

A Convenient Synthesis of Benz[*f*]Indene

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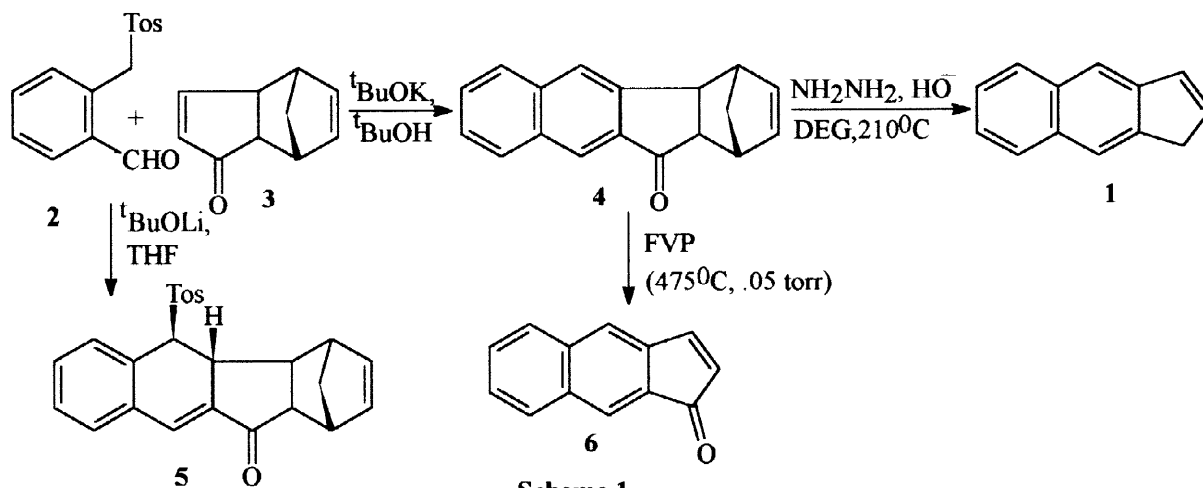
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Abstract : The crucial annulation of sulfone aldehyde **2** with enone **3** has led to an operationally simple two-step synthesis of benz[*f*]indene **1**, and its derivatives **8** and **9** involving a new rearrangement.

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The chemistry of benz[*f*]indenes has not been much explored. Benz[*f*]indene **1**, the parent member was first synthesized¹ in 1990 by Carpino et al as an intermediate in the preparation of newly introduced BIMOC protected amino acids². Subsequently, two more improved syntheses³ of this compound have appeared in the literature. We wish to report here a convenient two-step synthesis of **1**, from two readily available starting materials **2**⁴ and **3**⁵ (Scheme 1).

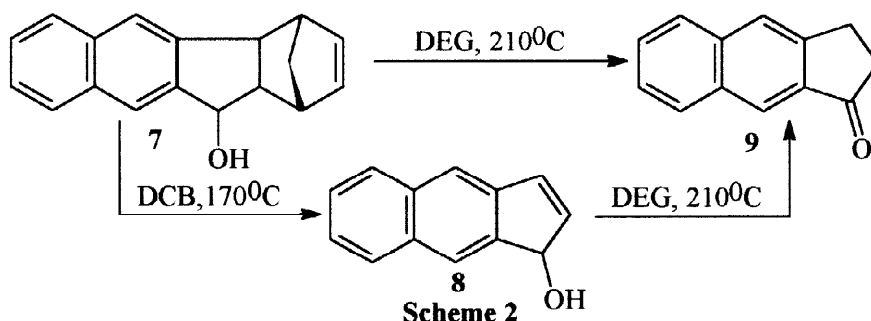


Scheme 1

In connection with our ongoing programmes⁶ on kinamycin antibiotics, we recently reported a methodology⁷ for the preparation of substituted benz[*f*]indenones, based upon sequential application of anionic [4+2] cycloaddition, and [4+2] cycloreversion. We intended to examine the same strategy for the preparation of benz[*f*]indene. But the planned annulation of sulfone aldehyde **2** with enone **3** proved to be very difficult, although such annulations⁸ have been utilized in the regiospecific syntheses of a variety of substituted fused aromatics. Under the standard conditions i.e. a strong base and an aprotic polar solvent, the reaction between **2** and **3** failed to provide the desired annulated product **4**. Alternatively, the attempted annulation in the presence of $t\text{BuOLi}$ in THF furnished a crystalline solid (~ 47%) which was tentatively characterized to be **5**. This product resisted various base-promoted attempts for aromatization of the central ring.

A thorough investigation of reaction conditions resulted in a procedure involving the use of 2 equiv. of $t\text{BuOK}$ in $t\text{BuOH}$ -methanol. Submission of the two reactants **2** and **3** to this condition at room temperature provided the desired product **4** in 84% yield. The product was collected by filtration, washed with water and used as such in the next step. Huang-Minlon reduction of **4** at 210°C in diethylene glycol (DEG) directly furnished benz[*f*]indene **1** (72%), which often condenses as a sublimate on the inside wall of the air condenser used.

In the light of rapid acquisition of the annulated product **4**, we further explored its utility. As shown in Scheme 2, it can be smoothly thermolysed to benz[*f*]indenone **6**⁹ (85%), and the corresponding alcohol derivative **7** to **8** (75%) at 170°C in *o*-dichlorobenzene (DCB) and **9**⁹ (87 %).



The heat promoted rearrangement of **8** to **9** is noteworthy in view of the little known chemistry of 1-indenols¹⁰. It is conceivable that the isomerization presumably proceeds via 1,5-sigmatropic carbinol hydrogen migration followed by tautomerisation. In a separate experiment indenol **8** was thermolysed to **9** in almost quantitative yield. Currently, we are exploring the use of this type of unprecedented rearrangement in the synthesis of psoralen derivatives. In summary, we describe an expeditious access to benz[*f*]indene and its derivatives without employing any tedious sequence.

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