

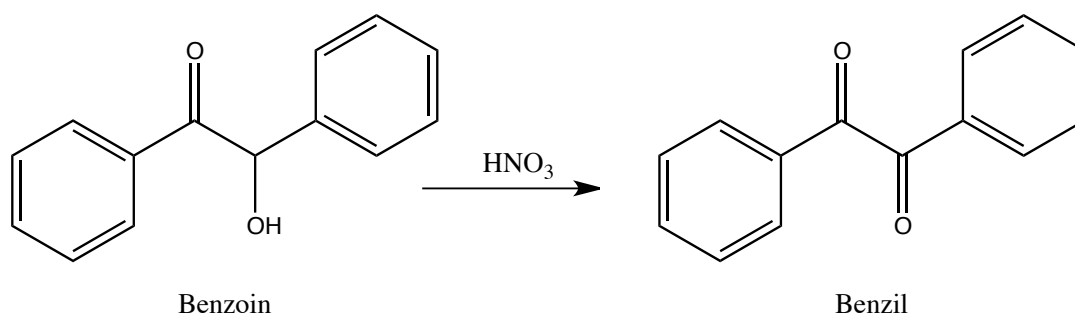
Oxidation of benzoin into benzil (n°39)

1. INTRODUCTION

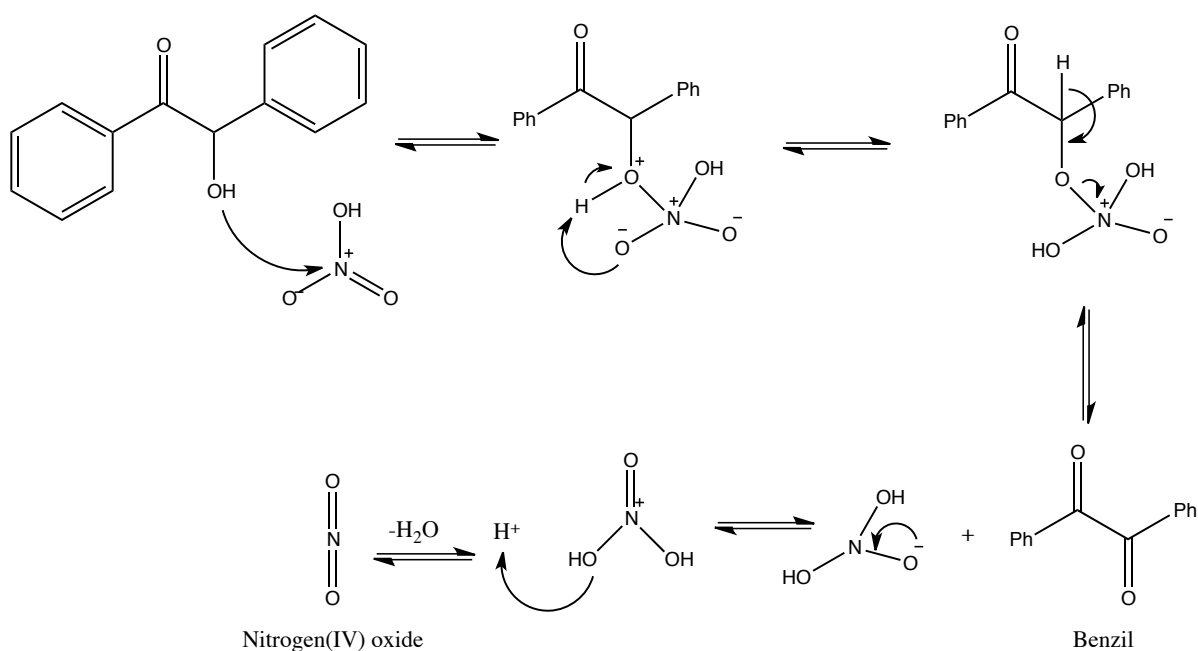
1.1) Purpose

The objective of this experiment is to oxidize benzoin into benzil in an acidic environment.

1.2) Scheme



1.3) Mechanism



2. PROCEDURE

2.1) Reaction

Reagents	molar mass [g/mol]	wt/vol taken	n [mmol]
benzoin	212.24	6.0g	28.3
acetic acid	60.05	30mL	excess
nitric acid	63.01	45mL	excess

In a 250mL triple-neck round bottom flask equipped with a refrigerator, 45mL of nitric acid, 30mL of acetic acid and 6g of benzoin were added. The solution was heated at 100°C and agitated until the red fumes were gone. The reaction was followed by the means of TLC (CH_2Cl_2 was the eluent). Then, the solution was transferred in a flask containing 150mL of cold water and agitated until the precipitate was formed.

2.2) Isolation

The solid product (yellow crystals) were filtered and washed with cold water and then recrystallized in ethanol.

3. DISCUSSION AND RESULTS

3.1) Observations

There was a strong release of NO_2 , identified by its red/dark orange fumes. Although the protocol said that the reaction should be finished after about an hour, almost two hours were necessary to its full completion (until the spot corresponding to the reagent disappeared from the TLC plate).

The obtained product has a bright yellow color.

3.2) Yield

molar mass [g/mol]	n_{th} [mmol]	n_{exp} [mmol]	yield [%]
210.23	28.3	17.5	62%

The obtained mass of the product was 3.6833g representing a yield of 62%, which is satisfactory, since the yield given by the protocol was 76% (4.5g). A possible loss might have occurred when washing the crystals with water before recrystallization.

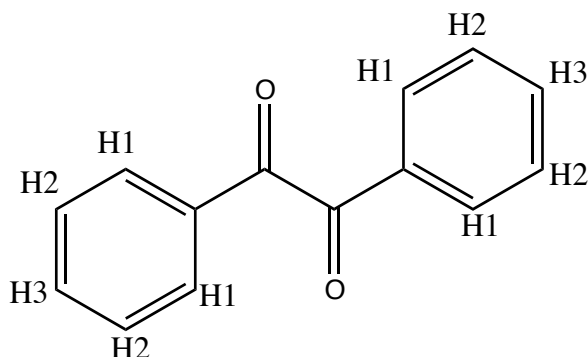
3.3) Additional analysis

- TLC plate, eluent: CH_2Cl_2 : $R_f=0.77$ (3.9/5.1 and 4/5.2)

- Melting point: mp=94.2-95.5 °C

4. SPECTROMETRY DATA

4.1) NMR ^1H (CDCl_3 , 400MHz)



The molecule is symmetrical; therefore the shifts are identical for the two “sides”.

bond	shift δ [ppm]	multiplicity	hydrogen
C-H	7.999-7.980	doublet	H1
C-H	7.696-7.658	triplet	H3
C-H	7.549-7.511	triplet	H2

The substituted groups ketone influence the most hydrogens in position ortho, then para and less of all, meta hydrogens. The coupling constant is exactly the same for all the hydrogens.

δ 7.99 (d, $J=7.6$ Hz, 4H); δ 7.68 (t, $J=7.6$, 2H); δ 7.53 (t, $J=7.6$, 4H)

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

1657; 1592-1578; 1209; 1173; 874; 716; 694-680; 639

Indeed there is a peak corresponding to the stretch of the ketone group $\text{C}=\text{O}$, but no peaks for the O-H that were in the benzoin. So the product is indeed benzyl.

5. REFERENCES

[1] *Travaux Pratiques de Chimie Organique 3^{ème} Semestre*, **21 Novembre 2011 – 16 Mars 2012**, 39

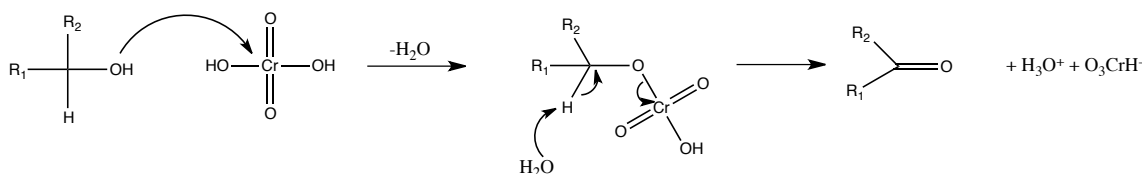
[2] Silverstein, Bassler, Morrill, *Spectrometric identification of organic compounds*

6. QUESTIONS

- 1) *What characteristic frequencies should you search in an IR spectrum of benzoin and benzyl?*

In the benzoin spectrum, you expect to see a peak at $3400\text{--}3300\text{ cm}^{-1}$ corresponding to the O-H stretch and in the benzyl spectrum, you should see a peak at 1715 cm^{-1} corresponding to the C=O stretch.

- 2) *What is the mechanism of the oxidation of a secondary alcohol by chromium trioxide?*



7. ANNEXES

IR spectrum, NMR spectrum