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Reaction of an Open-Chain Analogue of Reissert Compound Hydrofluoroborate Salt with Ethyl Acrylate. A Reinvestigation

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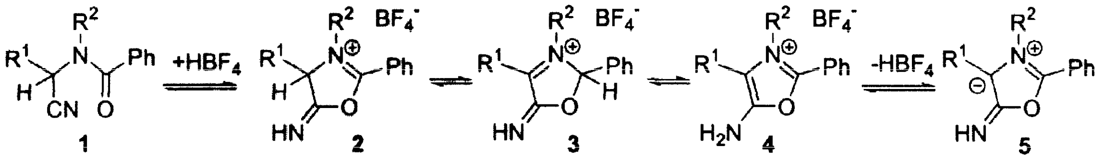
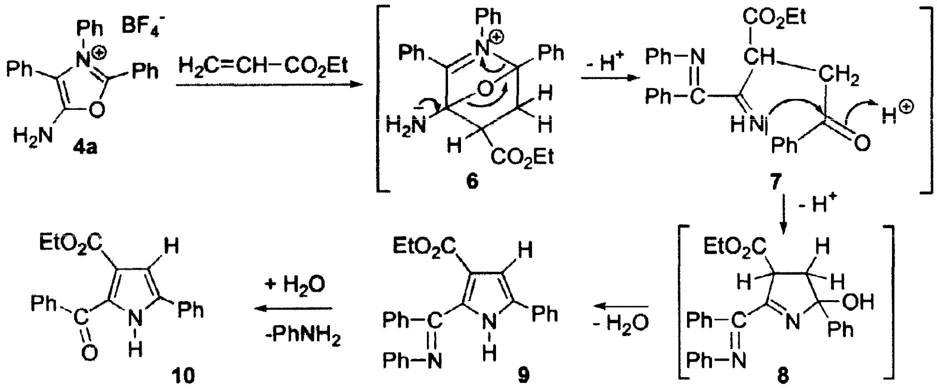
Abstract : The reaction of an open-chain analogue of Reissert compound hydrofluoroborate salt with ethyl acrylate does not give a [4+2] cycloadduct as previously described, but a [3+2] cycloadduct which evolves to a 2-pyridone **15**. © 1998 Published by Elsevier Science Ltd. All rights reserved.

The reactions of isoquinoline Reissert compound hydrofluoroborate salts with alkynes and alkenes was described by McEwen et al.[1] and our group.[2] Moreover, McEwen et al.[3] reported such reactions of some open-chain analogues of Reissert compound hydrofluoroborate salts. These salts can exist as a mixture of tautomeric forms **2-4**, of which **4** is the predominant one.[3] They are also presumed to be in equilibrium with the original compound **1**, the 1,3-dipolar species **5** and fluoroboric acid (scheme 1).



Scheme 1

McEwen et al.[3] claimed that olefins should react as dienophiles towards the heterodienes **4**. Thus, with ethyl acrylate and the salt **4a** ($R^1 = R^2 = Ph$), the presumed cycloadduct **6** should evolve via some complex condensation and rearrangement to give the ethyl 2-benzoyl-5-phenylpyrrole-3-carboxylate **10** (scheme 2).



Scheme 2

However, the structure **10** has never been proved.

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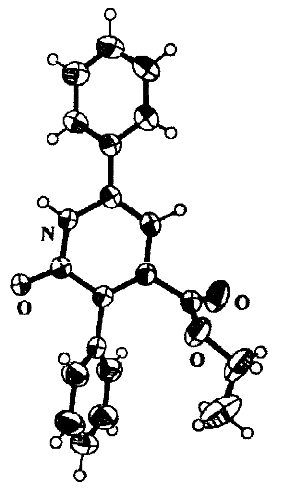
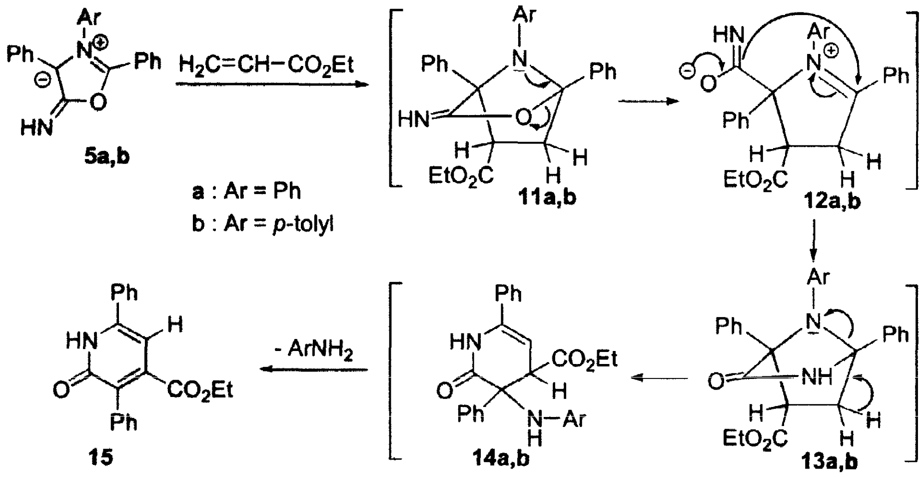
Repeating the reported procedure,[3] we have carried out the reaction of the mixtures **2a-5a** ($R^1 = R^2 = Ph$) or **2b-5b** ($R^1 = Ph$, $R^2 = p$-tolyl) with ethyl acrylate and did indeed obtain the same product (according to mp, IR and nmr spectra)[5]. However, the ^{13}C nmr data did not agree with the proposed structure **10** (scheme 2). An X-ray analysis allowed to identify its structure as the 2-pyridone **15**.[4,5]

Thus, the reaction of an open-chain analogue of Reissert compound hydrofluoroborate salt with ethyl acrylate does not lead to an initial [4+2] cycloaddition of heterodiene **4**. We have already reported on [3+2] cycloaddition reactions of an isoquinoline Reissert compound hydrofluoroborate salt with some alkenes.[2] It is reasonable to assume that the mesoionic species **5** undergoes a 1,3-dipolar cycloaddition with ethyl acrylate to give the [3+2] cycloadduct **11** (Scheme 3).



Crystal structure of **15**



Scheme 3

The opening of the cycloadduct **11** at the HN = C - O - bridge is assisted by the nitrogen electron pair of the pyrrolidine moiety and gives the transitory species **12**. This species **12** becomes the bicycle **13**, the opening of which leads to the 3,4-dihydro-2-pyridone **14**, a precursor of the final product **15**. The spectrometric data agree with this radiocrystallographically authentified structure.[5]

Work is in progress in order to isolate some of the postulated intermediaries **11-14** and also to generalize this new access to a 2-pyridone family.

REFERENCES AND NOTES

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2. Schmitt, G.; Laude, B.; Vebrel, J.; Rodier, N.; Theobald, F. *Bull. Soc. Chim. Belg.* **1989**, *98*, 113-23 ; Monnier, K.; Schmitt, G.; Laude, B. *Tetrahedron Lett.* **1992**, *33*, 1609-10.
3. McEwen, W.E.; Grossi, A.V.; MacDonald, R.J.; Stamegna, A.P. *J. Org. Chem.* **1980**, *45*, 130-8.
4. X-Ray crystallographic data, and the table of atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.
5. **15** : mp : 214°C (AcOEt) ; IR (cm^{-1}) : 1690 (CO), 1717 (CO), 3130 (NH). ^1H nmr ($CDCl_3$) : 0.96 (t, 3H, J = 7.1) ; 4.09 (q, 2H, J = 7.1) ; 6.79 (s, 1H) ; 7.30-7.82 (m, 10H) ; 12.89 (sl, 1H, NH). ^{13}C nmr ($CDCl_3$) : 13.4 (q, J = 126.9) ; 61.5 (t, J = 144.0) ; 103.6 (d, J = 170.9) ; 126.5-145.9 (10 signals for 15 C arom.) ; 164.2 (s) ; 167.5 (s).