

ARYL(INDOL-3-YL)BENZOINS

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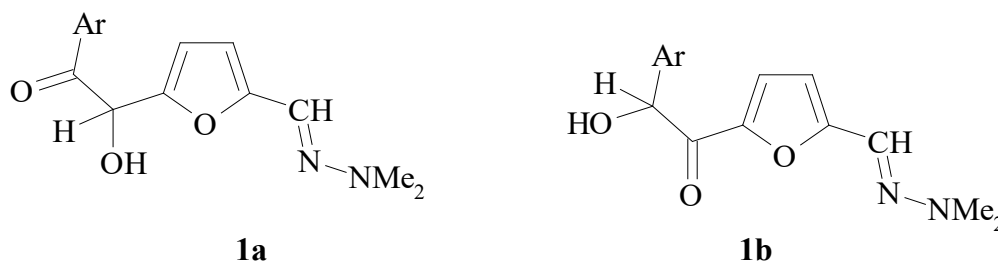
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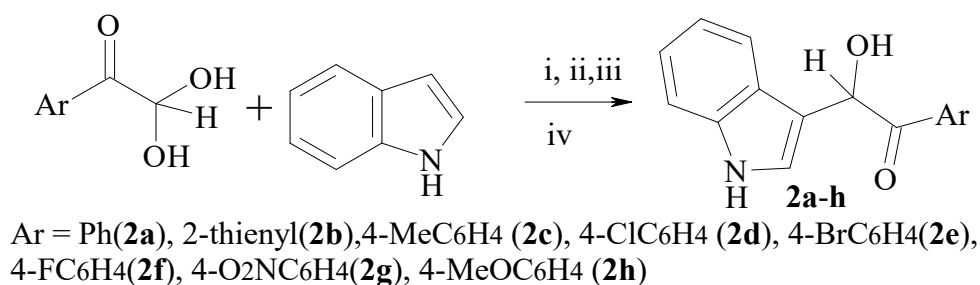
Unsymmetrical benzoin and aryl(hetaryl)benzoin exist in two isomeric forms, α -benzoin and β -benzoin for example aryl(furyl)benzoin **1a** and **1b** (Scheme 1, Ar = 4-ClC₆H₄), possess different stability.



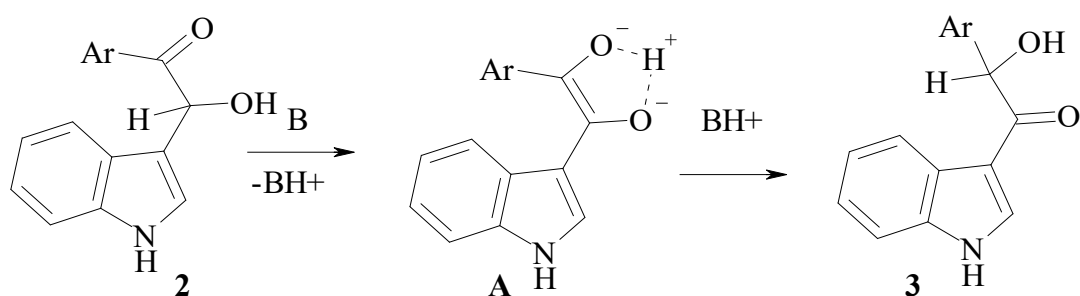
The development of efficient and general methodology for the synthesis of α -functionalized α -(indol-3-yl) ketones is highly desirable now. These compounds become relevant precursors for the preparation of biologically active molecules.

We had synthesized known α -benzoin **2a** and **2b** with moderate yields by reaction of indole with proper arylglyoxals in PhH at r.t. (ii) or in AcOH at rt (iv). α -Aryl(indolyl)benzoin **2c** has been synthesized in boiling PhH according to Zhungietu (i). α -Aryl(indolyl)benzoin **2d,e** had been synthesized as by known method (i), as in AcOH at r.t. during 1 h (iv). α -(4-Fluorophenyl)(indolyl)benzoin **2f** was obtained by 4-fluorophenylglyoxal interaction with indole in PhH at r.t. (ii). α -(4-Nitrophenyl)(indolyl)benzoin **2g** was obtained by interaction of 4-nitrophenylglyoxal hydrate with indole in acetic acid at 19°C during no more than 1 h. α -(4-Methoxyphenyl)(indolyl)benzoin **2h** was synthesized with moderate yield by

4-methoxyphenylglyoxal hydrate interaction with indole in boiling PhMe (Scheme 2).



We have found that α -benzoin, **2** readily isomerise into β -benzoin **3** in presence of bases (Scheme 3 (Et₃N (i), EtONa in EtOH (ii))):



(Ar = Ph (**a**), 2-thienyl (**b**), 4-ClC₆H₄(**d**), 4-Br-C₆H₄ (**e**)).

Structure of isomeric α -aryl(indolyl)benzoin **2** and β -aryl(indolyl)benzoin **3** was confirmed by data of ¹H and ¹³C NMR spectra and mass spectra. In ¹H NMR spectra of compounds **3** the chemical shifts of C(2)H indolyl proton and NH proton lie in more low field than chemical shifts of proper protons of α -benzoin **2**. Probably, this phenomenon is caused by conjugation of indol-3-yl moiety with carbonyl group in β -benzoin **3**.

In ¹³C NMR spectra of α -aryl(indolyl)benzoin **2** and β -aryl(indolyl)benzoin **3** the characteristic carbon shifts are shifts of CHOH carbon and C=O carbon atoms. In compounds **3** shift of C=O carbon lies in some upper field than of C=O carbon of α -benzoin **2** due to more conjugation of C=O group with 3-indolyl moiety. Shift of CHOH carbon for β -aryl(indolyl)benzoin **3** is observed in some lower field than that of α -aryl(indolyl)benzoin **2**. MS spectra of α - and β -aryl(indol-3-yl)benzoin also have some substantial distinctions.

Thus the synthetic route to β -aryl(indol-3-yl)benzoin **3** had been proposed.