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PARA-SELECTIVE FRIES REARRANGEMENT OF PHENYL ACETATE IN THE PRESENCE OF ZEOLITE MOLECULAR SIEVES

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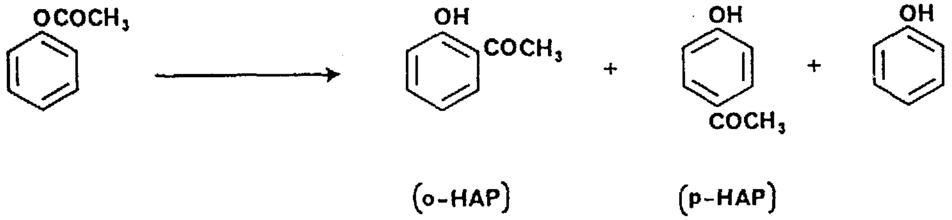
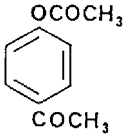
Summary: The Fries rearrangement of phenyl acetate is catalysed by acidic zeolites such as H-Nu-2 and H-ZSM-5, with selectivities of 2-6:1 in favour of para-substituted products.

The Fries rearrangement of phenyl esters affords a mixture of *o*- and *p*-hydroxyphenylketones, together with phenol as a hydrolysis product (Scheme). Extensive research over many years has established that the reaction can be catalysed by a variety of Lewis and Bronsted acids[1,2], with aluminium trichloride being the most widely used. An equimolar amount of $AlCl_3$ is generally required and it is consumed during work up. It is also known that the gas phase reaction can be catalysed by acidic zeolites at high temperatures(*ca* 400 °C)[3,4]. We now report that the liquid phase Fries rearrangement of phenyl acetate is catalysed by acidic high silica zeolites[5] (H-Nu-2[6], unknown structure; H-ZSM-5[7], *MFI* structure) which can be recovered, regenerated and reused, and furthermore that the process shows significant *para*-selectivity.

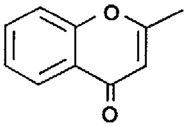


Scheme

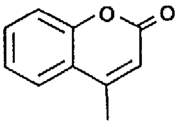
In a typical experiment phenyl acetate (7.5g) and the zeolite (1.5g) were heated together with stirring in the absence of solvent and the progress of the reaction monitored by g.c. and/or h.p.l.c. The results are presented in the Table. With H-Nu-2 after 24h at 170 °C the reaction mixture contained *p*-hydroxyacetophenone(*p*-HAP)(14%), *p*-acetoxyacetophenone (*p*-AAP)(5%), and *o*-hydroxyacetophenone (*o*-HAP)(4%), together with unreacted phenyl acetate (30%) and phenol (20%). (All percentages are by weight and refer to recovered product.) In the absence of the zeolite no reaction took place. The *p*-AAP may result from acetylation of *p*-HAP either by acetic acid formed by hydrolysis or by direct interaction with the phenyl acetate. The corresponding *ortho*-acetylated phenol was not detected. In contrast to normal Lewis and Bronsted acid catalysed Fries rearrangements under similar conditions there is pronounced *para*-selectivity, the ratio of *para*-products (*p*-HAP + *p*-AAP) to *o*-HAP being *ca* 4.3:1 (with $AlCl_3$ at 165 °C, neat, 70% *ortho*-product is obtained)[1]. Similar results were obtained at 210 °C (Table, entry 4) and in this case there were also traces (*ca* 1%) of 2-methyl-4-oxochromene(1) and 4-methylcoumarin(2). These may result from the facile intramolecular condensation of *o*-acetoxyacetophenone, thus accounting for its absence in the reaction mixture, or by reaction of *o*-HAP with phenyl acetate. Phenol formation can be attributed, at least in part, to the adventitious presence of water, a view supported by an experiment (Table, entry 2) with dried catalyst; this gave less phenol (13% *cf* 20%) but the amount of phenyl acetate converted was also reduced (45% *cf* 70%). It would also be formed as a by-product from the transesterification reaction between phenyl acetate and *p*-HAP.



(p-AAP)



(1)



(2)

Para-selectivity was also observed using H-ZSM-5 (Table, entries 3 and 5). Although the reaction is slower, with only 22% of phenyl acetate consumed after 24h at 170 °C, the preference for *para*-products was slightly greater (6.0:1). The excess phenyl acetate to zeolite (5:1 w/w) used in all the above experiments shows that the process is catalytic. Furthermore, after removal by centrifuging its activity was fully restored by heating at 500 °C for 24h. After 24h at 210 °C using regenerated H-Nu-2 the extent of reaction and product balance were the same, within experimental error, as those for the original sample (Table, entry 6).

When the reaction was repeated using H-Nu-10[8,9], reported to have the *TON* structure with one-dimensional 5.5 x 4.5 A channels[10] (*cf* H-ZSM-5 which has intersecting 5.4 x 5.6 and 5.1 x 5.5 A channels[11,12]) it proved to be slow and non-selective; after 54h at 210 °C only 12% of the ester had been consumed yielding 10% phenol and 2% of a 1:1 mixture of *ortho*-and *para*-products. As phenyl acetate is too large to enter easily the channels of H-Nu-10 and as there is certainly insufficient void space for the reaction to take place within the zeolite such reaction as occurred must have taken place at the zeolite crystal surface. Using Na-Y, a non-acidic zeolite, some hydrolysis occurred but no rearranged products could be detected (Table, entry 8). It can thus be concluded that for H-Nu-2 and H-ZSM-5 it is the acidic sites that account for the catalysis and the constraints of the zeolitic void space which give rise to *para*-selectivity.

These results can be compared with those of Olah et al[13] who utilised polymeric perfluorinated resin sulphonic acid (Nafion-H) as a reusable heterogeneous catalyst. Aryl benzoates were converted to *o*- and *p*-hydroxybenzophenones, but they reported that the corresponding reactions with acetate esters were unsuccessful. On re-examining this system we have found that Nafion-H *does* catalyse the Fries rearrangement of phenyl acetate (Table, entry 9). After 24h at 170 °C 83% of the ester had been consumed yielding 10% of a *ca* 1:1 mixture of *o*-HAP and *p*-HAP, together with a large amount of phenol (25%). The zeolites, particularly H-Nu-2 and H-ZSM-5, are therefore of comparable activity to Nafion-H, but in contrast show selectivity in favour of para-substituted products.

There is increasing evidence that zeolites will find widespread use in organic chemistry[14]. The results described in this communication support this view and illustrate one of their most important applications, the enhancement of para-selectivity in aromatic substitution reactions.

Table Influence of zeolites on the Fries rearrangement of phenyl acetate

Entry	Catalyst	Temp. (°C)	Reaction time (h)	Composition of recovered product (weight %)					
				PhOAc	*o*-HAP	*p*-HAP	*p*-AAP	PhOH	*para*:*ortho*
1	H-Nu-2[a]	170	24	30.5	4.3	13.8	4.7	20.5	4.3
2	H-Nu-2(dry)[b]	170	24	55.1	6.2	14.8	2.8	13.2	2.8
3	H-ZSM-5[c]	170	24	77.7	1.1	3.3	3.3	10.8	6.0
4	H-Nu-2	210	24	19.9	4.6	11.7	4.3	20.3	3.5
5	H-ZSM-5	210	24	66.8	3.7	6.0	6.0	13.3	3.2
6	H-Nu-2[d]	210	24	31.7	6.6	13.9[e]		25.2	2.1
7	H-Nu-10[f]	210	54	88.2	1.2	1.3[e]		7.2	1.1
8	Na-Y[g]	170	24	84.8	-[h]	-[h]		17.1	-
9	Nafion-H[i]	170	24	16.9	5.6	4.5[e]		25.2	0.8

[a] supplied by J.L.Casci, ICI Chemicals and Polymers Ltd (Si/Al=13.2)

[b] dried at 400 °C for 17h, stored *in vacuo* over P_2O_5, transferred to reaction flask under dry N_2

[c] synthesised according to EPA42225/1981 (Si/Al = 20.3)

[d] regenerated by heating at 500 °C for 24h

[e] combined yield of *p*-HAP and *p*-AAP

[f] supplied by A.Stewart, ICI Chemicals and Polymers Ltd (Si/Al = 54.5)

[g] from STREM Chemicals Ltd

[h] not detected (<0.1%)

[i] from Aldrich

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