



NOTE

Synthesis of Aryl Ketones *Via* Decarboxylation of Aromatic Acids Under Solvothermal Condition

K.M. LOKANATHA RAI^{1,*}, M. SURESH BABU¹ and K. BYRAPPA²

¹Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India

²Department of Studies in Geology, University of Mysore, Manasagangotri, Mysore-570 006, India

*Corresponding author: E-mail: dr.medurisuresh@yahoo.in

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Aryl ketones were prepared by the condensation of aromatic carboxylic acids with alkyl/aryl nitrile *via* the decarboxylation of carboxylic acids under solvothermal condition. All the compounds were characterized by comparing with standard samples prepared by the known literature method.

Key Words: Aryl ketones, Decarboxylation, Solvothermal.

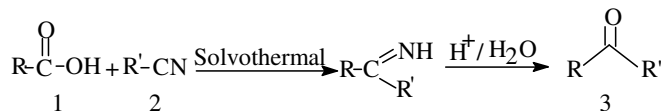
Acylation of aromatic carboxylic acids *via* decarboxylation plays an important role in organic synthesis¹. Usually, acylation of aromatic rings can be done using acyl halides in the presence of Friedel-Crafts catalysts like AlCl_3 and other catalyst like CuCl_2 and FeCl_3 . Decarboxylation of aromatic carboxylic acids is most often carried out by heating with copper and quinoline² and scanty of references are available for this type of reactions. Recent literature survey revealed that solvothermal conditions can be used for some of the organic reactions³. Recently, we have carried out few reactions under solvothermal condition. For instance, conversion of lactone to amide⁴ by heating the lactone with liquor ammonia in a sealed glass tube on water bath for 10-12 h. Intramolecular 1,3-dipolar cycloaddition of oxime with olefins *via* nitron intermediate was carried out successfully in a sealed tube at 100 °C using benzene as solvent⁵, while conversion of aldehyde semicarbazones to bishydrazones by thermolysis under reduced pressure was achieved in 90-95 % yield using ethanol as solvent⁶. The development of solvothermal reaction is of interest because they offer the possibility of environmentally benign reaction conditions by reducing the burden of organic solvent disposal. Solvothermal reactions⁷ can be defined as a reaction or transformation of reaction in a close system in presence of a solvent at a temperature higher than its boiling point. Consequently these reactions can be developed in supercritical or in sub critical conditions. Solvothermal process involve the heterogeneous chemical reaction, which occur at solid-liquid or solid-liquid-gas interfaces under high temperature and high pressure.

Melting points were recorded in open capillaries using Thoms Hoover apparatus and were uncorrected. The compounds were routinely checked for their purity by TLC using silica gel-G as adsorbent. IR spectra were recorded on Shimadzu FT 8300 spectrometer. ¹H NMR spectra were recorded on a Jeol 60 MHz FT NMR spectrometer using CDCl_3 as solvent.

Typical procedure for the preparation of acetophenone (3aa): In a typical experiment a mixture of benzoic acid (**1a**, 0.61 g, 5 mmol) and acetonitrile (**2a**, 0.32 g, 10 mmol) taken in a Teflon liner fixed into an autoclave was heated up to 100-150 °C for 8-10 h. The resulted solid mass was extracted with diethyl ether and washed with distilled water, 5 % sodium bicarbonate and distilled water. The organic layer was dried over anhydrous sodium sulphate and evaporated under vacuum to give imine in 90 % (0.53 g) yield. The imine was taken in 5 % HCl (10 mL) and heated upto 40 °C for few minutes and extracted with diethyl ether. The organic layer was washed with distilled water and evaporated on water bath to give acetophenone in 85 % (0.45 g) yield (Table-1).

This instigated us to carryout some interesting reaction. With this in mind, as a first step, we have made an attempt to carryout esterification of carboxylic acid with alcohols under solvothermal condition. As such it didn't materialize but in presence of acetonitrile as solvent, instead of getting esters we have got acetophenone in good yield. Probably the reaction goes *via* decarboxylation and the resultant phenyl radical will attack at the nitrile carbon with the formation of imine radical. This radical will pullout hydrogen from carboxylic acid to

form the imine. Isolated imine was then on hydrolysis gives corresponding ketone. Similarly we have prepared various imines by reaction of acids such as *p*-chlorobenzoic acid, *o*-toluic acid, *p*-nitrobenzoic acid and *o*-anisic acid with acetonitrile, benzonitrile and benzyl cyanide. These imines are then on hydrolysis by acid gives corresponding ketones (**Scheme-I**).



R = a) C₆H₅, b) *o*-CH₃-C₆H₄, c) *p*-OCH₃-C₆H₄, d) *p*-Cl-C₆H₄, e) *p*-NO₂-C₆H₄, f) *m*-OCH₃-C₆H₄, g) *m*-CH₃-C₆H₄; R' = a) CH₃, b) C₆H₅, c) C₆H₅-CH₂

Scheme-I: Synthesis of ketones **3**

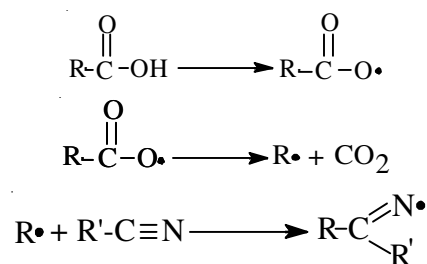
In a typical synthesis, equimolar quantities of benzoic acid and acetonitrile were taken in a stainless steel SS316 Morey type of autoclave (fabricated at the Department of Geology, University of Mysore, India) provided with a Teflon liner⁸ of 30 mL capacity and heated upto 100-150 °C for 8 to 10 h. The resultant solid mass on usual workup yields 85-90 % imine. The isolated imine on acidic hydrolysis gives acetophenone in 85 % yield. Products were identified by direct comparison (mixed m.p./mixed b.p., I.R. and ¹H NMR) with those of the samples prepared using literature procedures⁹. Typical examples of the reaction are compiled in Table-1 and the probable mechanism for the decarboxylation is as shown in **Scheme -II**.

TABLE-1
COMPILATION OF VARIOUS KETONES

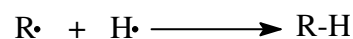
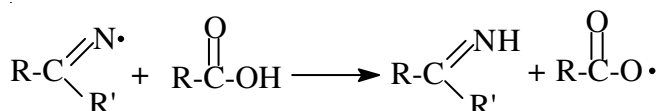
Ketone (3)	Time (h)	Yield (%)	m.p./b.p. (°C)		Appearance
			Obsv.	Lit.	
aa	8	85	201-203	202	Colourless oil
ba	9	88	213-214	216	Colourless oil
ca	9	89	37-39	39	White solid
da	8	90	234-236	236	Colourless oil
ea	9	84	79-81	80	White solid
fa	10	87	237-238	238	Colourless oil
gb	9	90	313-315	314	Colourless oil
ac	9	83	59-61	60	White solid
ab	8	86	46-48	49	White solid
bb	9	87	307-309	310	Colourless oil

Reaction mechanism:

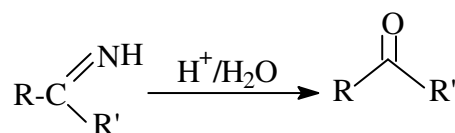
a) Chain initiation:



b) Chain propagation and termination:



Hydrolysis:



Scheme-II

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