

# A New Class of Benzoin Condensation Catalyst, the Bi-(1,3-dialkylimidazolidin-2-ylidenes)

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An electron-rich olefin  $[\overline{=CN(R)CH_2CH_2NR}]_2$  ( $R = \text{Me, Et, or } CH_2Ph$ ) is an effective catalyst (at  $< 1$  molar % concentration) for the benzoin condensation in aprotic non-polar media; the appropriate 2-arylimidazolidine is obtained at high dilution under stoichiometric conditions (olefin +  $2ArCHO$ ).

The formation of  $\alpha$ -hydroxyketones, an important class of compound with an extensive organic chemistry, *via* the benzoin or a related condensation, has received much attention.<sup>1</sup> The original catalyst was KCN in aqueous alcohol, although more recently other sources of  $CN^-$  (*e.g.*,<sup>2</sup>  $[NR_4][CN]$ ), or a thiazolium salt [including thiamine (vitamin B<sub>1</sub>) pyrophosphate],<sup>3</sup> in water or benzene (if a phase-transfer catalyst, such as *N*-laurylthiazolium bromide was used<sup>2</sup>) or a dipolar aprotic solvent, *e.g.*,  $Me_2SO-HCONMe_2$ ,<sup>4</sup> have proved effective for this key carbon-carbon bond-forming reaction.

We now find that electron-rich olefins, such as (**1a-c**), bearing primary alkyl substituents at the nitrogen atoms, are examples of a new class of highly active benzoin condensation catalyst, as illustrated in Table 1 for the conversion of  $2ArCHO$  into  $ArCH(OH)COAr$  (**2**). A noteworthy feature is the use of an aprotic non-polar reaction medium, and this combination of catalyst and solvent may prove to be useful for a wider range of C-C couplings.

In a typical experiment, a freshly prepared solution of bi-(1,3-dimethylimidazolidin-2-ylidene) (**1a**) (0.380 g, 1 mol %) and benzaldehyde (20.9 g) was placed in a pre-heated oil-bath at 60 °C under an inert atmosphere. The initial red colour of the solution was almost immediately discharged and within 1 min the reaction mixture had solidified. The product, benzoin (**2a**), was washed with ether and recrystallised from ethanol (17.6 g, 84%).

The catalytic activities of the electron-rich olefins (**1a-c**) compare very favourably with those claimed previously for other catalysts,<sup>1-4</sup> even though no attempts have yet been made to achieve optimisation.

A limitation, however, for reactions involving aldehydes containing an  $\alpha$ -hydrogen atom may be the basic character of the olefins (**1**). For example, we observe that acetaldehyde

affords aldol at ambient temperature in the presence of a trace of the olefin (**1c**), whereas by using the thiazolium salt

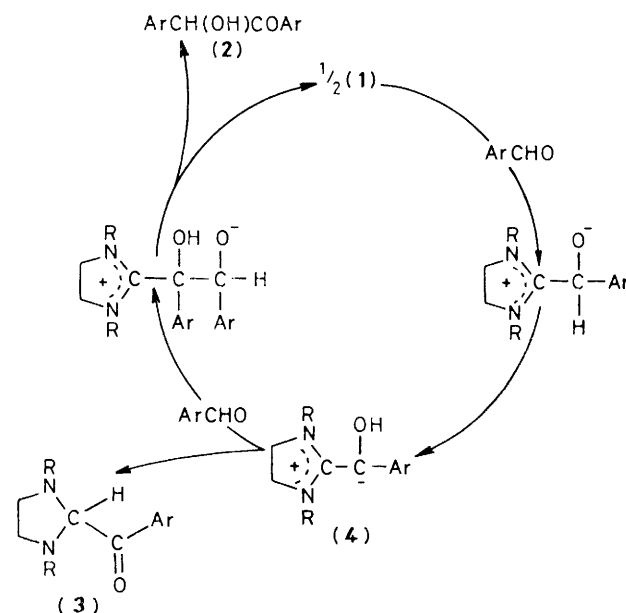
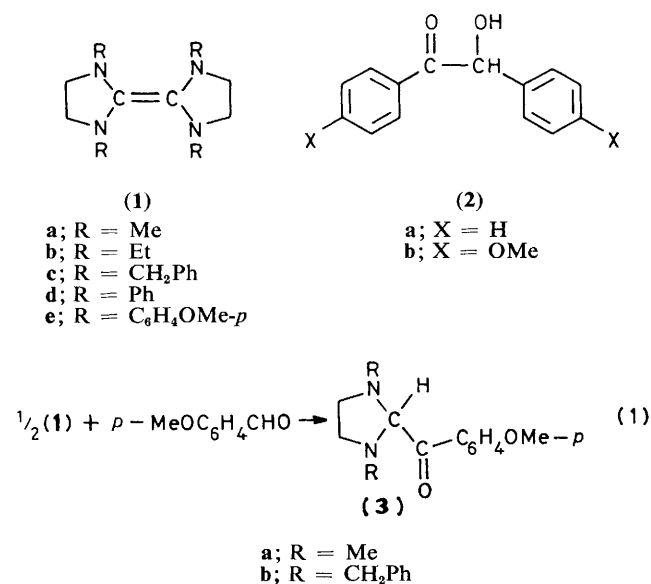
$PhCH_2N^+=CHSC(CH_2CH_2OH)=CMeCl^-$  a good yield of the acyloin was obtained at 80 °C under pressure (in the presence of triethylamine).<sup>3</sup>

The reaction conditions, reactant stoichiometry, and the nature of the substituents in either the aromatic aldehyde or the electron-rich olefin, have an important role in determining the nature and distribution of the product(s). Dilute solutions and appropriate reaction stoichiometries afford 2-arylimidazolidines (**3**) in good yield, equation (1). Indeed reaction (1) has a precedent: Wanzlick and Kleiner made the remarkable discovery that a tetra-aryl-olefin, such as (**1d**), is converted

**Table 1.** The benzoin condensation catalysed by some electron-rich olefins (**1a-1c**)

Catalyst (mol %)	Conditions <i>T</i> /°C; <i>t</i> /min	Yield of benzoin (%)
( <b>1a</b> ) (1.0)	60; 1	( <b>2a</b> ) 84 <sup>a</sup>
( <b>1a</b> ) (0.9)	80 <sup>b</sup> ; 30	( <b>2a</b> ) 76 <sup>a</sup>
( <b>1b</b> ) (0.5)	80 <sup>b</sup> ; 30	( <b>2a</b> ) 75 <sup>a</sup>
( <b>1c</b> ) (3.3)	130-140; 30	( <b>2a</b> ) 68 <sup>a</sup>
( <b>1a</b> ) (2.7)	60-90; 30	( <b>2b</b> ) 71 <sup>c</sup>
( <b>1a</b> ) (1.0)	100; 30	( <b>2b</b> ) 58 <sup>c</sup>
( <b>1c</b> ) (1.0)	100; 30	( <b>2b</b> ) 58 <sup>c</sup>

<sup>a</sup> Isolated yield. <sup>b</sup> In benzene. <sup>c</sup> Calculated from quantitative <sup>1</sup>H n.m.r. studies.



**Scheme 1.** A catalytic cycle for the electron-rich olefin-catalysed benzoin condensation.

into the 1,3-diaryl-2-arylimidazolidine by treatment with an appropriate aldehyde such as PhCHO or furfural.<sup>5</sup> Moreover they noted that using (**1e**) a trace of benzoin or furoin was a byproduct.

The catalytic activity of the olefin (**1**) is crucially dependent on the nature of the substituent R (Me ~ Et > CH<sub>2</sub>Ph >>> C<sub>6</sub>H<sub>4</sub>OMe-*p* > Ph). This is consistent with the catalytic cycle shown in Scheme 1, in which the 2-arylimidazolidine (**3**) results from ketonisation of the enol (**4**). Stabilisation of (**4**) by electron-donating substituents at nitrogen suppresses the conversion of (**4**) into (**3**). Compound (**4**) belongs to a family of masked acyl carbanions ArC<sup>-</sup>(X)OH, including X = CN or a thiazolium moiety; the reaction of this species with ArCHO is rate-limiting for the formation of the C-C coupled product (**2**).

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