

*Reprinted from*

# **JOURNAL OF THE INDIAN CHEMICAL SOCIETY**



Volume 89, No. 2, February 2012

---

*Published by*

**Indian Chemical Society**  
92, Acharya Prafulla Chandra Road  
Kolkata-700 009, India

## A route for synthesis of 1,3,5-trisubstituted naphthalenes by reaction of *ortho*-substituted benzyloisoquinolinium bromides with $\alpha,\beta$ -unsaturated ketones

K. C. Gupta<sup>a\*</sup>, Vandana Gupta<sup>a</sup>, A. K. Gupta<sup>a</sup>, V. K. Chaudhary<sup>a</sup>, S. K. Gupta<sup>a</sup>, S. Srivastava<sup>a</sup> and M. K. Gupta<sup>b</sup>

<sup>a</sup>Department of Chemistry, D. V. P. G. College, Orai-285 001, Uttar Pradesh, India

E-mail : guptakcdvc@rediffmail.com

<sup>b</sup>Department of Applied Chemistry, BIET, Jhansi, Uttar Pradesh, India

Manuscript received 10 August 2010, revised 02 March 2011, accepted 20 June 2011

**Abstract :** Three *ortho*-substituted cycloimmonium bromides : *ortho*-chlorobenzyloisoquinolinium bromide, *ortho*-bromobenzyloisoquinolinium bromide and *ortho*-nitrobenzyloisoquinolinium bromide have been prepared by the reaction of *ortho*-substituted benzyl bromide with isoquinoline in benzene in an atmosphere of nitrogen at reflux temperature in good yields. These isoquinolinium salts on reaction with base generated corresponding *ortho*-substituted benzyldeneisoquinolinium ylides *in situ*. The reaction of these salts or ylides with a wide range of substituted benzyldeneacetophenones in the presence of anhydrous  $\text{AlCl}_3$  or  $\text{ZnCl}_2$  in mixture of ammonium acetate and acetic acid gave 1,3,5-triarylnaphthalenes in good yields. Aluminium chloride or zinc chloride in acetic acid is used as cyclisation agent. The structures of naphthalenes were confirmed by elemental analysis, IR and NMR spectral data.

**Keywords :** Ylides, isoquinolinium ylides, isoquinolinium salts, dizonium salts, naphthalene.

### Introduction

Literature survey reveals that pyridinium,  $\alpha$ -picolinium phosphonium and arsonium ylides have gained considerable importance in the synthesis of acyclic, cyclic and heterocyclic compounds<sup>1-8</sup>. Thus our attention was directed towards utilization of isoquinolinium ylides for the synthesis of naphthalene derivatives. A convenient route in this regard was first reported by Krohnke's *et al.*<sup>4</sup> for the synthesis of diarylnaphthalene derivatives which involved the condensation of benzylpyridinium bromide with benzalacetophenone in presence of  $\text{ZnCl}_2$  in acetic acid. It was a convenient method<sup>4</sup> for synthesis of naphthalenes because it involved single step and gave better yield of products. Tewari and Gupta *et al.*<sup>8-10</sup> also extended the reaction of pyridinium ylides and reported the detailed experimental conditions for the preparation of 1,3-diarylnaphthalenes. We were prompted and encouraged by these reports to investigate an alternative route for the synthesis of naphthalene derivatives which involved the reaction of isoquinolinium salts and ylides with  $\alpha,\beta$ -unsaturated ketones. Herein, we reveal the results of our study leading to the synthesis of trisubstituted naphthalenes.

### Results and discussion

The reaction of *ortho*-substituted benzyl bromide with isoquinoline in benzene at reflux temperature under nitrogen atmosphere gave *ortho*-substituted benzyloisoquinolinium bromides (**1a-c**). The structures of these isoquinolinium salts (**1a-c**) were determined on the basis of IR and NMR data<sup>11,12</sup>. The NMR spectrum of salts **1a-c** showed a singlet at  $\delta$  6.35 typical of methylene protons and aromatic protons appeared in the range  $\delta$  6.85–8.35. The reactions of these salts **1a-c** were carried out with a wide range of  $\alpha,\beta$ -unsaturated carbonyl compounds in presence of anhydrous  $\text{AlCl}_3$  or  $\text{ZnCl}_2$  in presence of mixture of sodium acetate and acetic acid at 200 °C to give 1,3-diaryl-5-substituted naphthalenes (**5a-7m**) in 50–75% yields. It was, however, observed that the yields of the naphthalenes were dependent upon the nature of substituents attached to isoquinolinium salts (**1a-c**) as well as on  $\alpha,\beta$ -unsaturated ketones. The reactivity of salt **1c** was lower than salts **1a-b** because of electron withdrawing nature of  $\text{NO}_2$  group which stabilized carbanion formation. Hence, **1c** afforded lower yields of naphthalene derivatives than the salts **1a-b**.

The course of reaction seems to proceed via the intermediacy of betaine type derivatives **4** which is formed by