Regioselectivity of aniline and toluidine nitration with HNO_3 and H_2SO_4 in acetic acid

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ABSTRACT: The goal of this work is to study how the regioselectivity in aniline and toluidine nitration is affected by the resonance and induction effects of N-acetyl and N-succinimidil groups. Starting materials were protected with acetic and succinic anhydride, and nitration occured via S_EAr with a HNO_3/H_2SO_4 mixture in AcOH. Nitrated products were hydrolyzed and a sample of each experiment was analysed by HPLC. Aniline results show product distribution is controlled by both functional groups' *ortho/para* directing and +R effects, yielding similar percentages of 2-nitroaniline (23%) and 4-nitroaniline (76%). For 4-methylacetanilide, regioselectivity control is once again established by the +R effect, favoring the *ortho*-substituted product (97%). Since succinimide group is less activating than the acetamide group, reaction control is taken over by the methyl group, yielding 94% 4-methyl-3-nitroaniline. 3-methylacetanilide nitration yielded 91% 3-methyl-4-nitroaniline, which is a product favored by both +R effect of the acetamide group and +I effect of the methyl group. For N-(3-methylphenyl)-succinimide, the yield of 3-methyl-6-nitroaniline increased to 62% since the succinimide group has a weaker activating effect due to the electronic pull of its two carbonyl groups. For the N-(2-methylphenyl)-succinimide, product distribution was controlled by the alkyl group, with the main products being *ortho*/*meta* substituted, yielding 29% 2-methyl-3-nitroaniline and 55% 2-methyl-5-nitroaniline. This is due to the non-planar position between the succinimide group and the aromatic ring, nullifying its +R effect. For the acetanilide derivative, regioselectivity is controlled by its +R effect (45% 2-methyl-4-nitroaniline) and by the +I effect of the methyl group (33% 2-methyl-5-nitroaniline). Overall it was shown that the +R effect of the acetamide groups is stronger than that of the succinimide group. This is due to the presence of one more carbonyl group in the latter, which pulls electrons away from the aromatic ring by induction (-I effect) and by resonance (-R effect) deactivating the starting material to an EAS reaction. Experiments with the N-acetyl derivative also showed that +R effect is more important to regioselectivity control than the +I of the alkyl group. This was an expected result, as the non-shared electron pair of the nitrogen atom has a greater importance to the stabilization of the aromatic ring than the electron-donating role of the CH_3.

Keywords: nitration, aniline, regioselectivity, Electrophilic Aromatic Substitution

1. Introduction

1.1 State of the art

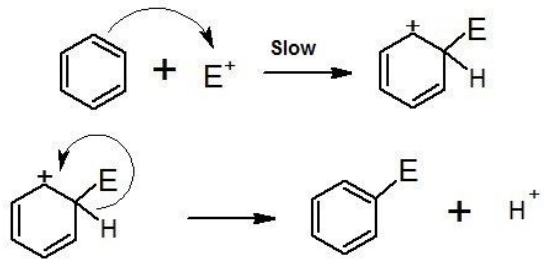
Nitration of aromatic compounds has been heavily studied since the 19th century due to its importance in several chemical industries. Nitro aromatic species are present in a wide range of value chains worth millions of Euros [1], from the pharmaceutical industry [2], used as intermediary in benzimidazole synthesis [3], to dye [4] and pesticide [5] precursors and many other uses. Given the large number of substracts used as starting material in these industries, and the even larger number of isomers that can be obtained during nitration, several synthetic routes have been developed with the objective of maximizing overall conversion of the reaction, as well as the selectivity of the desired

isomer. The classical nitration method is the use of an HNO_3/H_2SO_4 mixture in acetic acid, chloroform or dichloroethane. This synthetic route originates a great amount of acid effluents, hazardous to the environment. This generally leads to effluent treatment, which results in an extra cost to the company, reducing its profit. In order to keep up with the always growing environmental issues, new ways to produce nitro aromatic compounds at an industrial scale are being studied with the main concern being the necessity of synthesizing these compounds in mild conditions. The main processes include the use of transition-metal complexes as catalysts [6] [7], nitration salts [8] [9] and ozone mediated nitration [10]. Other nitro group sources have been investigated, such as $VO(NO_3)_3$ [11]. All these processes enable aromatic compound nitration in mild conditions that do not require the use of concentrated acids, extremely diminishing the environmental impact caused by the reaction. Other concern associated with the development of these new ways of producing nitro aromatic compounds is the desire to establish atom economical reactions that substantially reduce, or eliminate, the amount of effluents that have to be treated before they can be discharged.

However, the use of more expensive reactants and catalysts increases the process' overall cost. Moreover, these new synthetic routes have a much narrower range of application when compared to the classic HNO_3/H_2SO_4 method, and are more difficult to control, leading to unwanted and hazardous multi-nitrated sub-products, as shown by the process using $VO(NO_3)_3$ [11]. These problems are the reason why the classical nitration method which uses a mixture of concentrated nitric and sulfuric acids is still used worldwide in a great number of nitro aromatic compound industries [12] even with the associated environmental issues it carries.

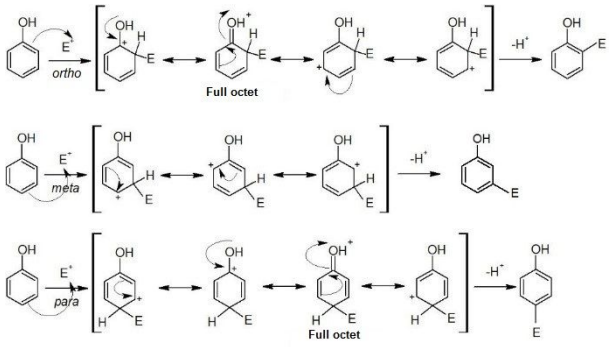
1.2. Electrophilic Aromatic Substitution

EAS is an organic reaction where an atom or group connected to the aromatic ring is substituted by another. This reaction occurs by a nucleophilic attack by the electron-rich aromatic ring on an electron-depleted electrophile in a two-step mechanism. The first step is the nucleophilic attack, connecting the aromatic ring to the electrophile, forming an arenium ion, stabilized by resonance. This is a slow step due to the momentary loss of aromaticity, and it determines the reaction's overall rate. The second step is the loss of the proton connected to the carbon atom where substitution occurred, thus reestablishing aromaticity.



Scheme 1 - EAS mechanism

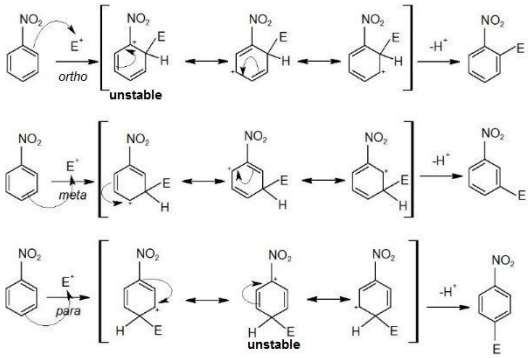
Regioselectivity is mainly affected by the aromatic ring's functional groups. These can either be activating or deactivating groups. Activating groups are electron donors by resonance (+R) or by induction (+I) and speed up the reaction by increasing the aromatic ring's electron density, making it more prone to attack an electrophile. Examples of these groups are NR_2, NH_2, OH and NHCOR. Activating groups are usually *ortho*/*para* directors due to the fact that *ortho* and *para* substituted species have one or more resonance contributors where all the atoms have a full octet.



Scheme 2 - Resonance contributors in an EAS mechanism with an activating group

These resonance contributors are very stable, which considerably decreases the activation energy necessary to form the intermediate complex. This significantly increases the reaction's overall rate, as EAS is kinetically controlled. The exception to this are halogen atoms, which form more stable intermediates in *ortho* and *para* substitution. However, they act as deactivating groups, due to a high electronegative property, attracting the aromatic ring's electron cloud, hence slowing the reaction.

In contrast, deactivating groups are *meta* directors, since *ortho* and *para* substituted products generate resonance contributors with a positively charged carbon atom connected to the deactivating group, highly destabilizing the arenium ion. Groups such as NO_2, SO_3H or COOR are extremely electronegative and attract electrons from the aromatic ring, decreasing its electron density. This results in a less activated ring, consequently leading to a much slower reaction.



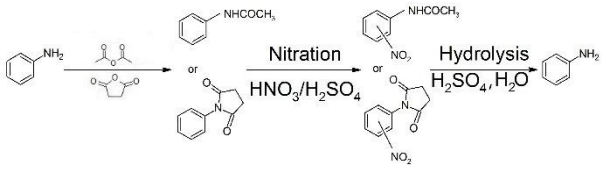
Scheme 3 - Resonance contributors in an EAS mechanism with a deactivating group

The fact that the NO_2 group is a deactivating group also explains why almost none multi nitrated byproducts were detected during every experimental procedure, since the presence of this group severely deactivates the aromatic ring for further nitration.

Regioselectivity is also affected by the steric hindrance stablished by both the functional group and the electrophile. Bulky groups tend to favor *para* substituted products, maximizing the distance between the functional group and the electrophile.

1.3. Nitration via HNO_3/H_2SO_4 in acetic acid

Using a mixture of concentrated nitric and sulfuric acids as nitrating agents is the ideal way of studying the reaction's regioselectivity since the reagents used are cheaper than those needed for other more complex processes. Furthermore, the reaction's mechanism is well known, simple (EAS) and does not require a catalyst. The occurrence of multi-nitrated byproducts was very limited in all of the experiments, which means the isomeric distribution is more reliable. Since this experiment took place at a laboratory scale, the amount of effluents was not a major concern, as the reactions were prepared with small amounts of reagents which led to small quantities of acid effluents that were neutralized or diluted in water prior to discharge. This synthetic route is also a quite easy and quick nitration mean, therefore allowing multiple experiments with the same starting material to ensure result repeatability. Given the main objective of this work was to understand how different functional groups affect the nitration of aniline and toluidine, and also because the amine group is very sensitive to harsh acidic conditions, the starting materials were protected via acetylation in the presence of acetic and succinic anhydride prior to nitration to prevent amine oxidation.

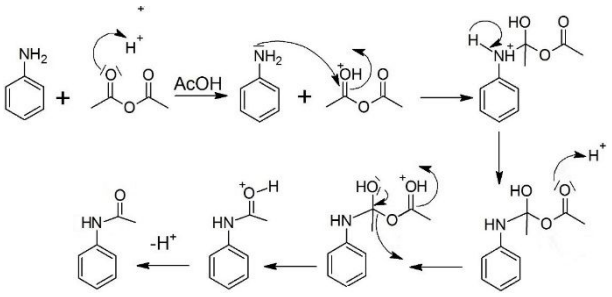


Scheme 4 – Experimental sequence

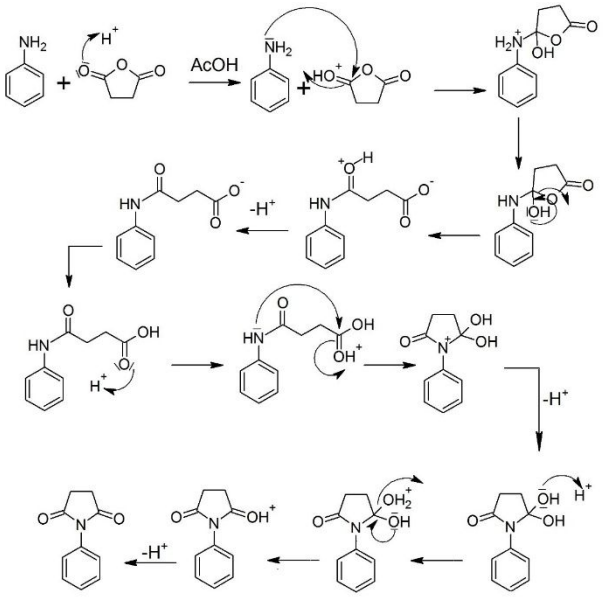
Acetylation with acetic anhydride has been used in many research works, either with nitration being carried out by HNO_3/H_2SO_4, as well as by the aforementioned processes. Studies' results show the expected acetamide group's *ortho/para* directing effect, resulting on *o:p* ratios of about 0,25 and no *meta*-substituted product being detected. These results are similar to those shown in the ozone mediated nitration and via nitration salts. The transition-metal complexes showed promise in obtaining *ortho*-substituted products, with *o:p* ratios of around 4,4. The use of $VO(NO_3)_3$ yielded equal parts of 2-nitroacetanilide and 4-nitroacetanilide products. Data regarding acetylation via succinic anhydride, however, is much scarcer, leading back to the early 20th century [13] when quantification methods were still not sufficiently well developed.

1.4. Mechanisms

The starting materials were protected with acetic and succinic anhydride, originating acetamide and succinimide derivatives, respectively.

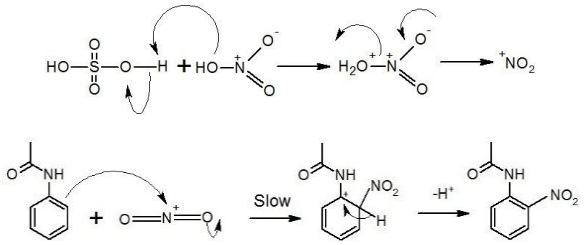


Scheme 5 - Amine protection with acetic anhydride



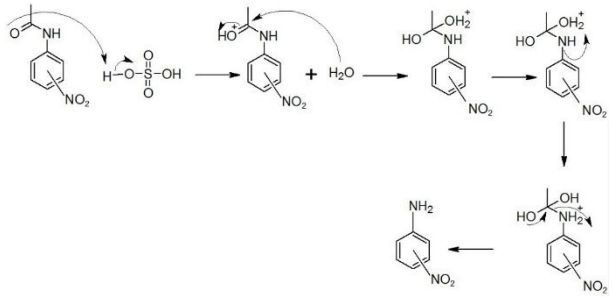
Scheme 6 - Amine protection with succinic anhydride

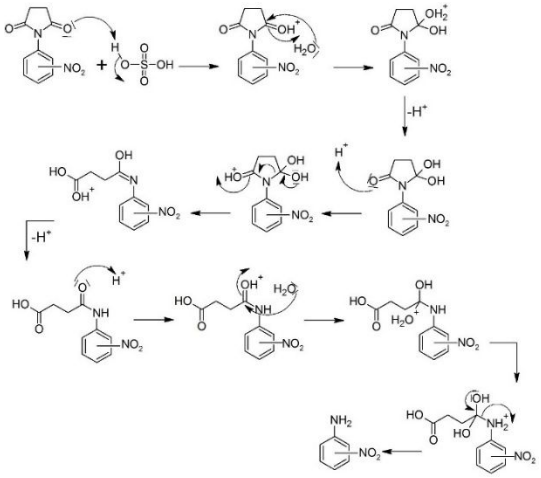
For the nitration reaction, nitric acid was protonated with sulfuric acid to produce the nitronium ion.



Schemes 7 and 8 – Nitronium ion formation and nitration mechanisms exemplified for *ortho* substitution

After nitration, the several isomeric mixtures obtained were submitted to hydrolysis with H_2SO_4 and water to re-establish the amine group.





Schemes 9 and 10 - Acetanilide and succinimide hydrolysis mechanism

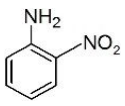
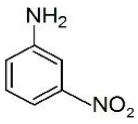
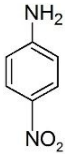
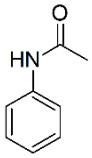
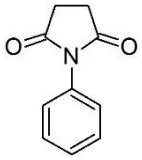
2. Results

Results obtained for each starting material allow to understand how the presence of different functional groups affect the nitrated products distribution in an EAS reaction. Both acetamide and succinimide groups act as electron donors by resonance (+R effect), whereas the alkyl group increases the aromatic ring electron density by induction (+I effect). These groups speed up the EAS reaction, favoring *ortho/para* substituted products.

Aniline

The mean results for aniline nitration are shown in Table 1.

Table 1 - Experimental results for aniline

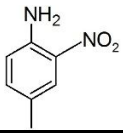
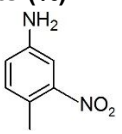
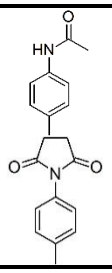
Starting material	Products (%)		
			
	**22**	**-**	**78**
	**24**	**2**	**74**

Acetanilide results show the expected activation of the *ortho* and *para* positions due to its +R property. The kinetically controlled reaction favors substitution in these positions, as it leads to an intermediate with all atoms having a full octet in one or more resonance contributors. The mean o:p ratio of 0,28 shown in Table 1 can be explained by the *para* position leading to a less hindered product. If steric hindrance did not have a role in product distribution, it would be expected to obtain an o:p ratio of 2, since there are two equivalent *ortho* positions where substitution may occur. These results were identical to those observed for N-phenyl-succinimide, as witnessed by the o:p ratio of 0,32. The slight increase of the *meta* substituted product can be explained by the weaker +R effect of the succinimide group compared to acetanilide due to the presence of two carbonyl groups. The succinimide group has more resonance contributors where the non-shared electron pair is delocalized to the carbonyl groups, giving it a –R effect, which, associated to the –I effect, decreases its +R effect.

p-toluidine

Nitration of p-toluidine led to the results displayed in Table 2.

Table 2 - Experimental results for p-toluidine

Starting Materials	Products (%)	
		
	**97**	**3**
	1	**99**

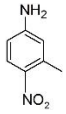
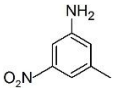
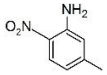
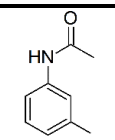
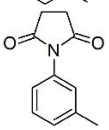
For p-toluidine, the –R and –I effects of both carbonyl groups present in the succinimide group

weaknesses its +R effect. Hence the reaction's control is mainly established by the methyl group, yielding almost exclusively 4-methyl-3-nitroaniline. As for the acetanilide derivative, the nitrogen atom's non shared electron pair has a greater control over regioselectivity than the methyl group's +I effect, thus explaining the 97% yield of 4-methyl-2-nitroaniline. This is an expected result, since a non-shared electron pair that can be delocalized by resonance through the aromatic ring, has a stronger effect in stabilizing the reaction's intermediary than the electron-inducing property of the alkyl group.

m-toluidine

As for m-toluidine nitration, product distribution is as shown in Table 3.

Table 3 - Experimental results for m-toluidine

Starting Materials	Products (%)			
				
	**-**	**91**	**-**	**9**
	**2**	**36**	**-**	**62**

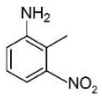
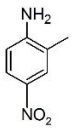
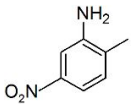
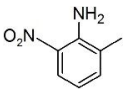
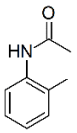
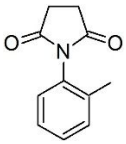
For the acetanilide derivative, nitration took place almost exclusively in the 4-position given it is activated by both the acetanilide group's +R and the methyl group's +I effects. Consequently, the second major product is 3-methyl-6-nitroaniline, once again activated by both functional groups. However, 3-methyl-4-nitroaniline percentage is much larger, due to the 4-position being a less steric hindered position than the 2 and 6-positions. Although results for the N-succinimidil derivative show mainly *ortho* and *para* substituted products, favored by both the succinimide and methyl groups, it is quite clear that reaction control was established by the alkyl group.

Contrary to the N-acetyl derivative experiments, 3-methyl-6-nitroaniline was the main product obtained, leading to the conclusion that the effect of the two carbonyl groups severely decreased the +R effect of the succinimide group, resulting in the methyl group's +I effect being stronger than the steric hindrance established by the volume of the succinimide group.

o-toluidine

Finally for o-toluidine, nitration with the HNO_3/H_2SO_4 mixture led to the results shown in Table 4.

Table 4 - Experimental results for o-toluidine

Starting Materials	Products (%)			
				
	**6**	**45**	**33**	**16**
	**30**	**9**	**56**	**5**

Results for 2-methylacetanilide show once again the prevalence of the acetamide group's +R effect, as shown by *ortho* and *para* substituted products adding up to *circa* 60% of the total product distribution. However, the second main product is 2-methyl-5-nitroaniline which is not favored by the acetamide group's +R effect, but by the alkyl group's +I effect. These results led to the conclusion that the difference between these effects is not as clear for o-toluidine as it was for both m-toluidine and p-toluidine. As for experiments with the succinimide derivative, reaction control was established exclusively by the CH_3 group. *Ortho* and *para* substituted isomers relative to the methyl group add up to around 90% of the nitration

products. These results are explained by the presence of the alkyl group in an adjacent position to the succinimide group, making it impossible for the aromatic ring and the functional group to assume planarity. This disables the possibility of the nitrogen atom's non-shared electron pair to be distributed through the aromatic ring, which cannot therefore stabilize the reaction's intermediate complex, canceling the succinimide group's +R effect. As the main product resulting from the HNO_3/H_2SO_4 nitration reaction was 2-methyl-5-nitroaniline, a chemical species used as a dye precursor [14] which is hard to separate from the other isomers, an experiment was made to purify a small sample of this isomer by recrystallization in EtOH. The recrystallization yield was 70% and HPLC analysis showed an increase in 2-methy-5-nitroaniline content from 65% to 94%.

3. Conclusions

Analyzing the experimental results as a whole, it is possible to see that acetamide groups' +R effect is the key contributor to product distribution for all starting materials. The main products obtained for N-acetyl derivatives were all *ortho/para* substituted relative to the acetamide group. The only case where the +I effect of the alkyl group was observed was in the 2-methylacetanilide experiments, where it was responsible for the second most common product yielded. This was an expected conclusion, as the kinetically controlled EAS reaction is more affected by a non-shared electron pair than by the presence of an electron-inducing group. For the N-succinimidil experiments however, the +I effect of the methyl group has a greater relevance to regioselectivity in all starting materials studied, due to the presence of two carbonyl groups, whose electron-attracting properties, either by induction (-I) or by resonance (-R) decrease its +R effect.

For the functional groups chosen to protect the amine, both yielded mainly *ortho* and *para* substituted products, except for the N-(2-methylphenyl)-succinimide (see Table 2). Again, this was an expected result due to the *ortho*/*para* directing property of both acetanilide and succinimide groups. Their ability to donate electrons to the aromatic ring by resonance grants them activating properties, increasing the reaction's rate. However, succinimide has two electronegative carbonyl groups that pull electrons away from the aromatic ring by induction and by resonance, whereas the acetanilide only has one. This makes acetanilide a more activated starting material for nitration. In theory, leaving the aniline unprotected would make it even more prone to nitration, since the NH_2 group has no electronegative atoms to attract electrons. However, amines are very reactive and would not sustain the harsh acidic conditions implemented.

The presence of the NO_2 group after nitration strongly deactivates the aromatic ring for further reactions, due to the positively charged nitrogen atom connected to the aromatic ring. This explains why no multi nitrated byproducts were detected during experimental procedure.

Comparing the experimental results to those shown in the literature for the aforementioned alternative nitration processes, it's possible to observe some differences, especially for o-toluidine. Acetanilide and succinimide derivatives yielded mainly 2-methyl-4-nitroaniline and 2-methyl-5-nitroanilines (see Table 2). Neither of these were observed in the research of ozone mediated and transition-metal complexes nitration, where the main product was 2-methyl-6-nitroaniline. The experimental results for aniline were very close to those found in the literature for other HNO_3/H_2SO_4 experiments, as well as for studies involving nitration salts and ozone mediated nitration, as shown by the

experimental *o:p* ratio of 0,25. For the use of transition-metal complexes, this ratio is inverted, yielding 80% 2-nitroaniline. For m-toluidine experiments via acetanilide, the results obtained are in line with those observed in other experiments with the acid mixture used in the laboratory, as well as for the use of nitration salts, where 90% 3-methy-4-nitroaniline was yielded. As for the succinimide experiments, the results are similar to those found for transition-metal complexes, since experiments showed 60% yield of 3-methyl-6-nitroaniline, close to the 55% claimed in the literature. As for p-toluidine, both derivatives studied showed very similar results to the nitration with salts and transition-metal complexes.

These results led to the conclusion that nitration via the classical mixture of HNO_3 and H_2SO_4 can still have an important role in nitro aromatic industries, leading to higher yields and purity levels for some of the products studied, as long as new methods of reducing or treating the acid effluents can be developed.

4. Experimental

Experimental techniques are based on those found in [15]. For each experiment, the quantities of the several reagents were calculated from the ones shown and the reactions' stoichiometry coefficients.

Reactions' progress was kept track by TLC.

Preparation of the acetanilide derivatives: Dissolve 0,11 mol of starting material (10,7 g aniline or 12,3 g toluidine) in 20 mL AcOH in a three-necked round bottom flask equipped with a magnetic stirrer, a thermometer, a dropping funnel and a reflux condenser. Add slowly through the dropping funnel an equimolar quantity of acetic anhydride without the temperature reaching 80 ^oC. Keep the mixture under stirring until it reaches room temperature and pour it over an ice bath. Keep stirring until full precipitation of the acetanilide derivative. Filter the solution under vacuum in a Büchner funnel and wash the solids with water. Leave the solids in a desiccator over night.

Preparation of the succinimide derivatives: Add 0,16 mol of starting material to 16 g of succinic anhydride in a tall glass beaker with a magnetic stirrer and a thermometer. Heat the mixture for 3 h until it reaches 200 ^oC and keep it at that temperature for one more hour. During the reaction water vapor is released, and the temperature should be decreased if crystals start to form on the top of the beaker by sublimation. Cool the mixture to about 70 ^oC and add enough EtOH/H_2O (1:1) to dissolve the solids. Cool to 0-10 ^oC by plunging the beaker in an ice bath and filter under vacuum in a Büchner funnel.

Nitration of the acetanilide and succinimide derivatives: Add 0,185 mol of the previously prepared compound to 25 mL of AcOH in a three-necked round bottom flask equipped with a magnetic stirrer, a thermometer, a dropping funnel and a reflux condenser. Add slowly through the dropping funnel 50 mL of concentrated H_2SO_4 and cool the mixture until it reaches a temperature of 0-5 ^oC by submerging the flask in a salt water and ice bath. Slowly add a mixture of 7 mL H_2SO_4 and 11 mL HNO_3 through the dropping funnel while keeping the mixture under 10 ^oC. Leave the mixture under stirring for 1 h at room temperature, or at 30 ^oC in the case of the succinimide derivatives, to complete nitration. Pour the solution in an ice bath and stir until full precipitation, filter under vacuum and wash the solids with water.

Hydrolysis of the nitrated products: Heat the nitro aromatic compounds with 30 mL of H_2SO_4 and 30 mL of H_2O under reflux for 45 min. Pour the solution over an ice bath and neutralize the nitroanilines with a 10% (%m/v) NaOH solution. Extract twice with 100 mL of ethyl acetate and dry the organic phase

with anhydrous sodium sulfate. Evaporate the ethyl acetate under vacuum in a rotary evaporator.

3,5-dinitrotoluene hydrogenation to 3-methyl-5-nitroaniline: Dissolve 0,6 g of sodium sulfide monohydrate ($Na2S{\cdot}H_2O$) in 5,15 mL of H_2O. Add slowly and with constant stirring 0,62 g of $NaHCO_3$. After total dissolution add 5,15 mL of MeOH, cool the mixture under 20 ºC, filter under vacuum and wash the solids with three 8 mL portions of MeOH. Mix 0,75 g of 3,5-dinitrotoluene with 5,15 mL of warm MeOH and add, with stirring, the NaSH solution previously prepared. Heat under reflux for 20 min and evaporate the majority of the MeOH. Pour the solution over an ice bath and filter the solids under vacuum. Wash the solids with water and recrystallize with a 25% MeOH aqueous solution.

Result analysis: Results were analised by HPLC in a Varian Pro Star Autosampler Model 410 apparatus equipped with Varian Microsorb-MV 100-5 C18 250x4,6 mm column and by ^1H, ^{13}C, HSQC and HMBC RMN in a Bruker UltraShield 400 MHz. The HPLC samples were prepared in MeOH (1 mg/mL) with an injection volume of 10 µL. The chosen mobile phase was a mixture of MeCN/H_2O at a 0,8 mL/min rate with an isocratic composition of 35/65. The isomeric distribution of the several mixtures was determined through calibration lines obtained for each starting material by preparing different mixtures of known concentrations of the different nitroaniline isomers available at the Laboratory. There were no 3-methyl-nitroaniline available, therefore it was necessary to run a chromatography column with one of the mixtures prepared to isolate the four possible nitrated isomers. A silica-gel column was used with a 50/50 petroleum ether/toluene mixture as eluent. The 3-methyl-5-nitroaniline was not detected, and it had to be obtained by hydrogenation of a small amount of 3,5-dinitrotoluene.

3-methyl-2-nitroaniline data: **^1H RMN ($CDCl_3$, 400 MHz) δ** 7,15 ppm (*m*, 5-C**H**, J = 7,8 Hz); 6,66 (*d*, 4-C**H**, J = 7,8 Hz) 6,58 (*d*, 6-C**H**, J = 7,4 Hz); 5,10 (*s*, N**H**$_2$); 2,46 (s, C**H**$_3$). **^{13}C RMN ($CDCl_3$, 400 MHz) δ** 143,0 ppm (C-1); 136,3 (C-2); 135,2 (C-3); 132,9 (C-4); 120,9 (C-5); 116,2 (C-6); 21,1 (**C**H_3).

3-methyl-4-nitroaniline data: **^1H RMN ($CDCl_3$, 400 MHz) δ** 8,02 ppm (*d*, 5-C**H**, J = 8,7 Hz); 6,71 (*s*, 2C**H**); 6,50 (*d*, 6-C**H**, J = 8,7 Hz); 4,25 (*s*, N**H**$_2$); 2,63 (s, C**H**$_3$). **^{13}C RMN ($CDCl_3$, 400 MHz) δ** 151,4 ppm (C-1); 139,8 (C-4); 137,9 (C-3); 128,3 (C-5); 116,9 (C-2); 111,9 (C-6); 22,2 (**C**H_3).

3-methyl-5-nitroaniline data: **^1H RMN ($CDCl_3$, 400 MHz) δ** 7,40 ppm (*s*, 4-C**H**); 7,30 (*s*, 2-C**H**) 6,71 (*s*, 2C**H**); 6,77 (*s*, 6-C**H**); 3,90 (*s*, N**H**$_2$); 2,34 (s, C**H**$_3$). **^{13}C RMN ($CDCl_3$, 400 MHz) δ** 149,4 ppm (C-1); 147,3 (C-5); 140,6 (C-3); 121,4 (C-4); 114,1 (C-2); 106,7 (C-6); 21,5 (**C**H_3).

3-methyl-6-nitroaniline data: **^1H RMN ($CDCl_3$, 400 MHz) δ** 7,97 ppm (*d*, 5-C**H**, J = 8,8 Hz); 6,49 (*d*, 4-C**H**, J = 8,8 Hz); 6,46 (*s*, 2-CH); 5,98 (*s*, N**H**$_2$); 2,28 (s, C**H**$_3$). **^{13}C RMN ($CDCl_3$, 400 MHz) δ** 147,3 ppm (C-3); 144,9 (C-1); 130,4 (C-6); 126,1 (C-5); 118,7 (C-2); 118,4 (C-4); 21,6 (**C**H_3).

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