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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 -sulphonylenamines² and β -iminosulphones³ 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 procedure⁴] with LiAlH₄ 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**).

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 HCO₂H or NaBH₄ 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 1

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 $-60^\circ C$], followed by warming to room temperature, resulted in the formation of dihydropyridine (6a)† (m.p. $164-165^\circ C$) 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).