First Isolation of 5-Amino-1-tosyl-*v*-triazolines from Tosylazide and Cyclic 1-Aminodienes

Donato Pocar, Maria Clara Ripamonti, Riccardo Stradi and Pasqualina Trimarco

Istituto di Chimica Organica della Facoltà di Farmacia,
Università di Milano, Viale Abruzzi 42, 20131 Milano, Italy

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By reacting the cyclic 1-aminodienes **1a-b** with tosylazide at low temperature, the corresponding *v*-triazolines **2a-b** were obtained. The structure of **2a-b** was assigned on nmr evidence. Compounds **2a-b** are the first examples of isolated 5-amino-1-tosyl-*v*-triazolines. The reversibility of the cycloaddition reaction was demonstrated.

J. Heterocyclic Chem., 14, 173 (1977).

Sir:

The reaction of enamines with arylsulfonylazides has been widely investigated (1). The compounds obtained have been explained as transformation products of unstable 5-amino-1-arylsulfonyl-*v*-triazoline intermediates which, heretofore, were never isolated.

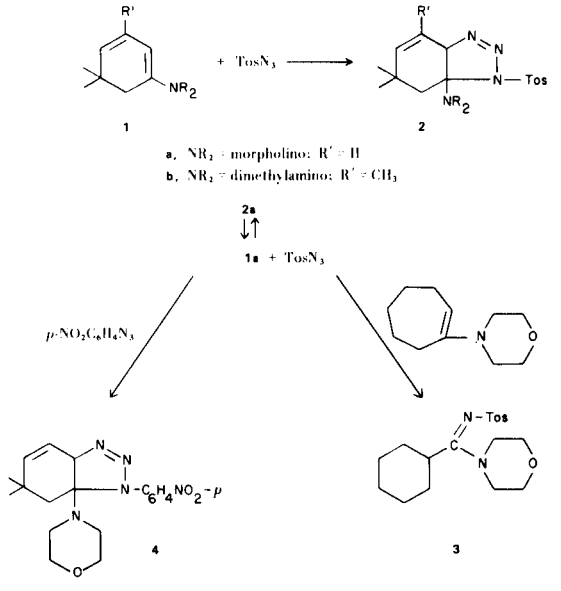
We now report that by reacting the enamines **1a-b** (2) with an equimolecular amount of tosylazide in diethyl ether at -20°, a precipitate of the corresponding *v*-triazolines **2a-b** was formed.

The products could be obtained in practically pure form by quick filtration and washing with cold ether (**2a**: 77%; m.p. 88-89°; **2b**: 34%; m.p. 59°).

Their structures were assigned on the basis of analytical (**2a**: *Anal.* Calcd. for $C_{19}H_{26}N_4O_3S$: C, 58.4; H, 6.65; N, 14.3. Found: C, 58.15; H, 6.4; N, 14.3. **2b**: *Anal.* Calcd. for $C_{18}H_{26}N_4O_2S$: C, 59.6; H, 7.2; N, 15.4. Found: C, 59.9; H, 7.15; N, 15.5.) and nmr data (δ, TMS: **2a** (deuteriochloroform/deuteriobenzene, 1:1, -5°): 0.97 (s, 2 CH_3); 1.84 and 2.65 (AB-system, CH_2, J = 14 Hz); 2.15 (s, aromatic-CH_3); 2.41 and 3.40 (2m, morpholine); 4.53 (d, -CH<, J = 2 Hz); 5.55 and 5.57 (AB-system, -CH=CH-C(H)-, J = 10 Hz); 7.00-8.00 (AA'BB'-system, aromatic); **2b** (deuteriochloroform, -20°): 0.95 and 1.04 (2s, 2 CH_3); 1.76 and 2.88 (AB-system, CH_2, J = 14 Hz); 1.90 (s, =C-CH_3); 2.19 (s, $N(CH_3)_2$); 2.41 (s, aromatic-CH_3); 4.52 (s, -CH<); 5.34 (s, =CH-); 7.20-8.10 (AA'BB'-system, aromatic).

In the solid state the triazolines were found to be stable for extended periods at room temperature. However, in solution (chloroform or benzene) **2a** and **2b** decompose rather quickly, even at 0°, with nitrogen evolution and formation of a very complex mixture of products from which we did not isolate until now any interesting compounds.

The cycloaddition reaction which affords **2a** and **2b** is reversible (3) and in solution the equilibrium between the triazolines and their components is evidenced by the azide (2130 cm^{-1}) band which is present in the ir spectrum of **2b** (in chloroform or dioxane) but is not detectable in the spectrum recorded in Nujol. Compound **2a** reacted with morpholinocycloheptene yielding the amidine **3** (the ex-



pected product from the reaction of the enamine and tosylazide (1)) and with 4-nitrophenylazide affording the triazoline **4** (4) derived from this azide and **1a**.

Further work is in progress to investigate in more detail the reactivity of this class of triazolines and to explain their unusual stability.

REFERENCES AND NOTES

(1) D. Pocar and P. Trimarco, *J. Chem. Soc., Perkin Trans. I*, 622 (1976) and references cited therein.

(2) The enamines were prepared by reacting 5,5-dimethyl-2-cyclohexenone and isophorone, respectively, with the appropriate amine and titanium tetrachloride (H. Weingarten and W. H. White, *J. Org. Chem.*, **31**, 4041 (1966), **1a**, b.p. 140°/25 torr; **1b**, b.p. 97°/25 torr. Enamine **1b** was found to be an equilibrium mixture (~ 50:50) of the two linearly conjugated (endo- and exocyclic) tautomers, according to the findings of N. F. Firrell and P. W. Hickmott (*J. Chem. Soc.* (B), 293 (1969)) on similar enamines.

(3) Other examples of reversible azide cycloaddition: F. Texier and J. Bourgois, *J. Heterocyclic Chem.*, 12, 505 (1975) and references cited therein.

(4) M.p. 162°. This product gave satisfactory analytical and spectral data and was also obtained by direct reaction of enamine **1a** with 4-nitrophenylazide.