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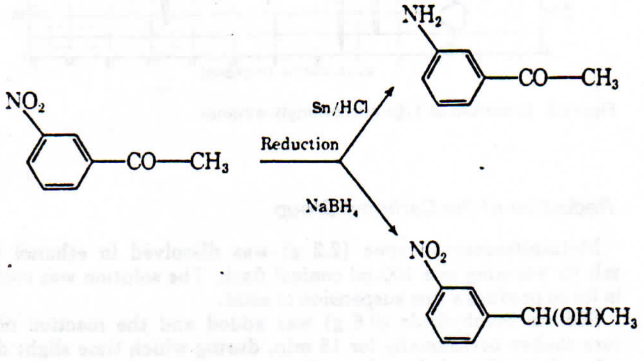
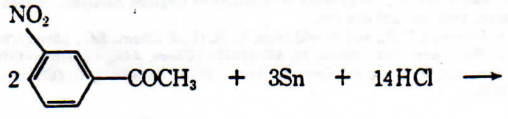
The Selective Reduction of Meta-(and Para-) Nitroacetophenone

By appropriate choice of reagent and reaction conditions a nitroketone can be selectively reduced to an aminoketone or a nitroalcohol, e.g.

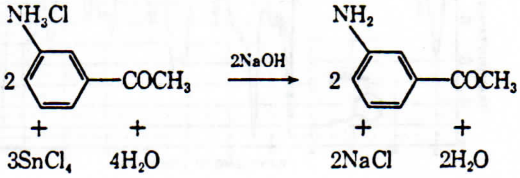


Aromatic nitro groups can be reduced to primary arylamines using various chemical reducing agents. The reducing agent and the solvent medium can be varied to suit the properties of the particular nitro compound and the arylamine. With nitroacetophenones it was found convenient to use tin and hydrochloric acid. This reagent does not also reduce the carbonyl group of *m*-(or *p*-)nitroacetophenone as would be the case if, for example, catalytic reduction was employed. In the reaction mixture the amine is converted to a chlorostannite or chlorostannate salt, (R-NH$_3$)$_2$ SnCl$_4$ or (R-NH$_3$)$_2$ SnCl$_6$.

Subsequent treatment with sodium hydroxide solution liberates the amine and forms water-soluble tin compounds, sodium stannite or stannate (Na$_2$SnO$_2$ or Na$_2$SnO$_3$)

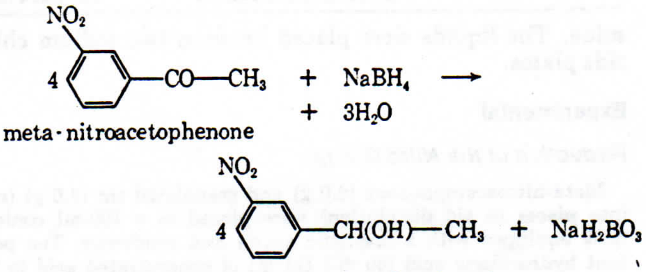


meta-nitroacetophenone



meta-aminoacetophenone

In ethanol, at room temperature, sodium borohydride will reduce aldehydes and ketones to the corresponding primary and secondary alcohols. It is quite selective and does not reduce other potentially reducible groups such as nitro compounds. It is a milder reducing agent and is more selective than lithium aluminium hydride and has been chosen for this reason. It has nevertheless high reducing capacity—one mole is able to reduce four moles of ketone



meta-nitroacetophenone

1-(m-nitrophenyl)-ethanol
or
meta-nitrophenyl methyl carbinol

The table represents the melting point or boiling point of the starting materials and products involved in this exercise. The infrared spectra (Figs. 1–6) are included since they demonstrably emphasize the formation or disappearance of the functional groups involved. The solid samples were incorporated into a pressed disk of potassium bro-

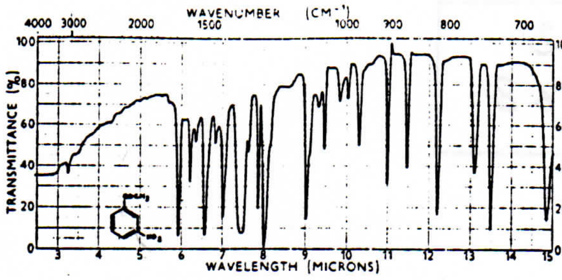


Figure 1. Spectrum of *m*-nitroacetophenone.

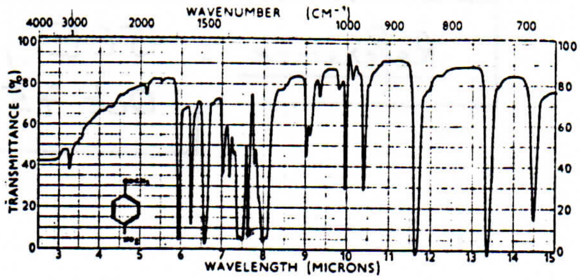


Figure 2. Spectrum of *m*-aminoacetophenone.

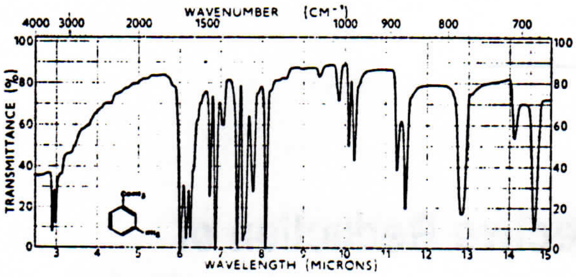


Figure 3. Spectrum of 1-(*m*-nitrophenyl)-ethanol.

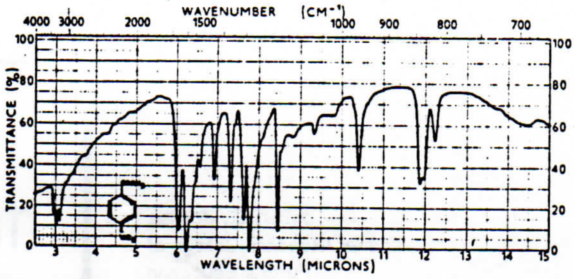


Figure 4. Spectrum of *p*-nitroacetophenone.

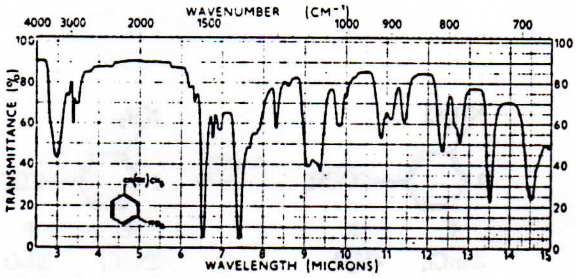


Figure 5. Spectrum of *p*-aminoacetophenone.

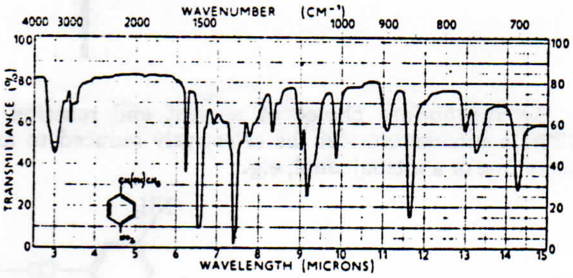


Figure 6. Spectrum of 1-(*p*-nitrophenyl)-ethanol.

Melting or Boiling Points of Starting Materials and Products

Starting Material	Product	m.p. (°C)	b.p.(°C)
m-nitroacetophenone		81	
	m-aminoacetophenone	96–97	
	1-(*m*-nitrophenyl)-ethanol	62	154–5 at 9 mm
p-nitroacetophenone		80	
	p-aminoacetophenone	106	
	1-(*p*-nitrophenyl)-ethanol		161–3 at 4 mm

mide. The liquids were placed between two sodium chloride plates.

Experimental

Reduction of the Nitro Group

Meta-nitroacetophenone (2.0 g) and granulated tin (4.0 g) (cut into pieces to aid dissolution) were placed in a 100-ml conical flask equipped with a magnetic stirrer and condenser. Ten percent hydrochloric acid (40 ml) (11 ml of concentrated acid to 29 ml of water) was added, and the mixture maintained in a boiling water bath on a magnetic stirrer hotplate for 1.5 hr. The cooled reaction mixture was filtered to remove any undissolved tin, and 40% sodium hydroxide (24 ml) was added to the filtrate, with stirring and cooling. The resultant yellow precipitate was filtered and washed with water. This was then dissolved in the minimum amount of hot water and the solution filtered hot to remove remaining tin salts. After recrystallization from water the dried *m*-aminoacetophenone had a melting point of 96–97°C.

Reduction of the Carbonyl Group

Meta-nitroacetophenone (2.2 g) was dissolved in ethanol (28 ml) by warming in a 100-ml conical flask. The solution was cooled in ice to produce a fine suspension of solid.

Sodium borohydride (0.6 g) was added and the reaction mixture shaken occasionally for 15 min, during which time slight discoloration occurred.

Water (20 ml) was added and the reaction mixture was heated to boiling to destroy any excess sodium borohydride. The cooled reaction mixture was extracted twice with ether (30 ml), and the combined extracts were dried over anhydrous sodium sulfate. Removal of the ether by distillation or rotary evaporation from a hot water bath gave a light-brown oil. The *m*-nitrophenyl methyl carbinol crystallized on cooling and scratching, and after recrystallization from toluene had a melting point of 62°C. Alternatively it can be distilled under reduced pressure, bp 154–5°C at 9 mm.

These reaction conditions apply equally to the reduction of *p*-nitroacetophenone to *p*-aminoacetophenone and *p*-nitrophenyl methyl carbinol.

General References

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