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János Farkas^a, Sándor Békássy^a, Béla Ágai^a, Marianna Hegedüs^a & François Figueras^b

^a Department of Organic Chemical Technology , Technical University of Budapest , H-1521, Budapest, Hungary

^b Institut de Recherches sur la Catalyse du CNRS, 2 Avenue Albert Einstein, F-69626, Villeurbanne, France

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ACYLATION OF RESORCINOL ON CLAY CATALYSTS

János Farkas¹, Sándor Békássy^{1*}, Béla Ágai¹, Marianna Hegedűs¹, François Figueras²

¹Technical University of Budapest, Department of Organic Chemical Technology, H-1521 Budapest, Hungary ²Institut de Recherches sur la Catalyse du CNRS, 2 Avenue Albert Einstein, F-69626 Villeurbanne, France

Abstract: Using a series of clay based catalysts (KSF, KSF/0, KP10, K10, K0, KS), resorcinol is acylated in 1,2-dichloroethane by phenylacetyl chloride with a heterogeneous catalytic procedure. The yield of 1-(2,4-dihydroxyphenyl)-2-phenyl-ethanone is in correlation with the specific surface area of the catalyst.

Friedel-Crafts acylation constitutes a very important class of reactions which is of common use in organic chemistry. These reactions are usually catalyzed by Lewis acids in homogeneous systems^{1,2}. Friedel-Crafts reactions can be well realized with the classical Lewis acid catalysts (e.g. AlCl₃), but recently the utilisation of solid acid catalysts has become current³⁻⁵ because of the environmental charge of the HCl and the metal ions formed following the disruption of the catalyst.

A characteristic group of Friedel-Crafts acylations is the acylation of phenolics, previously reported using 3 dimensional solid acids (ZSM-5, zeolite

^{*} To whom correspondence should be addressed. E-mail: bekas@oct.bme.hu

beta) as catalysts⁶⁻⁸. No data are published for direct acylation of phenolic compounds, in particular of polyphenols, with layered aluminosilicates having a larger, more accessible pore structure. Clay catalysts are useful in similar complex cases, e.g. for acetylation of benzo crown ethers⁹.

We have investigated therefore the possibilities of the solid acid catalysed acylation of resorcinol (1) with phenylacetyl chloride (2), not yet mentioned in the literature. The product achievable in this way is 1-(2,4-dihydroxyphenyl)-2phenyl-ethanone (3), which is an important intermediate in the pharmaceutical industry.



In industry the reaction is actually carried out with an equimolar AlCl₃ to resorcinol ratio.

Our objective was to investigate how acid catalysts of the K-series (KSF, KSF/0, KP10, K10, K0, KS – produced by Süd Chemie, Germany from mineral montmorillonite by different acid and heat treatments) are suitable for this reaction and to compare their catalytic and structural properties.

Results and discussion

General reaction conditions: Using a batch reactor, 1.1 g (10 mmol) 1 was acylated with 1.33 cm³ (10 mmol) 2 in 40 cm³ 1,2-dichloroethane as solvent at a temperature of 83.7 °C (boiling point of the solvent). The amount of the catalyst was always 0.5 g.



FIG. 1. Conversion of resorcinol on different montmorillonite based catalysts

The reactions were monitored by HPLC (C18 reversed phase column, methanol/water = 54/46 v/v as eluent). Before injection the samples were incubated (in methanol at 60 °C during 30 min) to transform the disturbing unreacted acid chloride into methyl ester. The internal standard was 2,4dinitrotoluene.

Performing the reaction with different catalysts, the final conversion of 1 was high, between 65 and 81 % (Fig. 1), while at these reaction times 2 has always completely reacted. Both the conversion and the selectivity has stabilised during a relatively short time, two hours, after that their variation has remained under the error limit of the experiments. In spite of this fact the reactions were continued and monitored for a longer time period to discover if there is a change in the quantity of the main product 3 and in the by-product profile.



FIG. 2. Comparison of different montmorillonite based catalysts in ring acylation of resorcinol (yield of 3 after three hours)

The highest conversion was reached using those catalysts (KS, K0, K10) which have shown the best yield of 3 (Fig. 2). As for the yield of 3, there is a great difference among the performance of the different catalysts. The lowest value was observed with KSF and KSF/0, while with KS the yield was much higher.

Because of the good conversions and the relatively poor yield of 3 we have identified the main by-product, formed in very high proportion. This compound is the O-monoacyl derivative (4) of 1 - it was independently prepared by Schotten-Baumann acylation and identified by IR and NMR spectroscopy. Under the reaction conditions of the acylation of resorcinol, in presence of catalyst, the by-product 4 does not transform at all into 3 even after a long reaction time. This suggests that the formation of 3 and 4 are parallel reactions.



FIG. 3. Relations of the yield of 3 and the specific surface area for different catalysts (reaction time 3 hours).

A correlation can be observed between the yield of 3 and the specific surface area of the catalysts (Fig. 3). The best yield was achieved with KS having the highest specific surface area, while KSF, the surface area of which is practically two orders of magnitude lower, can produce the less 3. This relation does not indicate that the yield depends only on the total surface area of the catalyst but that the different acid centers of the surface can influence the acylation reaction (see the KSF – KSF/0 difference).

To verify this assumption, Fe³⁺ ion exchange¹⁰ was carried out on the sufficiently active K10 catalyst which is available as commercial product. This ion exchange influences slightly the specific surface area, but it changes the

quality of the acid centers and considerably increases their number. The ion exchanged Fe^{3+} -K10 produces 30% yield at 75% resorcinol conversion and at complete transformation of **2**.

The introduced Fe^{3+} ion results –as in the acetylation of benzo-15-crown-5 crown ether¹¹ – in a large increase of the yield, which is doubled in this case.

Final conclusions: The acylation of resorcinol with phenylacetyl chloride can be realized in a heterogeneous process using a catalytic amount of the catalyst. This new method has several advantages: the separation of the catalyst is easy because of the heterogeneous system; the unpleasant AlCl₃ (its security problems and environmental pollution) can be eliminated; the catalyst is reusable after a simple regeneration. The yield of **3**, using different montmorillonite based catalysts, is in correlation with the specific surface area of the catalyst. Because of the beneficial effect of the Fe³⁺-exchange in K10, our investigations will be continued in this direction.

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