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[A0018]

# Intramolecular Nitrilimine Cycloadditions leading to the Pyrazolo[1,5-*a*][6,1]benzoxazonine and Pyrazolo[1,5-*a*][7,1]benzoxazecine Skeletons

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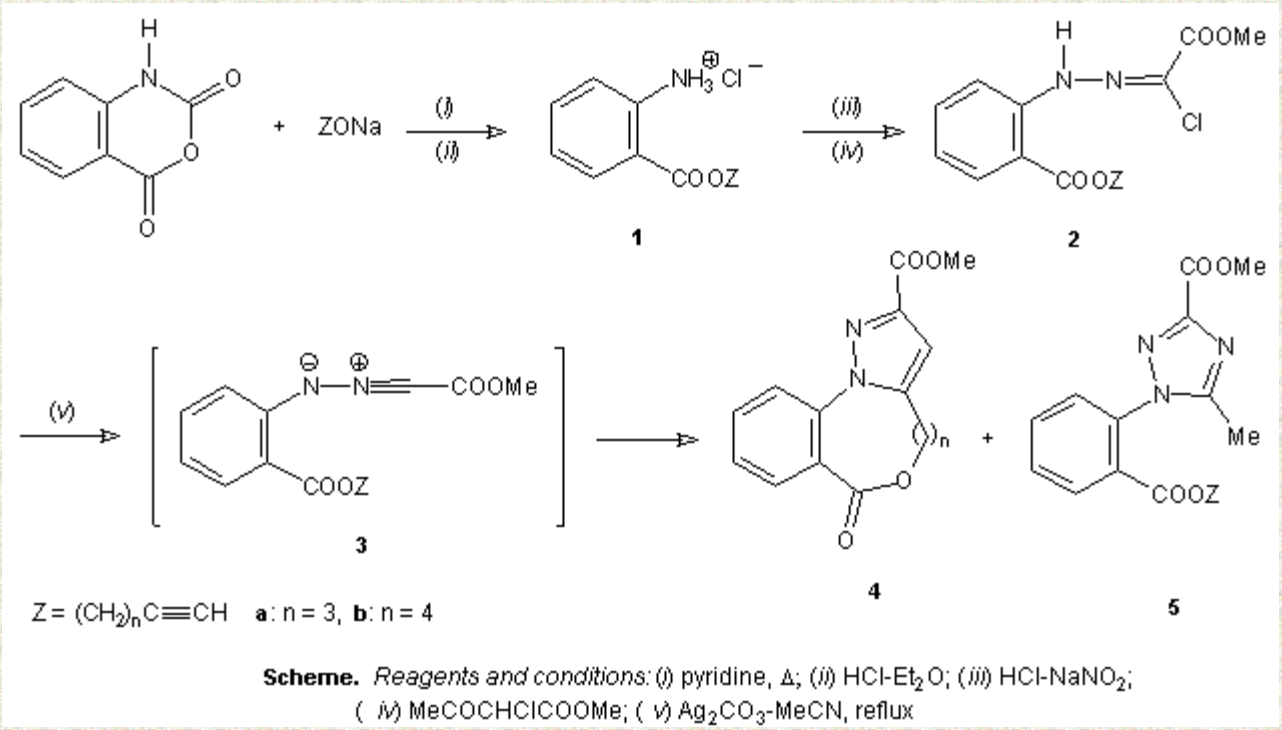
Intramolecular 1,3-dipolar cycloadditions represent a valuable tool in the synthesis of a large variety of heterocyclic systems containing a five- membered heterocycle fused or bridged to another hetero- or carbo-cyclic ring.[1] However, despite to the usefulness of this methodology, the examples in which is implied the formation of a medium-sized ring are still rare.[2,3]
A fruitful approach to the hitherto unreported pyrazolo[1,5-*a*][6,1]benzoxazonine and pyrazolo[1,5-*a*] [7,1]benzoxazecine skeletons is here reported, based on the intramolecular cycloaddition of properly chosen nitrilimines.
The hydrazonyl chlorides **2**, which we have devised as the precursors for the *in situ* generation of the nitrilimines **3**, were obtained starting from isatoic anhydride and the appropriate alkynols (see Scheme). The treatment of **2** with an excess of silver carbonate in refluxing acetonitrile gave the desired cycloadducts in good yields (see Table). It is to be added that, under the experimental conditions described above, the nitrilimines **3** underwent, as a side reaction, the 1,3-dipolar cycloaddition onto the solvent to give the triazole derivatives **5**.
In wiew of the well-known factors working against the formation of large-ring system,[4] the observed yields of cyclization can be considered worthy of noting.




**Scheme.** *Reagents and conditions:* (*i*) pyridine, Δ; (*ii*) HCl-$Et_2O$; (*iii*) HCl-$NaNO_2$; (*iv*) MeCOCHClCOOMe; (*v*) $Ag_2CO_3$-MeCN, reflux

**Table.** Treatment of Hydrazonyl Chlorides **2** with silver carbonate in refluxing acetonitrile.

| Entry | Time (h) | Products | Yield* (%) | Mp (°C) | IR (nujol) ($cm^{-1}$) | $^1$H-NMR *J* (Hz) |
|---|---|---|---|---|---|---|
| **a** | 7 | **4a**<br>**5a** | 41<br>15 | 148<br>171 | 1730, 1720<br>1730, 1710 | 2.30-2.55 (4H, m), 3.94 (3H, s), 4.95 (2H, br t), 6.69 (1H, s), 7.38-7.86 (4H, m)<br>1.70-1.85 (2H, m), 1.92 (1H, t, *J* 2.4), 2.18 (2H, dt, *J* 6.5, 2.4), 2.32 (3H, s), 3.94 (3H, s), 4.18 (2H, t, *J* 6.5), 7.32-8.21 (4H, m) |
| **b** | 3 | **4b**<br>**5b** | 60<br>15 | 110<br>146 | 1740, 1720<br>1730, 1710 | 1.70-3.00 (6H, m), 3.92 (3H, s), 4.74-4.98 (2H, m), 6.74 (1H, s), 7.40-8.30 (4H, m)<br>1.55-1.90 (4H, m), 1.95 (1H, t, *J* 2.5), 2.15 (2H, dt, *J* 6.2, 2.5), 2.31 (3 H, s), 3.92 (3H, s), 4.11 (2H, t, *J* 6.0), 7.20-8.20 (4H, m) |

***** Afetr chromatographic separation with dichloromethane-ethyl acetate (3:1) as eluent.

## References

1. A. Padwa, "*1,3-Dipolar Cycloaddition Chemistry*", Vol. II, p. 277-406, A. Padwa Ed.; Wiley-Interscience, New York, 1984.
2. G. Broggini, L. Garanti, G. Molteni, G. Zecchi, *J. Chem. Res.* **1995**, 385 (*S*), 2389 (*M*).
3. G. Broggini, L. Garanti, G. Molteni, G. Zecchi, *Org. Prep. and Proc. Int.* **1996**, *28*, 699.
4. M. A. Winnick, *Chem. Rev.* **1981**, *81*, 491.

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**Comments**

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