

Fries rearrangement of acetanilide over zeolite catalysts¹

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Abstract

Zeolites Y and Beta have been evaluated for the Fries type rearrangement of acetanilide (**1**) to the corresponding aminoacetophenones. Aniline was the major product but in the presence of added acetic anhydride the major product was *meta*-aminoacetophenone (**3**). The photo-Fries rearrangement was attempted for X, Y and Beta zeolites impregnated with **1**. In contrast to the catalytic rearrangement at elevated temperatures the major product was the *ortho*-aminoacetophenone (**2**). It appears that the selectivity for the *ortho* isomer improves at the expense of conversion with decreasing acidity. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective acetanilide (**1**) rearrangement to aminoacetophenones as shown in Fig. 1 represents a challenging but commercially relevant reaction. The *ortho*-aminoacetophenone (**2**) is probably the more interesting isomeric product of this reaction. Various *ortho* acyl substituted aniline derivatives are precursors to anti-inflammatory [1] and cardiovascular agents [2]. Other chemical synthesis applications for the *ortho* isomer as well as the *meta* (**3**) and *para* (**4**) isomers are anticipated.

The rearrangement of acetanilide to aminoacetophenones via thermal process has

been known for more than 80 years. However, there has been surprisingly little reported on this reaction since then. In 1957 [3], it was found that various Lewis acids such as ZnCl₂, SnCl₄, P₂O₅, AlCl₃, AlCl₃ + ZnCl₂ were catalysts for the acetanilide rearrangement. The best results were obtained with ZnCl₂ or a combination of AlCl₃ + ZnCl₂ catalyst where the *ortho*-aminoacetophenone was obtained in low yields. Subsequently, BiCl₃ was also found to catalyze the rearrangement of various substituted anilides [4]. More recently, TiCl₄, ThCl₄ and ZrOCl₂ were found to catalyze the Fries rearrangement of acetanilide to *para*-aminoacetophenone (**4**) as the major product [5]. It was proposed that the *ortho*-aminoacetophenone formed first followed by isomerization to the *para* product **4**.

It would appear from these results that Lewis acids catalyze the Fries rearrangement of **1**. It is

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¹ Dedicated to Professor Herman van Bekkum on the occasion of his 65th birthday.

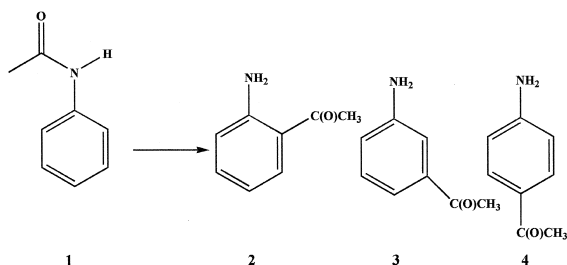


Fig. 1. Fries rearrangement of acetanilide (1).

also known that solid acids including the zeolite HY catalyze the closely related Hofman–Martius rearrangement of *N*-alkylanilines to ring alkylanilines [6]. Therefore, it was felt that zeolites could provide an acidic surface as well as steric constraints that might enhance regioselectivity, especially if an intermolecular mechanism were operative. It was hoped that a lesson could be learned from the extensive amount of work devoted to the Fries rearrangement of the analogous phenylacetate **5** to hydroxyacetophenones as shown in Fig. 2. For example the Hoechst–Celanese process for acetaminophen (**9**) which is one of the most popular over the counter analgesics, involves the Fries rearrangement of phenylacetate (**5**) to the *para*-hydroxyacetophenone (**7**). After the reaction of **7** with hydroxylamine followed by a Beckman rearrangement the acetanilide (**9**) is formed [7]. The phenylacetate rearrangement may be catalyzed by Lewis acids such as AlCl₃ or Bronsted acids such as HF. However, it is fairly clear that neither of these choices or similar acids would be regarded as environmentally friendly catalysts. Zeolites on the other hand could potentially solve the waste management or corrosion

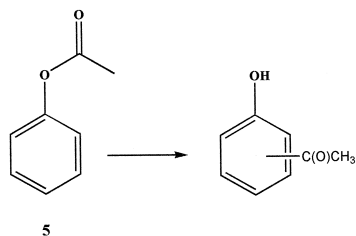


Fig. 2. Fries rearrangement of phenylacetate (5).

issues associated with metal halides or mineral acids. Zeolites of the type Beta [8–10], HY [9,11,12], ZSM-5 [9,11,13,12,14], ZSM-12 [9], Mordenite [9] and NU-10 [9] have been screened for the Fries rearrangement of phenylacetate. In most cases the major products observed were phenol (**6**) and a mixture of the *ortho* (**8**) and *para* (**7**) isomers where the latter dominates. The results would seem to reflect an intermolecular mechanism in most cases as evidenced by phenol and crossover products. Recently, the best selectivity for the Fries rearrangement of phenylacetate over zeolites was reported for a photochemical process [15]. In this case, X and Y zeolites were selective for the *ortho* isomer while ZSM-5 and ZSM-11 were selective for the *para* isomer. The photoreaction should involve a radical process in contrast to the thermal reaction which probably involves carbonium ions [16].

In the present study, we have tried to evaluate the possibility of running the Fries rearrangement of acetanilide (**1**) over different zeolites in both batch and flow type thermal processes. Additionally, we report the preliminary results for the photomediated rearrangement of **1** in zeolites. It has become apparent that the differences between acetanilide and phenylacetate are magnified inside the zeolites where the amino group has a higher affinity for the oxide surface than the phenol.

2. Experimental

Acetanilide, **1**, (Fluka) and standards for *ortho*-aminoacetophenone, **2**, *meta*-aminoacetophenone, **3**, and *para*-aminoacetophenone, **4**, (Aldrich) as well as TiCl₄ (Aldrich) were used as received. Zeolites Beta (Valfor, Si/Al = 25), NaY (Valfor, Si/Al = 5.1) and NaX (Aldrich) were calcined at 450°C prior to use. KX (6.3% K by wt.) was prepared by ion exchange of NaX. Two grams of NaX were stirred at RT in an aqueous 2 M KCl solution for 3 h, filtered,

washed and then the process repeated three more times. KY (6% K by wt.) was prepared by stirring 4 g of NaY in 100 ml of an aqueous 2 M KCl solution at RT overnight. CsX (2% Cs by wt.) was prepared by stirring 1 g of NaX in 100 ml of a 0.04 M CsCl solution overnight. CsY (2% Cs by wt.) was prepared by stirring 1 g of NaY in 100 ml of an aqueous 0.03 M CsCl solution at RT overnight. CoNaY was prepared by stirring 1 g of NaY in a 0.01 M aqueous cobalt chloride solution for 3 h at room temperature. The CoNaY was washed with deionized water, dried and calcined at 450°C.

Batch reactions were run in a round bottom flask under an atmosphere of helium or nitrogen while stirring. In a typical reaction the flask was charged with 0.5 g of calcined (450°C) zeolite catalyst and 2 g of acetanilide. The mixture was heated above the melting point while stirring. After cooling down, the contents of the flask were extracted with methanol or chloroform, centrifuged to remove catalyst and analyzed by gas chromatography. In the case of TiCl_4 , the reaction was basified with Na_2CO_3 and extracted with ethyl acetate.

Flow reactions were run using a quartz tube reactor having a 5 mm I.D. and a length of 200 mm, supplied with syringe pump and line with N_2 flow (0.4 l/h). In a typical reaction the tube was loaded with ~ 0.5 g of zeolite catalyst and activated for 1 h at 400°C in a flow of N_2 prior to reaction. For preparation of initial mixture sulfolane was used as a solvent.

The photochemical reaction was run in a 50-ml quartz flask (50 ml) using a RAYONET[®] (model RMR 600) reactor equipped with 8 UV-lamps (2537 Å) with a total power of 32 W. In a typical reaction, 0.5 g of calcined zeolite were impregnated with acetanilide by exposure to 0.01 g of **1** in 0.5–1.5 ml of dry acetonitrile at room temperature for several minutes. The solvent was evaporated at RT and the zeolite was dried further at 90°C for 0.5 h. The substrate-loaded zeolite was transferred to the quartz flask with 3 ml of hexane. The slurry was then irradiated for 1 h while stirring until the flask

reached $\sim 40^\circ\text{C}$. The products were extracted using acetonitrile for 1 h and the zeolites were separated by centrifugation.

Products were analyzed using an HP 5890 capillary gas chromatograph equipped with a flame ionized detector and a 'Heliflex' AT-1 capillary column (length 15 m; ID 0.53 mm; film thickness 5 μm). For analysis, a temperature program was used starting at 70°C for 1.5 min, followed by an increase to 140°C at a rate of 7°/min. The temperature was then raised to 250°C at a rate of 15°/min and maintained for 20 min.

3. Results and discussion

3.1. Batch and flow reactions

In a recent study of the Fries rearrangement of acetanilide using metal salts such as TiCl_4 as catalysts, the reaction was run batchwise at 160–180°C [6]. The acetanilide (**1**) melts at 113°C such that catalyst was simply dissolved in melted substrate. The products **3** and **4** melt at slightly lower temperatures while the *ortho* isomer **2** is a liquid at room temperature. An attempt was made to reproduce the previous results using TiCl_4 stirred in a melt of **1** over the temperature range of 100–220°C. However, after 30 min at 100°C ($\sim 20\%$ conversion) only some unidentified product was observed, while heating at 170°C ($\sim 50\%$ conversion) over the same time frame a few percent yield of aniline was obtained. Above 200°C, the degradation of **1** and the formation of coke becomes quite apparent. At the lower temperatures the formation of aniline suggests that the reaction might be losing the acylium ion in an intermolecular process. It is known that acetic anhydride reacts with aniline rapidly at room temperature to form the acetanilide **1**. It is also known that acetic acid improves the conversion of phenol to 2-hydroxyacetophenone [17]. Therefore, we added some acetic anhydride (10 mole% relative to TiCl_4) to the reaction. The effect was to lower

the conversions and no aniline was observed at 270°C. Additionally, the level of coking was reduced such that we could heat the reaction higher. After heating at 260°C for 1.5 h we obtained a 21% yield of the *meta*-aminoacetophenone isomer. This was somewhat unexpected but may be the result of trace amounts of water which in turn would form HCl in the mixture and protonate the aniline generating a weak *meta* director. In the presence of acetic anhydride we also saw crossover products such as the acylated acetanilide. So the source of extra electrophile eliminates aniline but generates over substituted byproducts. Although the conditions of this batch reaction did not appear promising it was decided to try a Co(II) exchanged NaY as the catalyst. Above 250°C, 100% conversion was achieved but the only products were small amounts of aniline and condensed products. The addition of acetic anhydride to the reaction eliminated aniline as a product and generated the *meta* isomer in low yields. Zeolite Beta was also tried under these conditions and comparable results were obtained. Therefore, the batch reactions were abandoned in favor of gas phase reactions in a flow reactor.

Since zeolite Beta has been one of the more promising catalysts for the Fries rearrangement of phenylacetate [9,10,18], we continued to evaluate the conversion of **1** over this zeolite but in a flow reactor. The reactor was filled with 1–2 mm particles from crushed pellets of zeolite Beta. The feed solution was 9.0 wt.% acetanilide dissolved in sulfolane. Sulfolane is a high boiling, polar solvent that has been used in zeolite Beta catalyzed rearrangements of phenylacetate [18]. In that case, the *para* isomer **7** was favored in the sulfolane solvent. Small amounts of the *para* isomer **4** were also observed in the temperature range of 280–380°C over zeolite Beta. However, the principal product in this reaction is aniline. The addition of acetic anhydride to the feed (7% by wt.) resulted in the *meta* isomer **3** being the major product as shown in Table 1. If the contact time

Table 1
Rearrangement of **1** over zeolite Beta in the presence of acetic anhydride^a

| Temperature (C) | Conversion % | % Yield 3 | % Yield 4 | Ratio 3/4 |
|-----------------|--------------|------------------|------------------|------------------|
| 175 | 63 | 47.2 | 15.7 | 3 |
| 230 | 63.4 | 42.5 | 17.5 | 2.4 |
| 280 | 66.8 | 40.5 | 18.3 | 2.2 |
| 330 | 53.3 | 34.8 | 18.5 | 1.9 |
| 360 | 55.1 | 29.9 | 18.7 | 1.6 |

^a0.10-g zeolite beta activated at 420°C, acetanilide/acetic anhydride molar ratio was 1:1 and N₂ was the carrier gas (30 ml/min).

is increased fourfold then at 175°C the only product is *meta*-aminoacetophenone. It should also be noted that with time on stream (> 60 min) severe coking becomes apparent. This is consistent with the thermal instability of the *meta*-aminoacetophenone which begins to convert to an unknown product above 100°C. In contrast, both products **2** and **4** show only trace levels of conversion in the temperature range of 100–300°C.

It appears that the formation of a *meta* substituted product from a catalytic Fries type rearrangement of phenyl acetates or acetanilides has not yet been reported. Normally, the hydroxyl or amino group would be *ortho* or *para* directors, however, the ammonium ion should be regarded as at least a weak *meta* director. If one examines some of the literature for zeolite catalyzed alkylations of aniline [19–29] any ring alkylation appears in the *ortho* or *para* positions. However, under strongly acidic conditions the *ortho* or *para* isomers can rearrange to *meta* isomer [19]. It may be that *p* → *m* isomerization is occurring in our case but it is more likely that an intermolecular process is at work such that formed aniline is protonated or interacts strongly with the zeolite surface.

3.2. Photochemical reactions

The selectivity issues associated with the electrophilic substitutions in the catalytic Fries process might be resolved in a photochemical reaction that should be radical in nature. Fol-

Table 2
Results for the photo-Fries rearrangement of **1** over NaY

| Solvent | Products ^a | | | | Conversion Mol% | Nonextracted 1 Mol% | Ratio <i>o/p</i> |
|--------------------------------|-----------------------|----------|----------|----------|--------------------|-------------------------------|------------------|
| | Aniline | 2 | 3 | 4 | | | |
| Chloroform | 4.6 | 1.3 | 0.6 | 0.3 | 9.4 | 65 | 5.0 |
| Acetone | 0.2 | 2.0 | 0.0 | 0.7 | 3.9 | 18 | 2.8 |
| Water | 0.8 | 2.0 | 0.0 | 0.0 | 3.7 | 38 | — |
| Methanol | 1.3 | 3.4 | 0.0 | 1.0 | 5.9 | 79 | 3.4 |
| Sulfolane | 0.4 | 3.9 | 0.2 | 1.5 | 9.5 | 42 | 2.6 |
| <i>t</i> -Butanol | 1.2 | 3.5 | tr. | 0.7 | 7.2 | 55 | 4.8 |
| <i>t</i> -Butanol ^b | 2.0 | 5.2 | 0.0 | 2.2 | 12.8 | 43 | 2.4 |
| Cyclohexane | tr. | 1.7 | 0.0 | 0.0 | 2.3 | 71 | — |
| Hexane | 2.3 | 4.0 | 0.1 | 0.8 | 9.8 | 47 | 5.0 |
| Acetonitrile | 4.6 | 7.7 | 0.1 | 4.3 | 22.4 | 70 | 1.8 |

^aIn mmol $\times 10^3$.

^bExtraction for 4 h with pyridine.

lowing the recent report of Pitchumani et al. [15] on the photo-Fries rearrangement of phenylacetate in zeolites we attempted to mimic somewhat their conditions. This meant that irradiation of the solid zeolite impregnated with acetanilide was expected to provide a rather poor yield. Therefore, we had to find a solvent in order to suspend the zeolite during irradiation and not extract the substrate from the zeolite. For a series of tested solvents the order of activity was acetonitrile > *n*-hexane > cyclohexane \sim *t*-butanol \sim sulfolane > methanol > benzene > water > acetone > chloroform where the only detectable product was *ortho*-aminoacetophenone and traces of aniline. Interestingly, the solubility of acetanilide was not a factor since **1** is insoluble in the nonpolar hexane and cyclohexane. The irradiation of **1** in these solvents also serve as the blank experiments for the intrazeolite reactions. The reaction

was then run using NaY (Si/Al = 5.1) impregnated with acetanilide in the same series of solvents as shown in Table 2. In all cases except for *n*-hexane and cyclohexane the products were analyzed directly. In the case of the *n*-hexane and cyclohexane the insoluble substrate and products were extracted with acetonitrile. In all cases, the major product was the *ortho* isomer with varying amounts of the *para* isomer. This selectivity is similar to that observed for the photoreaction of phenylacetate over NaY [15]. Additionally, only trace amounts of the *meta* isomer produced in the catalytic reaction at elevated temperatures was observed. Although these results look promising we have a problem with our mass balance. It would appear that a significant amount of unreacted acetanilide as well as an indeterminate amount of products remain adsorbed in the zeolite after the extraction procedure. The presence of **1** inside the

Table 3
Results for the photo-Fries rearrangement of **1** over X and Y zeolites in *n*-hexane

| Zeolite | Products ^a | | | | Conversion Mol% | Nonextracted 1 Mol% | Ratio <i>o/p</i> |
|---------|-----------------------|----------|----------|----------|--------------------|-------------------------------|------------------|
| | Aniline | 2 | 3 | 4 | | | |
| NaX | 2.6 | 5.0 | 0.0 | 2.7 | 13.9 | 44 | 1.8 |
| KX | 0.4 | 3.3 | 0.0 | 0.7 | 5.9 | 42 | 4.7 |
| CsX | tr | 1.0 | 0.0 | 0.1 | 1.3 | 36 | 10.0 |
| KY | 1.6 | 1.8 | 0.0 | 0.2 | 4.9 | 39 | 9.0 |
| CsY | 1.4 | 1.9 | 0.0 | 0.2 | 4.7 | 32 | 9.5 |

^aIn mmol $\times 10^3$.

Table 4
Results for the photo-Fries rearrangement of **1** over zeolite Beta

| Solvent | Products ^a | | | | Conversion Mol% | Nonextracted 1 Mol% | Ratio <i>o/p</i> |
|---------------------------|-----------------------|----------|----------|----------|--------------------|-------------------------------|------------------|
| | Aniline | 2 | 3 | 4 | | | |
| Cyclohexane | 0.0 | 0.0 | 0.0 | 0.0 | | 95 | |
| Hexane | 0.0 | 0.2 | 0.0 | 0.2 | 0.6 | 77 | 1.0 |
| Pyridine | 0.0 | 0.5 | 0.0 | 0.0 | 0.7 | 46 | |
| Acetonitrile | 0.0 | 1.6 | 0.0 | tr. | 2.1 | 92 | |
| Acetonitrile ^b | 2.1 | 1.8 | 0.0 | 0.5 | 5.9 | 82 | 3.6 |

^aIn mmol $\times 10^3$.

^bExtraction with pyridine for 4 h.

zeolite can be verified by infrared spectroscopy but any other occluded molecules have not been identified. The entry for *t*-butanol in Table 2 illustrates that the use of a stronger base than acetonitrile can extract additional substrate and product from the zeolite pores and further indicates that the reaction occurs inside the zeolite. It should also be noted that products **2**, **3** and **4** preabsorbed in the NaY do not appear to undergo any photoconversion as evidenced by GC analysis. However, the zeolite with occluded **2** and **4** turns yellow and the zeolite with **3** turns pink in color. Approximately, 90% of **2**, 70% of **3** and 50% of **4** could be extracted using our procedure. The problem of strong adsorption is exemplified by experiments with ZSM-5 where regardless of Si/Al ratio (56–130) no observable products and only trace amounts of substrate could be extracted from the zeolite. The plan is to repeat these experiments using silicalite in order to see if the *para* selectivity found with phenylacetate [15] can be realized for acetanilide.

In order to render the NaY less acidic, the Na⁺ was ion exchanged for K⁺ and Cs⁺ as well and the analogous NaX series was also prepared. Table 3 shows the results in hexane as a solvent. It appears that as the general acidity decreases the amount of substrate and products that can be extracted increases. Additionally, the ratio of *ortho* to *para* isomer increases. 90% selectivity for **2** is comparable to some of the best results obtained for the photo-Fries rearrangement of phenylacetate over X and Y zeo-

lites [15]. Unfortunately, as the relative acidity decreased the conversion also decreased. Longer irradiation times improved the conversions at the expense of selectivity.

For a comparison with the catalytic reactions at elevated temperatures the photoreaction was carried out over impregnated zeolite Beta as shown in Table 4. The zeolite Beta (Si/Al = 25) is more acidic than the NaY catalyst and the difficulty in extracting product from the pores is correspondingly greater. The selectivity for this large pore zeolite also appears to be in favor of the *ortho*-aminoacetophenone. The photo-Fries rearrangement inside zeolite host materials has promise, however, for substrates such as acetanilide we still need to determine a composition that would allow complete recovery of organics from the pores. It would appear that zeolites with little or no acidity would be preferred.

4. Conclusions

It appears that the Fries type rearrangement of acetanilide over zeolite catalysts is a much more difficult reaction compared with the analogous phenylacetate. The strong affinity for aniline and the substituted aniline products complicates the reaction. Nevertheless, it has been shown that acetanilide can be converted to *meta* and *para*-aminoacetophenone in a catalytic process at elevated temperatures. The photo-Fries rearrangement appears to be more selective for

the *ortho*-aminoacetophenone in the large pore zeolites. Although the yields are low the possibility of a selective process merits further investigation of the Fries type rearrangement over zeolite catalysts.

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