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Indium mediated Barbier reactions of 1,2-diones: a facile synthesis of α -hydroxy ketones

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Abstract

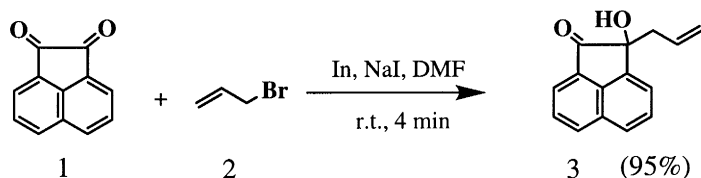
Indium mediated allylation and cinnamylation of 1,2-diones with the corresponding bromides in the presence of sodium iodide produce α -carbonyl homoallylic alcohols in excellent yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Barbier reactions; indium; diones.

Ever since the discovery of indium mediated Barbier reactions of aldehydes and ketones by Araki et al.,¹ there has been considerable interest in this area.² A variety of functional groups such as anhydrides,³ acid chlorides,⁴ imides,⁵ activated alkenes,⁶ alkynes,⁷ cyclopropenes⁸ etc. has been subjected to indium mediated C–C bond forming reactions. However, except for the reports involving azetidinones,⁹ there has been no work on indium mediated reactions of 1,2-diones.

In the context of our general interest in the chemistry of 1,2-diones,¹⁰ an exploration of the indium mediated allylation of such compounds was carried out and our preliminary results indicating the utility of this process in the synthesis of α -hydroxy carbonyl compounds are reported here. It is worthy of mention that α -hydroxy carbonyl compounds are useful intermediates in synthesis.¹¹

Our studies were initiated with the reaction of allyl bromide with acenaphthenequinone in the presence of indium and sodium iodide in DMF which furnished 95% of the corresponding α -hydroxy carbonyl compound **3** (Scheme 1).



Scheme 1.

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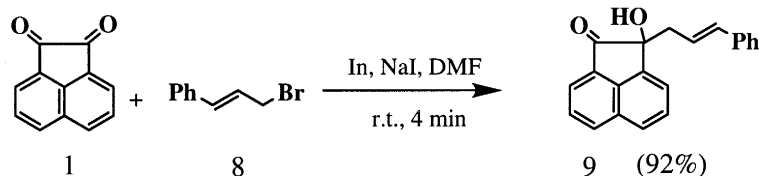
This procedure¹² offers a more convenient alternative to the Lewis acid mediated allylation using allyl tin compounds.¹³ In order to assess the generality of the process, the reaction was studied with a variety of 1,2-dicarbonyl compounds and the results are summarised in Table 1.

Table 1
Allylation of diones

Entry	Diones	Product	Yield ^a	Reaction conditions
1			97%	NaI, DMF, 5 min
2			95%	NaI, DMF, 10 min
3			95%	NaI, DMF, 2 min
4			96%	NaI, DMF, 4 min

^a isolated yield.

Subsequently, it was found that the acenaphthenequinone undergoes facile cinnamylation¹⁴ also under similar conditions, as illustrated by Scheme 2.



Scheme 2.

This reaction also appears to be general (Table 2). In certain cases, cinnamylation affords regioisomeric mixtures of products which are separable. It may be noted that cinnamylation leading to both α and γ isomers in certain cases is in keeping with the characteristic behaviour of other substituted allyl organometallics.¹⁵ However, in the case of indium mediated Barbier reactions, Araki¹⁶ has suggested that the steric environment of the carbonyl group may be responsible for the formation of the α -cinnamylated product.

In conclusion, we have observed that the indium mediated allylation and cinnamylation of 1,2-diones in the presence of NaI provides a rapid and operationally simple method for the synthesis of α -hydroxy carbonyl compounds which may prove to be the method of choice. Further work is in progress.

Table 2
Cinnamylation of diones

Diones	Product(s), Yield(s)	Reaction conditions
4	 25% 50%	NaI, DMF, 25 min
5	 88%	NaI, DMF, 10 min
6	 85%	U.S.,* DMF, NaI, 7 min
7	 55% 25%	U.S.,* DMF, NaI, 25 min

*Ultrasonication.

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- Typical experimental procedure: A mixture of the 1,2-dione (1 mmol), allyl bromide (1.55 mmol) indium powder (Aldrich chemicals) (1.05 mmol) and sodium iodide (1.55 mmol) in dimethylformamide (3 mL) was stirred at 25°C until completion of the reaction (TLC). The reaction mixture was quenched with a few drops of 1N HCl and extracted with diethylether. Evaporation of the solvent followed by purification of the product by silica gel column chromatography provided the pure product.

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14. Data of the product **9**. IR (KBr): 3474, 1695, 1595, 1339, 1195, 970, 746 cm^{-1} . ^1H NMR (CDCl_3) δ : 2.70(1H, m), 2.95(1H, m), 3.4(1H, b, -OH), 6.13(1H, m), 6.37(1H, d), 7.13–7.18(5H, m), 7.61–8.08(6H, m); ^{13}C NMR 42.03, 79.79, 120.98, 122.25, 122.69, 125.36, 126.29, 127.42, 128.32, 128.48, 128.74, 130.67, 132.03, 134.99, 137.05, 139.44, 141.32, 205.17; CHN calcd: C(83.98), H(5.37). Observed: C(83.86), H(5.44).
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