

## A Novel 3,4-Dihydro-5-methylene-1,2,4-triazole and its Reactions with Acrylonitrile and Sulphene (Thioformaldehyde *S,S*-Dioxide) to form Spiroaziridines

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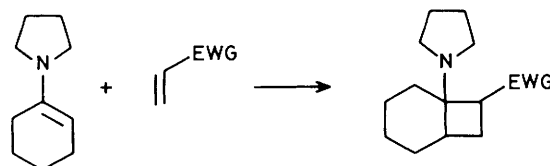
The dihydro-1,2,4-triazole (2), prepared by oxidation of the amidrazone (1), reacts with acrylonitrile and with sulphene ( $\text{CH}_2=\text{SO}_2$ ) to afford spiroaziridines (5) and (6), respectively.

Enamines react readily with a variety of reactive alkenes to afford cyclobutane derivatives,<sup>1</sup> as illustrated in Scheme 1. We have prepared the 5-methylene-3,4-dihydrotriazole (2) by the sequence of reactions in Scheme 2, involving oxidative cyclization of the amidrazone (1) as the key step.<sup>†</sup> 3,4-Dihydro-5*H*-1,2,4-triazoles are very rare compounds<sup>‡</sup>

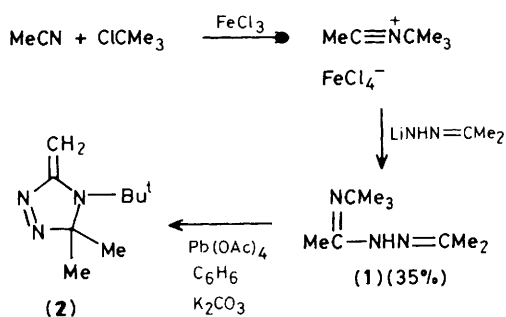
<sup>†</sup> We adopt the nomenclature recommended (D. G. Neilson, R. Roger, J. M. W. Heatlie, and L. R. Newlands, *Chem. Rev.*, 1970, **70**, 151, and references therein) for systems capable of tautomerism according to the equation  $\text{R}^1\text{C}(\text{NR}^2)_2=\text{NNR}^3_2 \rightleftharpoons \text{R}^1\text{C}(\text{=NR}^2)\text{NR}^2\text{NR}^3_2$  and refer to them as amidrazones. The equilibrium position for (1) is not known. Compound (1) and/or its tautomer may be named *N*<sup>1</sup>-isopropylidene-*N*<sup>3</sup>-*t*-butylacetamidrazone.

<sup>‡</sup> To the best of our knowledge, there are only ten 3,4-dihydro-1,2,4-triazoles reported in the literature. Eight are either 3*H*-pyrazolo[5,1-*c*][1,2,4]triazoles or 3*H*-[1,2,4]triazolo[4,3-*b*]indazoles (G. Ege and K. Gilbert, *Tetrahedron Lett.*, 1979, 1567) and only two are monocyclic (but highly fluorinated) systems [H. A. Brown, U.S. Pat. 3,326,889 (Cl. 260—192), 1967; *Chem. Abstr.*, 1967, **67**, 64407d].

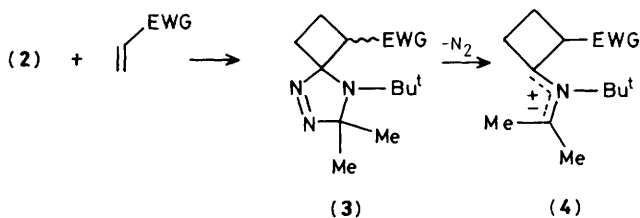
and (2) is the only member with an enamine functional group. By analogy with precedents<sup>1,3</sup> (Scheme 1), the enamine (2) was expected to react with Michael acceptors to form spirocyclobutanes (3) which, by thermal loss of  $\text{N}_2$ , would lead to azomethine ylides (4) (Scheme 3). Treatment of (2) with neat acrylonitrile at 50—80°C afforded (5) as a 1 : 1 mixture of diastereoisomers (88% yield), presumably by the steps of Scheme 3, followed by closure of the ylide (4) (EWG = CN). Separation of the diastereoisomers (5) was achieved with analytical g.c. columns but not, as yet, on a preparative scale.



Scheme 1. EWG = electron-withdrawing group throughout.

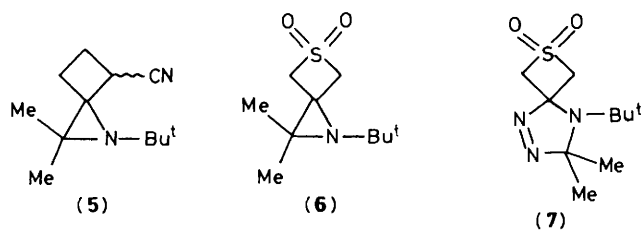


Scheme 2



Scheme 3

Gradual addition of methanesulphonyl chloride to a solution of (2) and triethylamine in ether at ice temperature, followed by stirring for 4 h at room temperature, afforded (6), m.p. 78.5–80°C (from petroleum), in 40% yield, probably *via* (7), formed by initial cycloaddition of (2) to sulphene ( $\text{CH}_2=\text{SO}_2$ ) generated *in situ*.<sup>3</sup> The sense of cycloaddition of (2) to sulphene, to form (6) ultimately, was expected on the basis of analogy,<sup>3,4</sup> and the fact that (6), formed at room temperature, did not contain (7) indicates that loss of  $\text{N}_2$  from (7) is a facile process.



Structures (2), (5), and (6) were fully supported with  $^1\text{H}$  n.m.r.,  $^{13}\text{C}$  n.m.r., i.r., u.v., and mass spectra.

The straightforward synthesis of (2) and its reactions with acrylonitrile and with sulphene point to a new entry to azomethine ylide intermediates (4) for mechanistic or synthetic work. For example, compounds such as (2) offer an alternative route to spiroaziridines of the type reported by Cookson and coworkers.<sup>5</sup>

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Received, 17th July, 1986; Com. 1006

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