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Reaction of 2-Benzoyl-1,2-Dihydroisoquinaldonitrile Hydrofluoroborate Salt with some 1,4-Quinones

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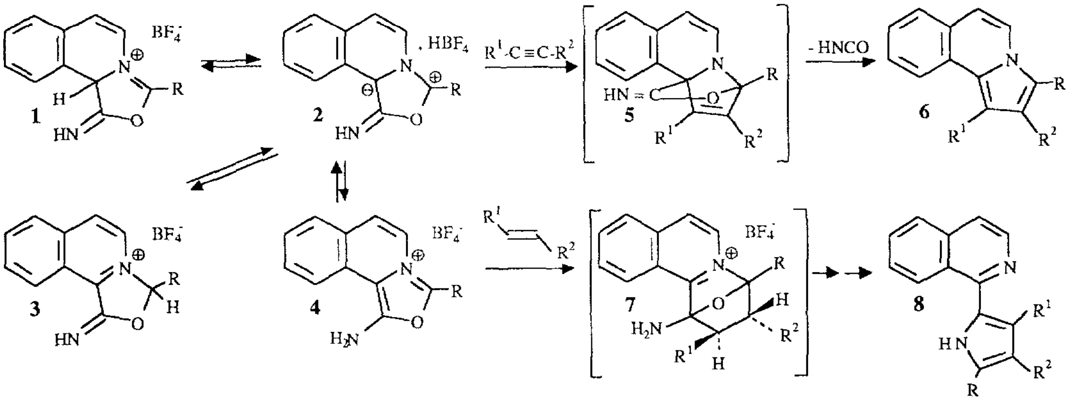
Key Words : 1,3-Dipolar cycloaddition ; 1,4-Quinones ; Reissert hydrofluoroborate salt.

Abstract : In all reactions studied up to the present time with olefins, the Reissert hydrofluoroborate salts have given only the Diels-Alder adducts. With 1,4-benzo- and naphtoquinones, we have found evidence for 1,3-dipolar cycloaddition. The structure of cycloadducts was determined from spectroscopic data and specified by a radiocristallographic study.

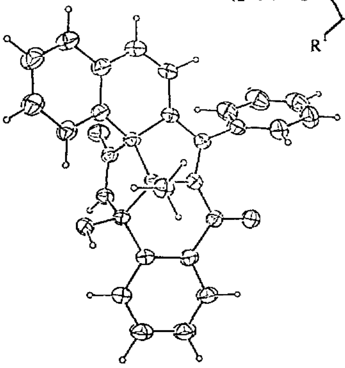
Evidence has been presented that solutions of the hydrofluoroborate salts of 2-acyl-1,2-dihydroisoquinaldonitrile (Reissert compounds) consist of equilibrium mixtures of **1**-**4**, the latter being the major component.[1,2]



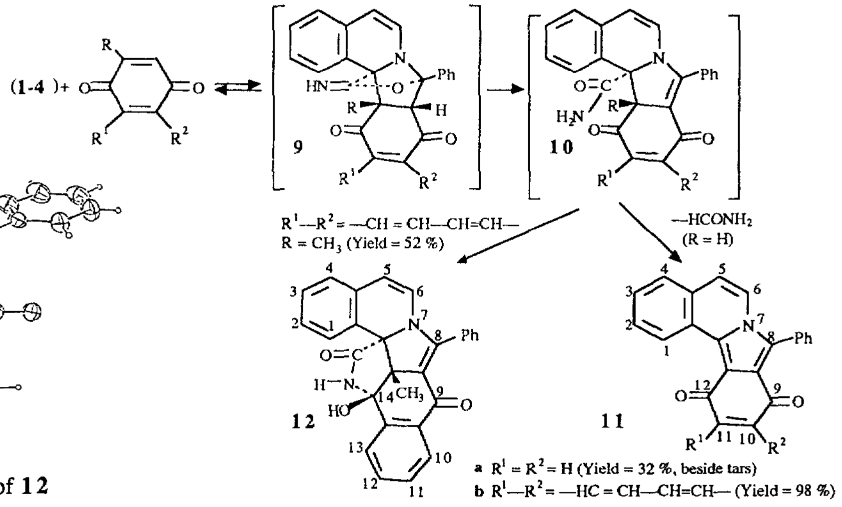
According to McEwen and coworkers,[2] these salts undergo 1,3-dipolar cycloadditions with alkynes wich trapped the species **2** and give pyrrolo[2,1-a]isoquinoline **6**, via the cycloadduct **5**. Acid-catalyzed condensation-rearrangement reactions of these salts, the initial step of which being a Diels-Alder reaction involving **4** as heterodiene, occur with alkenes to yield substituted 2-[1-isoquinolinyl]pyrroles **8**. The olefin reactions take place with both monosubstituted and 1,2-disubstituted ethylenes, and also when either electron-donating or electron-withdrawing (only ethylenic esters were used) substituents are bonded to the ethylene moiety. McEwen and coworkers claimed that these reactions and general in nature.[2]

We report here reactions of an hydrofluoroborate salt (R = Ph) with three 1,4-quinones and found that the reaction was not a Diels-Alder but a 1,3-dipolar cycloaddition. These cycloaddition reactions are reversible, so it is reasonable to assume that the equilibrium mixture of **1-4** can undergo the initial step of both types of reaction with each quinone. Since the inital competing cycloadditions are reversible, their continuation depends on the relative velocities of the first irreversible steps. The easy loss of ketonic α-H atom from the cycloadduct **9** leads to the transition species **10**. If R = H, conversion of **10** (involving only loss of $HCONH_2$) gives an aromatic product **11**. If R = CH_3, the amidic rest of **10** cannot be eliminated and the NH_2 group reacts with the ketonic moiety to give the compound **12**. The radiocrystallographic structure of **12**[3] confirms the 1,3-dipolar cycloaddition.

The reactions were carried out in a DMF solution of the reactants (mole to mole) at 0°C for 3 h. The mixture was poured into water and then extracted with ether. This solution was dried (Na_2SO_4), the solvent evaporated and the residue crystallised in an appropriate solvent.[4]



Crystal structure of **12**



Thus, we have discovered a 1,3-dipolar cycloaddition of a Reissert salt with olefins in an acidic medium. The search for other 1,3-dipolarophilic olefins to oppose towards the munchnone imine **2** is now in progress.

REFERENCES AND NOTES

1. Cook, M. J.; Katritzky, A. R.; Page, A. D.; *J. Am. Chem. Soc.*, 99, 165-169, (1977).
2. McEwen, W. E.; Cabello, C. C.; Calabro, M. A.; Ortega, A. M.; Stott, P. E.; Zapata, A. J.; Zepp, C. M.; Lubinkowski, J. J.; *J. Org. Chem.*,**44**, 111-117 and refererences cited therein, (1979).
3. X-Ray crystallographic data, lists of refined coordinates and e.s.d's are deposited at the Cambridge Crystallographic Data Centre.
4. **11a** : mp 252°C (EtOH) ; IR (cm^{-1}) : 1656 (C=O). ^1H nmr ($CDCl_3$) : 6.67 (d, 1H, J = 10.2) ; 6.90 (d, 1H, J = 10.2) ; 7.04 (d, 1H, J = 10.5) ; 7.52-7.75 (m, 9H) ; 10.26 (d, 1H, J = 6.9) ; **11b** : mp > 270°C (toluene) ; IR (cm^{-1}) : 1663 (C=O). ^1H nmr ($CDCl_3$) : 7.05 (d, 1H, J = 9.5) ; 7.52-7.80 (m, 11H) ; 8.13 (d, 1H, J = 10.2) ; 8.43 (d, 1H, J = 10.2) ; 10.47 (d, 1H, J = 10.3) ; **12** : mp 222°C (n-PrOH) ; IR (cm^{-1}) : 3350 (OH); 3300 (NH); 1690 (C=O); 1630 (C=O) ; ^1H nmr ($DMSOd_6$): 1.30 (s, 3H, CH_3) ; 3.39 (s, 1H, OH) ; 5.58 (d, 1H, J=9.2) ; 6.4 (d, 1H, J=9.2); 7.08-7.6 (m, 9H) ; 7.68 (d, 1H, J = 7.6) ; 7.85 (d, 1H, J = 8.7) ; 7.98 (d, 1H, J = 8.7) ; 8.30 (d, 1H, J = 9.2) ; 9.22 (s, 1H, NH).

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