Synthetic Approaches towards 5*H*-Indeno[1,2-*b*]pyridines

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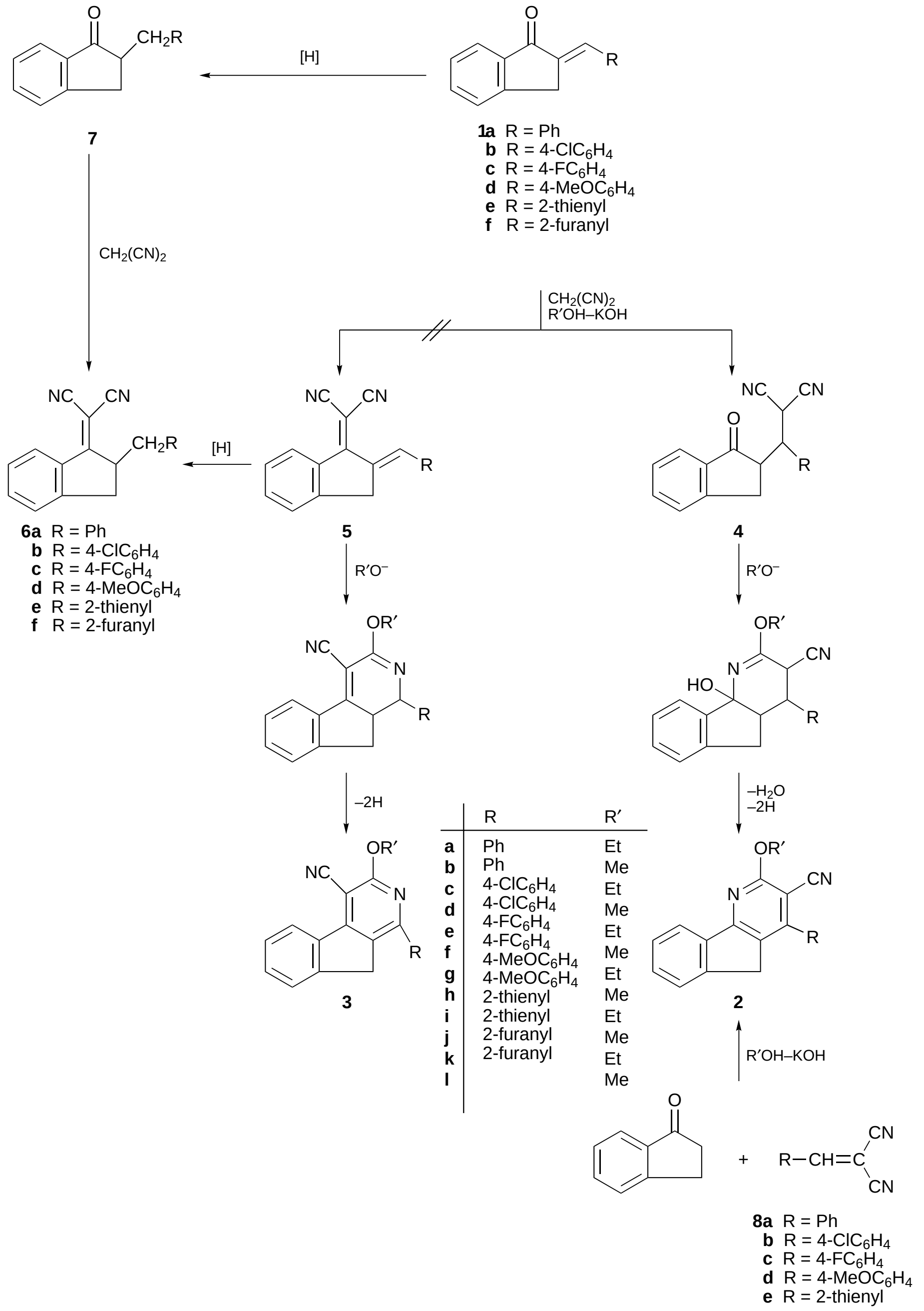
Reaction of the 2-arylmethylidene-2,3-dihydro-1*H*-inden-1-ones **1a–f** with malononitrile in alcoholic KOH affords 2-alkoxy-4-aryl-5*H*-indeno[1,2-*b*]pyridine-3-carbonitriles **2a–l** and (2-arylmethyl-2,3-dihydro-1*H*-inden-1-ylidene)dicyanomethanes **6a–f.**



	R	R′
a	Ph	Et
b	Ph	Me
c	4-ClC$_6$H$_4$	Et
d	4-ClC$_6$H$_4$	Me
e	4-FC$_6$H$_4$	Et
f	4-FC$_6$H$_4$	Me
g	4-MeOC$_6$H$_4$	Et
h	4-MeOC$_6$H$_4$	Me
i	2-thienyl	Et
j	2-thienyl	Me
k	2-furanyl	Et
l	2-furanyl	Me

Scheme 1

The reactions of α,β-unsaturated ketones with methylene compounds activated by a nitrile function, particularly malononitrile, have been the subject of many publications. Although the reaction was first investigated using sodium methoxide,[1] other organic basic catalysts such as morpholine[2–4] or piperidine[5,6] have been found to be useful in allowing the isolation of the mono-Michael adducts. Depending on the reaction conditions many interesting products were obtained. Thus, the reaction was used to synthesize 2-amino-3-cyano-4*H*-pyrans,[5,6] cyclohexane derivatives[2,6–9] and pyridine analogues.[6,9,10]

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In the present work the reaction of a number of 2-arylmethylideneindan-1-ones **1a–f** with malononitrile as a possible route for the synthesis of indenopyridinecarbonitrile derivatives was investigated. Thus, **1a–f** were reacted with malononitrile in alcoholic KOH to give colourless products. Based on analytical and spectral data, the structure of these products was assigned either as 5*H*-indeno[1,2-*b*]pyridines **2a–l** or the isomeric 9*H*-indeno[2,1-*c*]pyridines **3a–l**.

The isolated pyridines were established as being **2** rather than **3** on the basis of their independent synthesis *via* base catalysed addition of indan-1-one to arylmethylidenemalononitriles **8** in alcoholic KOH solution.

The formation of **2a–l**, presumably, takes place *via* Michael addition of the active methylene compound to the β-carbon of the unsaturated system affording the intermediate adducts **4**. Alkoxide attack on one of the nitrile groups, followed by dehydration and subsequent dehydrogenation, affords the condensed pyridines **2**.

A by-product **6a–f** was isolated in each case, the structure of which was based on IR, ^{1}H and ^{13}C NMR spectral and elemental analytical data. The formation of **6** presumably takes place through the reduction of the arylmethylidenes **1** or **5** and may be concerted with the dehydrogenation process that gives the indenopyridines **2** or **3**.

Techniques used: Elemental analysis, IR, ^{1}H and ^{13}C NMR

References: 19

Table 1: Physical properties of the products

Table 2: Spectroscopic properties of the products

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