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Synthesis of pyridinium ylides and simulation of their 1,3-dipolar cycloaddition mechanism

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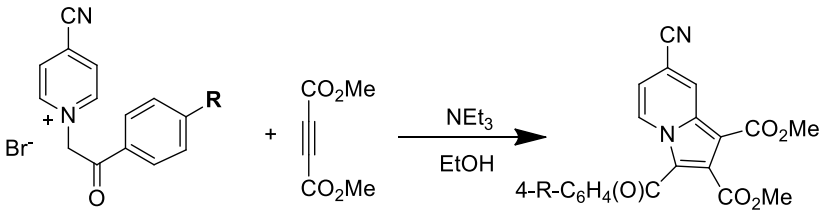
Experimental

Melting points were determined with a micro-Koffler apparatus and are uncorrected. NMR spectra were recording on Bruker-300 MHz or Bruker DRX-500 MHz. Mass spectra were obtained on a Finnigan MAT in INCOS 50 quadrupole massspectrometer. High resolution mass spectrometry: Instrument Ser# micrOTOF 10248. Flash chromatographies were performed with silica gel 60 (Acros) and tls with 60 F 254 silica gel (Merck).

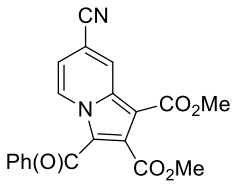
3-Cycloaddition of pyridinium ylides to dimethyl lacetylenedicarboxylate 3. General procedure.



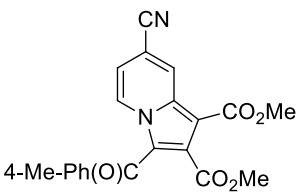
1a-e **3** **7a-e**

R = H (**a**), Me (**b**), MeO (**c**), F (**d**), NO_2 (**e**)

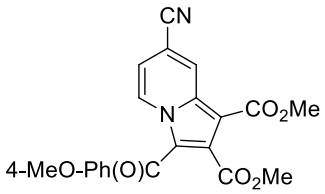
To the mixture of quaternary salt (**1a-e**) (3.3 mmol) and alkyne **3** (4 mmol) in 20 ml of ethanol, Et_3N (4.0 mmol) was added dropwise at 20 °C with stirring. The reaction mixture was left for 24 h, the precipitate of adduct (**7a-e**) was filtered, washed with EtOH and dried in air at room temperature.



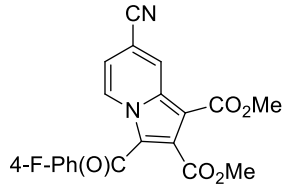
Product 7a. Yield 56%, mp 123-126 °C (decomp.), rose solid. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.31 (s, 3H, CO_2Me); 3.34 (s, 3H, CO_2Me); 7.12 (d, *J* = 5.6 Hz, 1H, ArH); 7.44-7.72 (m, 5H, PhH); 8.89 (s, 1H, ArH); 9.52 (d, *J* = 5.6 Hz, 1H, ArH). EIMS *m/z* 362 [M]+.



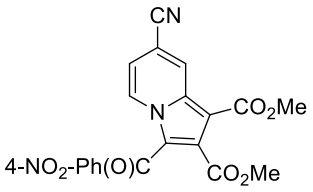
Product 7b. Yield 52%, mp 156-158 °C (decomp.), rose solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H, Me); 3.36 (s, 3H, CO_2Me); 3.91 (s, 3H, CO_2Me); 7.10 (d, *J* = 5.6 Hz, 1H, ArH); 7.29 and 7.51 (2d, *J* = 7.6 Hz, 4H, ArH); 8.84 (s, 1H, ArH); 9.46 (d, *J* = 5.6 Hz, 1H, ArH). EIMS *m/z* 376 [M]+.



Product 7c. Yield 58%, mp 152-153 °C (decomp.), red solid. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.85 (s, 3H, CO_2Me); 3.86 (s, 3H, CO_2Me); 3.89 (s, 3H, MeO); 7.05 (d, *J* = 7.6 Hz, 2H, ArH); 7.46 (d, *J* = 4.6 Hz, 1H, ArH); 7.68 (d, *J* = 7.6 Hz, 2H, ArH); 8.71 (s, 1H, ArH) ; 9.12 (d, *J* = 4.6 Hz, 1H, ArH). EIMS *m/z* 392 [M]+.

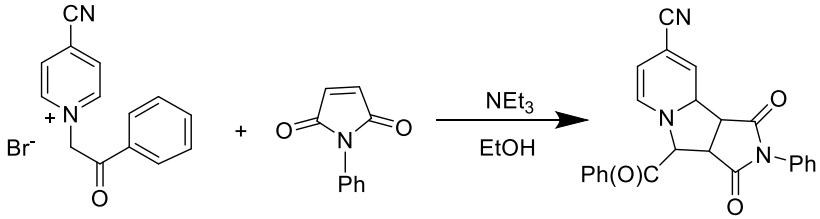


Product 7d. Yield 47%, mp 116-118 °C (decomp.), rose solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 3H, CO_2Me); 3.91 (s, 3H, CO_2Me); 7.15-7.74 (m, 5H, ArH); 8.79 (s, 1H, ArH); 9.48 (d, *J* = 5.6 Hz, 1H, ArH). EIMS *m/z* 380 [M]+.

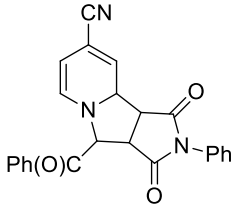


Product 7e. Yield 34%, mp 170-174 °C (decomp.), red-brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.39 (s, 3H, CO_2Me); 3.93 (s, 3H, CO_2Me); 7.22 (d, *J* = 5.6 Hz, 1H, ArH); 7.55 and 8.36 (2d, *J* = 7.6 Hz, 4H, ArH); 8.81 (s, 1H, ArH); 9.73 (d, *J* = 5.6 Hz, 1H, ArH). EIMS *m/z* 407 [M]+.

1,3-Cycloaddition of 1a to *N*-phenylmaleinimide. General procedure.



To the mixture of quaternary salt **1a** (3.3 mmol) and *N*-phenylmaleinimide (3.5 mmol) in 20 ml of ethanol, Et_3N (3.5 mmol) was added dropwise at 20 °C with stirring. The mixture was left for 24 h, the precipitate of adduct **8** was filtered, washed with EtOH and dried at room temperature.



Product 8. Yield 95%, mp 176-180 °C (decomp.), yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.62 (t, *J* = 7.6 Hz, 1H, CH); 3.87 (d, *J* = 7.6 Hz, 1H, CH); 4.85-4.98 (m, 1H,CH+1H, ArH); 5.51(s, 1H, CHCOPh); 6.19 (m, 1H, ArH); 6.28 (d, *J* = 4.6 Hz, 1H, ArH); 7.21-8.11(m, 10H, 2Ph). EIMS *m/z* 395[M]+.