does not allow the penetration of TMHQ to the vicinity of acidic protons; eventually the formed molecule of TPh would congest pores. That is why zeolites with broad pores or dominant surface acidity were mainly studied as possible heterogeneous catalysts.

The data given in Table 2 show, that even montmorillonite alone (catalyst KSF), with its relatively high surface acidity and multilayer structure, has proved little selectivity in the formation of TPh. About 20% of TMHQ could be isolated from the products, i.e. its conversion reached less than 80%. In reality, all of IPh was dehydrated; TPh content in product being only 7.4 wt. %, which translates into a yield of only 6.4%. Acidic protons of montmorillonite in fact stimulated mainly unwanted side reactions of IPh and TMHQ. Montmorillonite with an addition of  $\text{ZnCl}_2$  (catalyst EPZ-10) afforded up to 95% TMHQ conversion, with IPh conversion at about 85%. The TPh content in raw product increased up to 43.2%. Since for some alkylation and the acid-catalyzed reactions it is recommended to activate the EPZ-10 catalysts at 260° C for 15 h, the reaction of TMHQ and IPh was also tried with such catalysts. Unfortunately in our reaction this type of activation has negative influence on the desired reaction. The gathered data indicate that the addition of  $\text{ZnCl}_2$  to acidic montmorillonite improved the conversion of TMHQ, suppressed side reactions of IPh and enhanced formation of TPh.

The HY catalyst, possessing wide pores and acidic protons, though affording lower conversion of TMHQ (~ 57% at 72% conversion of IPh), gave significantly higher TPh content in the raw product (34.2%) than in either experiments using alumina or montmorillonite alone. On the other hand, catalysts Rudex, possesses protons active enough to afford increased TMHQ conversions (more than 90%) as well as those of IPh (~ 88%). Also the TPh content in raw products was higher (67.3 wt. %).

The results of experiments with heterogeneous catalysts alone indicate that strongly acidic protons are active in transformation reactions of TMHQ and IPh, it is nonetheless insufficiently selective as far as the formation of TPh is concerned. Increasing the amount and acidity of protons present at the catalyst thus enhances the rate of transformation reactions of

TMHQ and IPh, unfortunately towards the unwanted side reactions. In order to verify this assumption a strong organic acid (formic acid) and a medium strong mineral acid (phosphoric acid) were added to the EPZ-10 catalyst. Since these acids contained a small amount of water, the water distilled off the reaction mixture was slightly higher than the theoretical amount, arising from dehydration of IPh. Addition of HCOOH did not affect the conversion of TMHQ, the TPh content in raw product fell to 23.6%. Conversely, addition of phosphoric acid increased the TPh content in raw product to 68.3 wt. % at slightly lower TMHQ conversion.

Since addition of ZnCl<sub>2</sub> proved beneficial in case the EPZ-10 catalyst, in the next series of experiments it was added, in various amounts, to each heterogeneous catalyst used. Table 3 summarizes the results achieved with EPZ-10 enriched with ZnCl<sub>2</sub>, while Table 4 presents results obtained with the rest of mixed catalysts. As can be seen from data in Table 3, increasing the amount of added ZnCl<sub>2</sub> practically does not affect the conversion of raw materials, even though it improves the selectivity of formation of TPh. The addition of 7 molar % of ZnCl<sub>2</sub>, for instance (TMHQ : IPh : ZnCl<sub>2</sub> = 1 : 1 : 0,07) gave in fact the same result as using EPZ-10 without zinc dichloride (Table 2 and 3). The only difference was that EPZ-10 gave by 2.5% higher TPh content in the raw product. After filtration, purification and recycling the EPZ-10 catalyst an addition of the same amount ZnCl<sub>2</sub> afforded comparable results. Data in Table 4 indicate that an addition of ZnCl<sub>2</sub> to each studied heterogeneous catalyst improves mainly the selectivity of TPh formation, reflected in higher TPh content in the raw product. The highest (92.7 wt.%) TPh content thereby was achieved by a combination of Rudex and ZnCl<sub>2</sub>. In order to achieve such result, Rudex had to be repeatedly washed with diluted HCl. The facts stated above confirmed once again high selectivity of ZnCl<sub>2</sub> and low selectivity of acidic protons.

Table 3 Effect of addition of ZnCl<sub>2</sub> to the EPZ-10 catalyst on preparation of  $\alpha$ -tocopherol by the reaction of isophytol (41,4 g) with 2,3,5-trimethylhydroquinone (21g) in 50 ml of boilingbutyl acetate.

Catalyst / amount [g]	water <sup>b</sup> [g]	TMHQ <sup>a</sup> [g]	Weight of raw TPh [g]	TPh content wt. %]	TPh yield [%]
EPZ10 <sup>c</sup> /2,1	1.0	7.0	51.5	39.2	33.9
EPZ10 /2,1 +ZnCl <sub>2</sub> /0,42	2.5	1.5	55	53.4	49.4
EPZ10 /2,1 +ZnCl <sub>2</sub> /0,63	2.4	1.0	55	67.7	62.7
EPZ10/2,1 +ZnCl <sub>2</sub> /0,63/	2.3	1.0	53	66.9	59.7
EPZ10(2,1) +ZnCl <sub>2</sub> /0,84	2.3	2.0	54	71.4	64.9
EPZ10 /1,1 +ZnCl <sub>2</sub> /1,3	2.5	1.0	55	85.5	79.4

a- Amount of TMHQ, isolated after the reaction

b- Amount of azeotropically separated water, maximum theoretical amount 2.5 g.

c- Activated at 260° C

Table 4 Effect of ZnCl<sub>2</sub> addition to the heterogeneous catalysts on preparation of  $\alpha$ -tocopherol by the reaction of isophytol (41,4 g) with 2,3,5-trimethylhydroquinone (21g) in 50 ml of boiling butyl acetate.

Catalyst / amount [g]	water <sup>b</sup> [g]	TMHQ <sup>a</sup> [g]	Weight of raw TPh [g]	TPh content wt. %]	TPh yield [%]
HY/2,1+ ZnCl <sub>2</sub> /0,84	2.5	–	56	84.8	79.7
HY/1,1 + ZnCl <sub>2</sub> /1,0	1.8	2.0	56.5	79.2	75.3
Rudex/2,1+ ZnCl <sub>2</sub> /0,84	2.5	1.8	58.4	80.2	78.8
Rudex/1,05 <sup>c</sup> ZnCl <sub>2</sub> (1,3)	2.5	1.5	54.5	92.7	85.1
Al <sub>2</sub> O <sub>3</sub> /2,1+ ZnCl <sub>2</sub> /2,34	1.5	1.0	49	67.8	55.9
KSF /1,05+ ZnCl <sub>2</sub> /1,3	2.5	0.5	56.7	87.9	83.9

a- Amount of TMHQ, isolated after the reaction

b- Amount of azeotropically separated water, maximum theoretical amount 2.5 g.

c- Washed with solution of HCl

## **Conclusion**

The obtained results indicated that solid catalytic systems in combination with zinc dichloride can be used in preparation of TPh from IPh and TMHQ. Acidic heterogeneous catalyst montmorillonite (in commercial form as EPZ-10 and KSF), zeolite HY, alumina and natural aluminosilicate-bleaching clay (Rudex) were tested. The acidity of mentioned catalysts allows achieving high conversions of IPh and TMHQ, but in comparison with  $\text{ZnCl}_2$  their selectivity is low. The yield of  $\alpha$ -tocopherol achieved by  $\text{ZnCl}_2$  alone is nearly the same as the yield achieved by using Rudex or KSF impregnated with  $\text{ZnCl}_2$ . This allows reduction of the amount of used  $\text{ZnCl}_2$ , which after reaction should be isolated from the waste waters, because of its unpleasant ecological influence. The best results (85 % yield of TPh) were obtained by combination of  $\text{ZnCl}_2$  and Rudex washed by aqueous solution of HCl. The yield of TPh over  $\text{ZnCl}_2$  alone was 83.8 %, by combination of  $\text{ZnCl}_2$  and KSF 83.9 %.

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