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Fries Rearrangement of Esters in Montmorillonite Clays:Steric control on selectivity

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Abstract: In the Fries rearrangement of phenyl and naphthyl esters in clay interlayer, framework aluminium acts as a Lewis acid, catalysing the rearrangement. An increase in the size of migrating group/substrate causes an increase in the formation of 2-isomer. © 1997 Elsevier Science Ltd.

INTRODUCTION

Clays, modified clays and clay-based reagents are extensively employed[1a-m] as media/reagents for a wide range of organic functional group transformations. Fries rearrangement of phenyl benzoate catalysed by a Lewis acid as anhydrous aluminium bromide[2] in homogeneous solution (chlorobenzene) produced a mixture of 2- and 4-hydroxybenzophenones (*ortho*/*para* ratio ~1.0). Phenyl benzoate, however, when heated in the absence of a solvent, at 140°C and higher temperature rearranges exclusively to the 4-isomer. 4-Biphenylyl biphenyl-4-carboxylate under similar conditions,[3] yields 2-isomer as the exclusive product in homogeneous solution. Recently, we have reported[4a-c] the Fries rearrangement of phenyl 4-toluenesulphonate[4a] in clay microenvironment, wherein the 2-isomer is obtained as the major product. This prompted us to undertake a clay-catalysed Fries rearrangement of aryl esters (**Scheme 1**) and to have a closer look at the effect of the migrating group/substrate size on the product distribution, when placed within the clay interlayer.

EXPERIMENTAL

K10-Montmorillonite obtained from Aldrich was used as such. Cation-exchanged montmorillonite clays were prepared by stirring 1g of natural clay with 25ml of 1M solution of appropriate salt (nitrate or chloride) for three days. It was then filtered, washed repeatedly with distilled water and dried at 60°C. Esters were prepared by literature routes.[5a]

In a typical experiment, 0.2g of the ester was mixed with an equal amount of K10-montmorillonite or cation-exchanged montmorillonite clay in a round bottomed flask and placed in an oil bath for 5 hours at 140°C. After extracting with chloroform, the reaction mixture was analysed by HPLC

(Shimadzu LC-8A modular HPLC system with reverse phase ODS-column, UV-detector at 254nm and methanol as the mobile phase). Products 4-hydroxybenzophenone, 2-and 4-hydroxyacetophenones were commercially available samples. 2-Hydroxybenzophenone was prepared according to the literature.[5b] Products from naphthyl esters were isolated by column chromatography. They were identified by spectral methods and also by HPLC.

RESULTS AND DISCUSSION

The percentage conversion and the relative yields of the various products are presented in table 1. In the case of phenyl acetate, the rearrangement proceeds very smoothly with K10-montmorillonite and also with Na^+-exchanged montmorillonite clays as catalysts yielding the 4- isomer exclusively (Table 1). Presence of extralattice Brönsted and Lewis acidic sites as in H^+ and Al^{3+}- exchanged clays does not alter either the conversion or the product distribution, in comparison with K10-montmorillonite. The maximum acid strengths[6] of the various clays are $-8.2 \geq H_o$ for K10-, H^+ - and Al^{3+} - montmorillonites. A much lesser acidity $+3.3 \geq H_o > +1.5$ is reported[6] for Na^+ -exchanged montmorillonite. When the catalyst is present in a two-fold excess, an increase in the amount of the 2- isomer is observed. With phenyl benzoate, though the 4- isomer is still the major product, there is formation of the 2- isomer as well as phenol. When the 4-position is blocked with methyl- (or) methoxy-substituents, migration of benzoyl group to the *ortho*-position takes place. With naphthyl esters, in all the three cases, 2- isomers are the only products.

Fries rearrangement of phenyl benzoate in the presence of anhydrous $AlBr_3$ is shown to proceed simultaneously by two mechanisms.[2] The first one, involving a π-complex, leads exclusively to *ortho*-migration in an intramolecular process. A second pseudo-intramolecular mechanism leads to *ortho*- & *para*-migration with an ion-pair type intermediate. Later, the same group of workers based on detailed studies using isotopically labelled phenyl benzoates, have shown[7] that formation of *ortho*- isomer is intermolecular. In the present work also, a similar binding between the nucleophilic centres of the ester and the electron-deficient aluminium present in the framework, acting as Lewis acid may be visualised (**Scheme 2**). Previous reports[2] point out that Fries rearrangement is catalysed essentially by Lewis acids, though, however, H^+ played a significant but not a critical role (protonation inducing a strong polarization within the molecule, with a consequent weakening of the C-O bond) in affecting the reactivity and products distribution. Initial coordination at the carbonyl oxygen will be more common, a factor supported by spectroscopic evidences[8] of the rearrangement of phenyl benzoate catalysed by aluminium bromide in solution. Subsequent cleavage of the complex leaves an ion pair, in which the acyl or sulfonyl fragment migrates to the 2-(or) 4- position. Absence of effect of extralattice Brönsted and Lewis acidic sites (as with H^+ and Al^{3+} - exchanged clays) and decreased acidity (as with Na^+ -exchanged clay) points out the importance of framework aluminium present in the octahedral layer as the major player in this reaction. Many Lewis acid-catalysed reactions[9] are also found

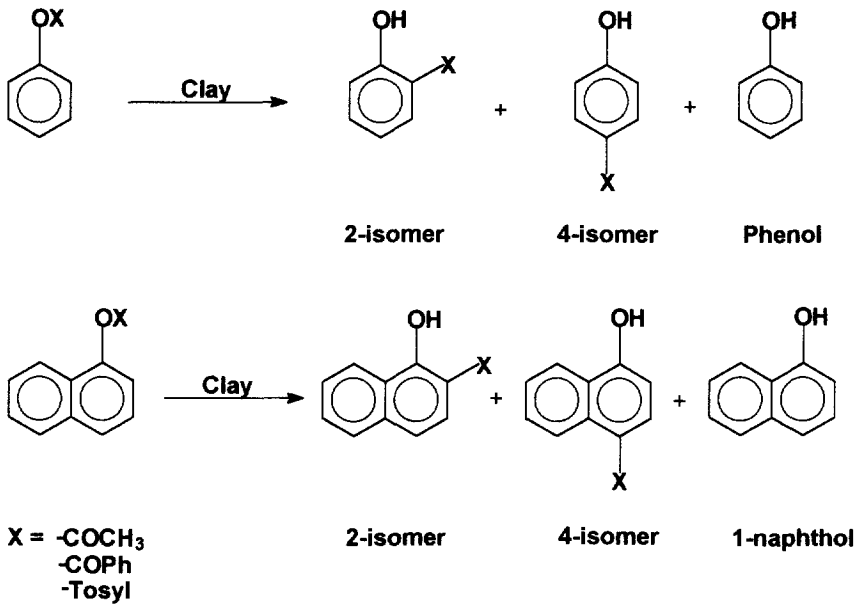
Table 1. Percentage Yield and Product Distribution in the Fries Rearrangement of Esters in Clay Microenvironment[a]

Clay		Conversion (%)	Percentage of products		
			2-isomer	4-isomer	phenol/1-Naphthol
			Phenyl acetate		
K10-Mont.	(1:1)[b]	88	03	85	--
Na^+-Mont.	(1:1)	81	--	81	--
H^+-Mont.	(1:1)[c]	100	--	100	--
Al^{3+}- Mont.	(1:1)	100	--	100	--
K10-Mont.	(1:2)	100	18	82	--
Al^{3+}-Mont.	(1:2)	100	12	88	--
K10-Mont.	(1:3)	100	16	84	--
			Phenyl benzoate		
K10-Mont.	(1:1)	90	10	62	18
Na^+-Mont.	(1:1)	94	24	64	06
H^+-Mont.	(1:1)[c]	100	09	77	14
Al^{3+}-Mont.	(1:1)	100	12	74	14
K10-Mont.	(1:2)	100	10	80	10
Al^{3+}-Mont.	(1:2)	100	08	80	12
			Phenyl *para*-toluenesulphonate[d]		
K10-Mont.	(1:1)	100	88	12	--
H^+-Mont.	(1:1)[c]	100	86	14	--
Al^{3+}-Mont.	(1:1)	100	92	08	--
			1-Naphthyl acetate		
K10-Mont.	(1:1)	72	69	--	03
Na^+-Mont.	(1:1)	66	62	--	04
H^+-Mont.	(1:1)[c]	81	72	--	09
Al^{3+}-Mont.	(1:1)	61	58	--	03
			1-Naphthyl benzoate		
K10-Mont.	(1:1)	43	43	--	--
Na^+-Mont.	(1:1)	45	40	--	05
H^+-Mont.	(1:1)[c]	73	65	--	08
Al^{3+}-Mont.	(1:1)	61	53	--	08
			1-Naphthyl *para*-toluenesulphonate		
K10-Mont.	(1:1)	67	62	--	05
Na^+-Mont.	(1:1)	63	57	--	06
H^+-Mont.	(1:1)[c]	68	55	--	13
Al^{3+}-Mont.	(1:1)	64	58	--	06

[a]Error limit ± 3% ,[b]Substance:Clay ratio, [c]K10-Montmorillonite exchanged with 2N HCl with a view to increase the extralattice Brönsted acidic sites, [d]Data from reference 4a.

to occur very efficiently in the presence of cation-exchanged montmorillonites and the reactivity is attributed to the Lewis acidity of the clay interlayer. These observations lead us to propose a major role for Lewis acidic sites of clays in catalysing this rearrangement with a small contribution from Brönsted acidity mainly in the latter stages of the rearrangement.

The orienting influence can be best understood from the nature of the migrating group. With a smaller acyl group, migration inside the clay interlayer to the thermodynamically more stable 4- position is facile. When the clay catalyst is present in excess, both the nucleophilic centres in the substrate are complexed



Scheme 1

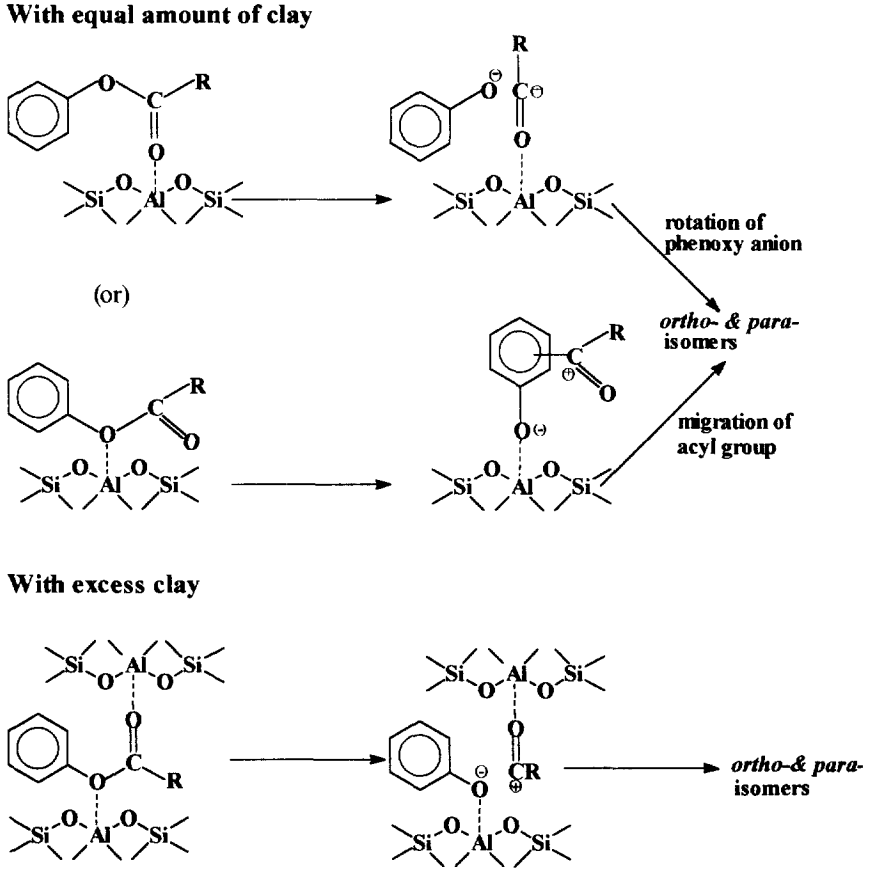
separately (**Scheme 2**). This renders the mobility of the ion-pair more difficult, thus paving the way for the formation of the 2-isomer also.

In phenyl benzoate, though the 4- isomer is still the major product, there is formation of the 2- isomer also. This may be attributed to the decreased mobility (within the clay interlayer) with a bulkier benzoyl group, compared to the acetyl group. It is interesting to observe the presence of phenol also, which is not formed in the other two cases. This may be due to the greater stability of benzoyl group which makes the clay-bound phenoxy group more prone to the attack by the interlayer water (or) H^+ generated from it. In the case of phenyl 4-toluenesulphonate, with a more bulkier sulphonate migrating group, steric effects exert their presence more effectively and 2- isomer formation is the major course of the reaction.

This steric influence on the products distribution is also demonstrated with the nature of the substrate. With more bulkier naphthyl esters (acetates, benzoates & *para*-toluenesulphonates) also, the rearrangement is regiospecific and 2- isomers are the exclusive products. Even with a smaller acetyl group,

formation of 2-isomer as the exclusive product illustrates clearly the manifestation of steric control of the rearrangement, when present in the restricted environment of clay interlayer.

Support for this conclusion of dependence of *ortho/para* ratio on the size of the migrating group/substrate in a constrained environment comes from other results also. In the Orton rearrangement of N-Chloroacetanilide in clay interlayer,[10] the 4- isomer is the major product. This is in accordance with our conclusion of steric control on selectivity as in this case the migrating group is a much smaller chloronium ion, which directs itself to the thermodynamically more stable 4- position. In the case of benzyl phenyl ethers[11] when the migrating group is a bulkier more reactive benzylcarbonium ion, 2-isomer is observed as the major product.



Scheme 2

This results discussed above amply illustrates the catalytic efficiency of clays and also the susceptibility of the rearrangement to steric effects in the migrating group/substrate, which is more pronunced when the substrates are present in a more constrained environment of the clay interlayer.

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