β-Arylsulphonylvinylamines: Synthesis and Use in a New Route to Dihydropyridines

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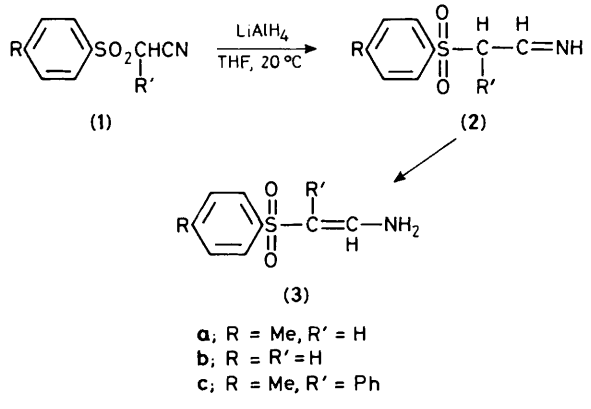
The title compounds are obtained by reduction of arylsulphonylmethyl cyanides and can be used as α-aza-allyl anion synthons in a new route to dihydropyridines.

Enamines certainly rank among the most versatile reagents for carbon–carbon bond formation.[1] Although several *N*-substituted β-sulphonylenamines[2] and β-iminosulphones[3] have been described, the parent β-sulphonylvinylamines are unknown and synthetic applications of β-sulphonylenamines have been very limited thus far.[2] We present here the synthesis of β-sulphonylvinylamines and their use in a new dihydropyridine formation.

The reduction of *p*-toluenesulphonylmethyl cyanide (**1a**) [prepared in 60% yield *via* a phase transfer catalysed modification (using tetrabutylammonium bromide) of an existing procedure[4]] with $LiAlH_4$ in tetrahydrofuran (THF) at 20 °C unexpectedly gave β-(*p*-toluenesulphonyl)vinylamine (**3a**) as a slightly yellow crystalline compound (m.p. 92–94 °C) in a quantitative yield (Scheme 1). Similarly, (**3b**) was obtained from (**1b**).

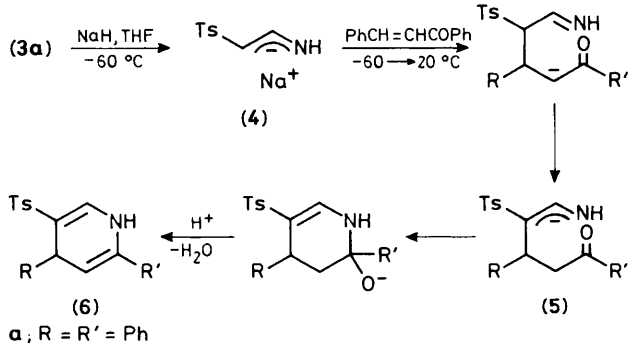


Scheme 1

N.m.r. data indicate *trans*-olefin stereochemistry (*J* 13 Hz) and show a 55.3 p.p.m. olefinic carbon shift difference for (**3a**), reflecting the presence of a strongly polarized double bond in these new 'push–pull' olefins.

The reduction of (**1**) apparently stops at the imine stage (**2**), owing to an immediate tautomerization to the enamine form (**3**). No trace of imine (**2**) or β-tosylethylamine could be detected; (**3a**) and (**3b**) are not reduced to arylsulphonylethylamines by HCO_2H or $NaBH_4$ in acidic media, reagents commonly used in enamine reductions.

This method also gives access to β-substituted β-arylsulphonylvinylamines lacking an α-substituent, enamines that



Scheme 2. Ts = tosyl.

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are otherwise not easily obtained.[3] Thus (**1c**) (R′ = Ph) gives (**3c**) (R′ = Ph) in 80% yield.

The multifunctional character of β-arylsulphonylvinylamines may be used to advantage in a variety of syntheses. This is exemplified by their use as a sulphonyl-stabilized α-aza-allyl anion synthon in a new route to dihydropyridines.

The addition of chalcone to a solution of (**4**) [prepared from (**3a**) and NaH in THF at −60 °C], followed by warming to room temperature, resulted in the formation of dihydropyridine (**6a**)‡ (m.p. 164—165 °C) in 65% yield (Scheme 2). Similarly, 4-phenylbut-3-en-2-one gave (**6b**) in 70% yield.

The formation of (**6**) is rationalized in Scheme 2. Initial Michael addition is followed by intramolecular proton transfer to the new aza-allyl anion (**5**) which cyclizes, and dehydrates to dihydropyridine (**6**).

Despite the extensive use of α-sulphonyl-β-aza-allyl anions in heterocyclic synthesis,[5] the isomeric α-aza-allyl anions have scarcely been investigated.[2,3,6] The procedures described here provide a viable alternative to obtain new dihydropyridines. Dehydrogenation or sulphinic acid elimination of (**6**) can open new routes to substituted pyridines.

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‡ *N.m.r. spectroscopic data* for (**6a**) ($CDCl_3$). ^1H: 2.32 (s, 3H), 4.70 (d, *J* 5 Hz, 1H), 5.08 (dd, *J* 5, 2 Hz, 1H), 6.25 (br.d, *J* 6 Hz, 2H), 7.01 (d, *J* 8 Hz, 2H), 7.10 (s, 5H), 7.38 (s, 5H), 7.44 (d, *J* 8 Hz, 2H), 7.66 (d, *J* 6 Hz, 1H). ^{13}C: 21.3, 40.3, 104.8, 110.5, 125.1, 126.3, 127.2, 128.1, 128.2, 128.7, 129.0, 133.9, 135.2, 137.2, 139.2, 142.4, 145.2 (co-production of isomeric 1,2-dihydropyridine was observed in a few cases).

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