

NOTE

A Novel Method for Reduction of a Double Bond by using a Microwave Oven

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The reduction of tetralone benzylidene derivatives (**I-A** and **I-B**) was carried out to give the corresponding benzyl derivatives (**II-A** and **II-B**) in a microwave oven. Higher yields are obtained in much lesser time than that obtained in conventional method.

Key words: Reduction, double bond, microwave oven.

Kulkarni and co-workers¹ had investigated new approaches for building up of tetracyclines and naphthacenes. The general scheme of the synthesis of hexahydro-naphthacenes involved the condensation of an α -tetralone-3-carboxylic acid with an aromatic aldehyde to give benzylidene derivative. Benzylidene could not be cyclized by any method like using P_2O_5 or polyphosphoric acid. Therefore it was reduced or hydrogenated using catalytic hydrogenation, to the corresponding benzyl-tetralone carboxylic acid. It was then cyclized to give a hexahydro-naphthacene-5,11-dione. The reduction was carried out at high pressure (20–40 lb/sq. in) using hydrogen gas and Raney Ni. In some cases the reaction required 6 h.

We have investigated a new method for reduction of benzylidene derivatives of tetralone using a microwave oven. It was found that the reduction can be carried out in less time than catalytic hydrogenation.

Microwave heating has become the standard method for many organic reactions². The *in-situ* generation of heat is efficient for significant reduction. There is improvement in yield and also decrease in reaction time. For finer control of the microwave energy input into small scale reaction mixture a beaker containing water was placed next to the reaction vessel inside the oven. This helped in capturing a significant amount of microwave energy thereby reducing the energy supplied to the reaction mixture.

The present paper discusses the reduction of benzylidene derivatives (**II-A** and **II-B**) using Raney nickel as a catalyst and ammonium vanadate as a hydrogen donor in ethylene glycol as a solvent³. Benzylidene derivatives were prepared by condensation of tetralone with aromatic aldehydes using the method used by Kulkarni and co-workers⁴.

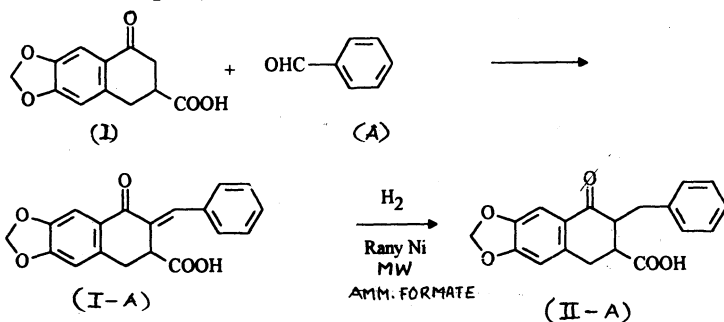
A tetralone, 3-carboxy-1-keto-1,2,3,4-tetrahydronaphthalene (**I**) was condensed with anisaldehyde (**A**) and pyridine-3-aldehyde (**B**) to give the corresponding tetralone-benzylidene derivatives (**I-A**) and (**I-B**) respectively. These benzylidene derivatives were further subjected to reduction to give the corresponding benzyl derivatives (**II-A** and **II-B**).

General Procedure

Reduction of 3-Carboxy-2-(4-Methoxy-Benzylidene)-1-Keto-6,7-Methylenedioxy-1,2,3,4-Tetra-hydronaphthalene (I-A) to give 3-Carboxy-2-(4-Methoxy-Benzyl)-1-Keto-6,7-Methylenedioxy-1,2,3,4-Tetrahydronaphthalene (II-A)

The reaction was carried out at 10% energy level of the microwave oven (Domestic BPL BMO700-T). The microwave oven was modified for use as a water condenser. A beaker containing 500 mL of water was kept inside the oven.

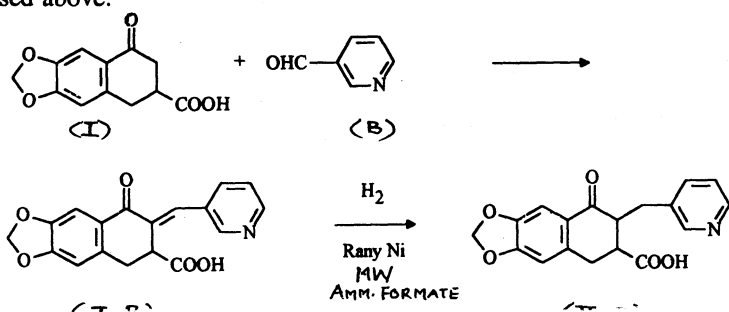
In a two-necked round bottom flask equipped with a water condenser was taken 2 g (0.0056 mole) of 3-carboxy-2-(4-methoxy-benzylidene)-1-keto-6,7-methylenedioxy-1,2,3,4-tetrahydronaphthalene (I-A) in about 25 mL of ethylene glycol. To it was added 1.79 g of ammonium vanadate, 0.6 g of Raney nickel and 1-2 KOH pellets. The reaction mixture was irradiated in a microwave oven for a predetermined period of time. The reaction was monitored by testing the reaction mixture at certain intervals with conc. H_2SO_4 (benzylidene gives dark coloration with conc. H_2SO_4).



The reaction was completed within 2 h. The reaction mixture was cooled and was filtered to remove the catalyst. The filtrate was diluted with water and then acidified with dil. HCl, when solid separated out. It was filtered, washed with water and then crystallized using ethanol : water mixture to give a white solid.

Reduction of 3-Carboxy-2-(Methylidene-3-Pyridyl)-1-Keto-6,7-Methylenedioxy-1,2,3,4-Tetra-hydronaphthalene (I-B) to give 3-Carboxy-2-(Methyl-3-Pyridyl)-1-Keto-6,7-Methylenedioxy-1,2,3,4-Tetrahydronaphthalene (II-B)

Reduction of 3-carboxy-2-(methylidene-3-pyridyl)-1-keto-6,7-methylenedioxy-1,2,3,4-tetrahydro naphthalene (I-B) was carried out in the same way as discussed above.



In the above reaction it was observed that the ratio of 0.3 : 1 (by weight) for Raney nickel and the substrate worked well. Also for each reducible group 5 equivalents of ammonium vanadate gave good results.

Conventional Method for Reduction of Benzylidene

In this method the reduction was carried out using 'Parr Apparatus' for hydrogenation⁵. Hydrogen gas was used as a hydrogen donor. A high pressure of 40 lb./sq. inch was required for completion of reaction. The detailed procedure is as follows:

Benzylidenes (II-A and II-B) 2 g each were taken in a reaction vessel along with 2 g of Raney nickel and 2 g of KOH in methanol as a solvent. The pressure of 40 lb/sq. inch was applied to the reaction mixture and hydrogen gas was allowed to pass into the reaction mixture. The reaction was carried out for 6 h. After the reaction got over (tested with TLC) the reaction mixture was filtered to separate the catalyst. The filtrate was then acidified with dil. HCl with external cooling when a white solid separated out. It was filtered, washed with water and crystallized from ethanol-water mixture.

The comparison of the products obtained from the above two methods is given below:

Compound No.	Microwave irradiation		Parr apparatus	
	Reaction time (h)	Yield (%)	Reaction time (h)	Yield (%)
II-A	2	58	6	28
II-B	2	55	6	27

The compounds (II-A and II-B) synthesized using microwave oven were found to be identical in all respects with the compounds synthesized by conventional method using Parr apparatus. m.p., Co-IR, Co-TLC were found to be the same.

It was found that the reactions carried out in a microwave oven were very rapid, clean with good yield and better quality. Also the risk of using hydrogen gas is eliminated in a microwave oven method.

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