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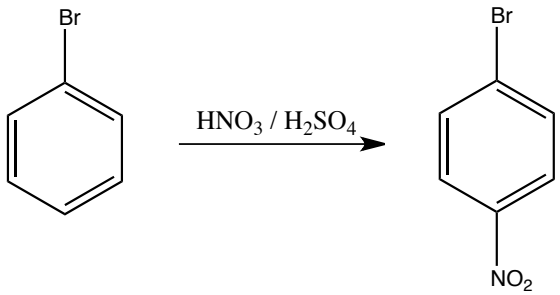
Nitration of bromobenzene (n°28)

1. INTRODUCTION

1.1) Purpose

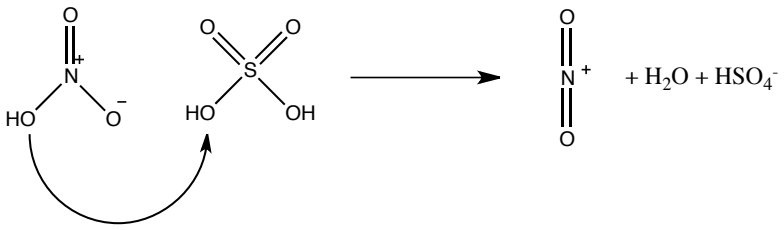
The objective of this experiment is to synthesize the p-bromonitrobenzene (bromo-1-nitro-4-benzene) out of bromobenzene, by nitration.

1.2) Scheme

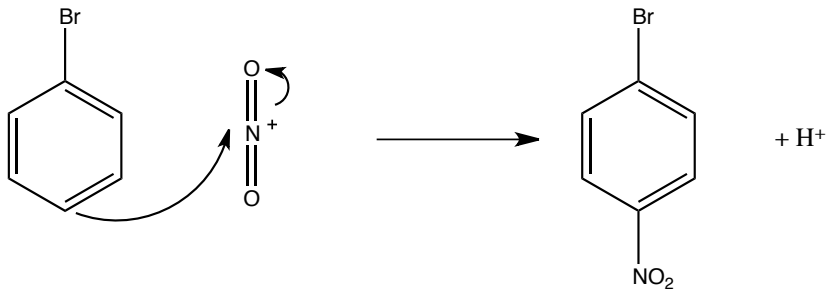


1.3) Mechanism

The first step is the formation of the NO_2 from the nitric acid:



The second step is the nucleophile attack of the bromobenzene on the NO_2. The temperature is moderated to avoid the formation of ortho and meta products:



2. PROCEDURE

2.1) Reaction

In a 100mL twin-neck bottom flask a mixture of nitric acid and sulfuric acid was prepared (cooled down with an ice bath). The flask was then equipped with a thermometer (not to let the temperature go over 50-60°C) and a refrigerator. Bromobenzene was added in small proportions (1mL at a time) through the refrigerator and the solution was well agitated between each addition. Then, the solution was heated for 20min at 100°C. After heating, the mixture was left to cool down a little and then poured on 150g of ice. The crystals left on the flask were dissolved in 10mL of hot ethanol and added to the suspension.

2.2) Isolation

The solid product was isolated by filtration, washed 3 times in water and recrystallized in 50mL of ethanol.

3. DISCUSSION AND RESULTS

3.1) Observations

When the bromobenzene was added, the solution turned yellow. The final product was also yellow crystals.

3.2) Yield

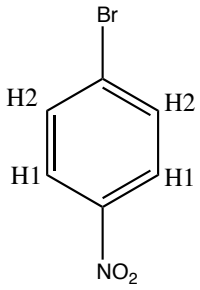
molar mass [g/mol]	n_{th} [mmol]	n_{exp} [mmol]	yield [%]
202.99	76	35.0	46%

7.1124g of final product were collected at the end of the reaction. That represents 46% of yield, which is in similar to the yield indicated by the protocol: 55% (8.5g).

4. SPECTROMETRY DATA

4.1) NMR ^{1}H ($CDCl_3$, 400MHz)

The molecule is symmetrical; therefore the hydrogens on each side of the molecule are equivalent.



Br has a stronger unshielding effect than the nitro group, therefore the peaks corresponding to H2 are more on the left.

bond	shift ∂ [ppm]	multiplicity	hydrogen
C-H	8.134-8.098	Doublet of triplets	H1
C-H	7.721-7.684	Doublet of triplets	H2

The coupling is strong, so there is a roof effect. Also, we observe doublets of triplets and not just doublets because of the ^{4}J coupling.

δ 8.116 (dt, J=9.2Hz, J=2.4 Hz, 2H); δ (dt, J=9.2Hz, J=2.4 Hz, 2H)

4.2) IR (neat, cm^{-1})

1508; 1470; 1342-1310; 1277; 1104; 1065; 837; 736; 674

The peaks corresponding to the aromatic nitro substituent are observed at 1508 cm^{-1} and 1342-1310 cm^{-1}. Therefore the product indeed was obtained.

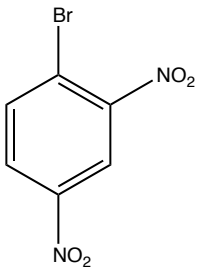
5. REFERENCES

[1] *Travaux Pratiques de Chimie Organique 3ème Semestre*, **21 Novembre 2011 – 16 Mars 2012,** 27
[2] Silverstein, Bassler, Morrill, *Spectrometric identification of organic compounds*

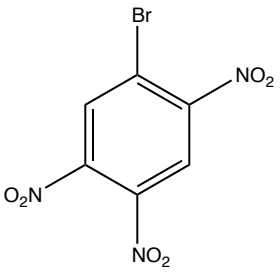
6. QUESTIONS

1) *What secondary product is expected if the reaction is made at a higher temperature?*

   At higher temperature, we expect to see more than one nitro group substituted on the bromobenzene.



1-bromo-2,4-dinitrobenzene



1-bromo-2,4,5-trinitrobenzene

2) *Why do we only isolate the p-bromonitrobenzene by recrystallization of the final product in ethanol?*

The p-bromonitrobenzene must be less soluble in EtOH (in cold solution). The solubility depends on the polarity and since the 1-bromo-2,4-dinitrobenzene is more polar, if it was formed, than it stayed solubilized in ethanol. Finally, there is very little chance that 1-bromo-2,4,5-trinitrobenzene was formed under the experiment conditions.

7. ANNEXES

IR spectrum, NMR spectrum