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Condensation Reactions of 2-Acetylpyridine and Benzaldehydes: New Cyclohexanol Products and an Improved Synthesis of 4′-*p*-Tolyl-2,2′:6′,2″-terpyridine

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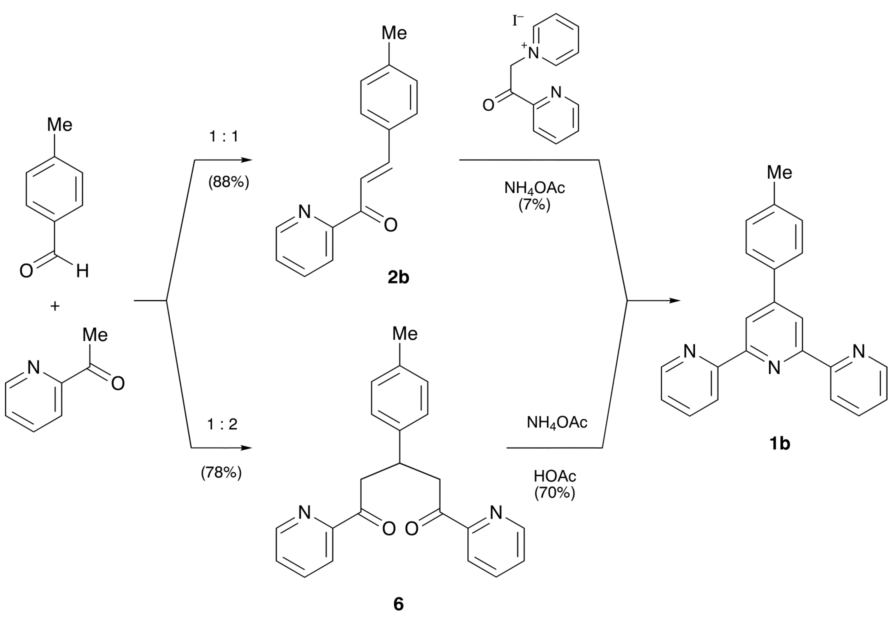
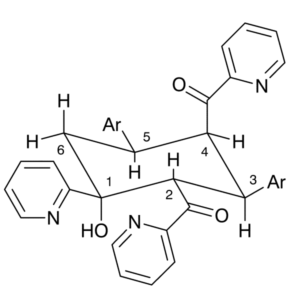
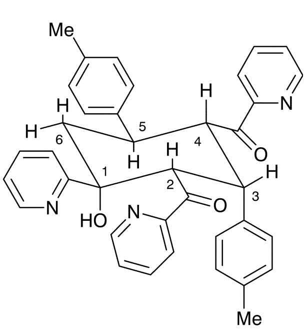
Condensations of 2-acetylpyridine with *p*-tolualdehyde and 4-*tert*-butylbenzaldehyde furnish three new cyclohexanol 3:2 condensates (**3d,e** and **7**), including a new diastereomer, and open a better route to 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (**1b**) *via* the new 2:1 condensate, 1,5-di(2-pyridyl)-3(4-methylphenyl)pentane-1,5-dione (**6**).



2,2′:6′,2″-Terpyridines are useful ligands in coordination chemistry.[1] The 4′-aryl derivatives **1** are accessible by the Kröhnke route[2] through the chalcone derivatives **2** which, in turn, result from the base-catalysed condensations of 2-acetylpyridine with benzaldehydes. Recently, however, novel 3:2 acetylpyridine–benzaldehyde condensation products (**3a–c**) were instead isolated.[3] 4-*tert*-Butylbenzaldehyde differed in forming a 3:1 condensate[3] though a 3:2 product had been reported earlier,[6] albeit without description.



3a Ar = 4-BrC$_6$H$_4$
b Ar = 4-ClC$_6$H$_4$
c Ar = 3,4-(MeO)$_2$C$_6$H$_3$
d Ar = 4-Bu^{t}C$_6$H$_4$
e Ar = 4-MeC$_6$H$_4$



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In our hands, *p*-*tert*-butylbenzaldehyde gave a 60% yield of the 3:2 product **3d**. Its stereochemistry was established by comparative NMR (Table 1). The reaction of *p*-tolualdehyde and 2-acetylpyridine at 1:1 ratio produced the chalcone **2b** (88%) but its reaction with the Kröhnke reagent[2] and NH$_4$OAc led to a poor yield of the known[7] terpyridine **1b** (7%).

In an alternate route,[3,6,8] a 1:2 tolualdehyde–acetylpyridine ratio led to diketone **6** (78%). Two byproducts were also isolated in a separate reaction. One was the 3:2 condensate **3e** (8%). The other (6%) was a diastereomer of **3e**. Extensive NMR work, including conclusive NOESY spectra, was used to assign it structure **7** with the unprecedented (1*RS*, 2*SR*, 3*SR*, 4*SR*, 5*RS*) configuration.

Diketone **6** was transformed to terpyridine **1b** in 70% yield (55% overall). This route is a significant improvement over the published syntheses[7] with no risk of contamination by the 6′-*p*-tolyl-2,2′:4′,2″ isomer.

The identities of all new compounds were confirmed by mass spectra and elemental analyses.

Techniques used: ^{1}H and ^{13}C NMR, FAB-MS, elemental analysis

References: 8

Tables: 1 (Chemical shifts and coupling constants for 3:2 condensation products)

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