

## Intramolecular 1,3-Cycloadditions of Nitrile Ylides Bearing an Acetylenic Function

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Treatment of amides **1a,b** with thionyl chloride followed by reaction with triethylamine gave 1,4-dihydro[1]benzopyrano[4,3-*b*]pyrrole derivatives (**4a,b**) arising from intramolecular 1,3-cycloaddition of intermediate nitrile ylides (**3a,b**).

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Sir:

As recently reviewed (2,3), 1,3-dipolar substrates containing a dipolarophile function can undergo intramolecular 1,3-cycloadditions leading to fused or bridged ring heterocycles. Studies on functionalized nitrile ylides, however, have shown mainly electrocyclic ring closures (4,5) or intramolecular carbene-type 1,1-cycloadditions (6-8). An authentic intramolecular 1,3-cycloaddition is involved only in the photoisomerization of 2-methyl-2-(4-pentenyl)-3-phenyl-2*H*-azirine to 5-methyl-2-phenyl-4,5-trimethylene-1-pyrroline (9) and, perhaps, in that of 3-phenyl-4,5-trimethylene-2-isoxazoline to 2-phenyl-4,5-trimethylene-2-oxazoline (10). In this context, we now wish to report intramolecular 1,3-cycloadditions of nitrile ylides bearing an acetylenic function.

Amide **1a** (m.p. 121-122°), prepared from 2-(2-propynyloxy)benzoyl chloride (m.p. 86°) and 4-nitrobenzylamine, was treated with an excess of thionyl chloride (10 moles, 1 hour at 80°) with the aim of synthesizing the iminochloride **2a**. In reality, isolation and characterization of the latter compound was not possible since it is easily hydrolysed in air as well as thermally decomposed to give 2-(2-propynyloxy)benzoyl nitrile (m.p. 76°) and 4-nitrobenzyl chloride (11). Nevertheless, the crude product arising from the reaction of **1a** with thionyl chloride was treated with triethylamine in boiling benzene (3 moles, 2 hours). Column chromatography of the resulting mixture gave 2-(4-nitrophenyl)-1,4-dihydro[1]benzopyrano[4,3-*b*]pyrrole (**4a**) (deep red crystals, dec. > 280°) in 18% yield with respect to the starting amide.

The structure **4a** is supported by the following data: ir (nujol) 3360 cm<sup>-1</sup> (NH); nmr (DMSO-*d*<sub>6</sub>) δ: (12) 5.29 (2H, s, CH<sub>2</sub>O), 6.7-8.3 (9H, complex signal, ar and CH=), 11.85 (1H, broad s, NH); mass spectrum: *m/e* 292.

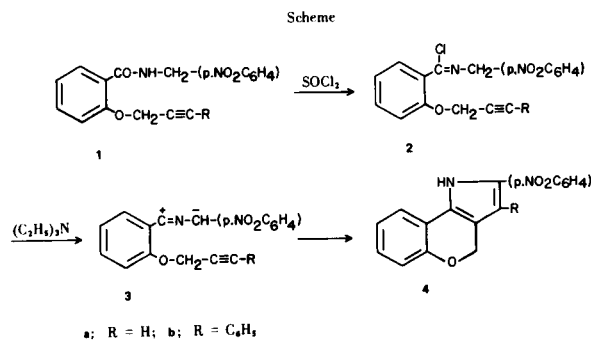
*Anal.* Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>: C, 69.85; H, 4.14; N, 9.59. Found: C, 69.76; H, 4.05; N, 9.36.

Analogous results were obtained starting from amide **1b** (m.p. 140-141°). In this case, however, the final product

**4b** (deep red crystals, dec. > 250°) was isolated in a very low yield (6%). The following data are available for **4b**: ir (nujol) 3350 cm<sup>-1</sup> (NH); nmr (acetone-*d*<sub>6</sub>) δ: (12) 5.20 (2H, s, CH<sub>2</sub>O), 6.7-8.2 (13H, complex signal, ar), 11.8 (1H, broad s, NH); mass spectrum: *m/e* 368.

*Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 74.99; H, 4.38; N, 7.61. Found: C, 74.86; H, 4.00; N, 7.39.

As illustrated in the Scheme, the formation of **4a,b** is well accounted for by the intermediacy of nitrile ylides **3a,b**, whose intramolecular 1,3-cycloaddition is probably facilitated by entropy factors due to the spatial proximity of the reaction partners. Steric hindrance by the phenyl group in the case of **3b** may explain the lower yield of cyclization.



### REFERENCES AND NOTES

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(11) This behaviour is consistent with a general decomposition pattern of *N*-alkyliminochlorides [W. J. Hickinbottom, "Reactions of Organic Compounds", Longmans, New York, N.Y., 1957, p. 343].

(12) With tetramethylsilane as an internal standard.