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SHORT COMMUNICATIONS

Ylides Synthesis by Oxidative Coupling of Pyridine Bases with Methylene Active Compounds

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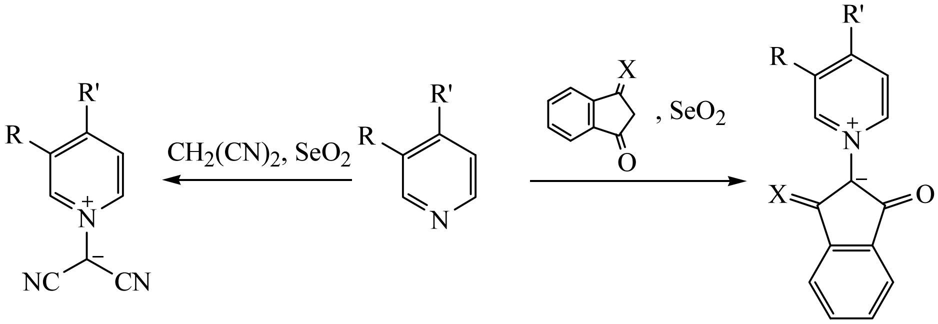
Ylides prepared from puridine bases and methylene active compounds, primarily malononitrile and 1,3-indanedione, are already known for a long time. The most common method of these ylides generation is the reaction of pyridine bases with oxides of tetracyano-ethylene [1, 2] and 2-dicyanomethylene-1,3-indanedione [3]. A synthesis was also described of 3-hydroxymethylpyridinium dicyanomethylide from 3-hyderoxymethylpyridine and malononitrile in the presence of of iodobenzene diacetate and sodium methylate [4], and a synthesis of an ylide from pyridine and 2-bromo-1,3-indanedione [5].

We found that pyridinium ylides **Ia, Ib, IIa–IIe** readily form in sufficiently good yields at treating pyridine bases (pyridine, 3-picoline) with methylene active compounds (malononitrile, 1,3-indanedione, and 2-dicyanomethylene-1,3-indanedione) in the presence of selenium dioxide (see the scheme).

The reaction should be performed by slowly adding the solution of methylene active compound to SeO_2 dissolved in the pyridine base; it was formerly shown that the simultaneous mixing of malononitrile, pyridine base, and SeO_2 resulted in formation of the corresponding bases pentacyanopropenides [6]. We presume that in this reaction carbene intermediates intermediately form generated from the corresponding methylene active compounds; these intermediates react further with excess pyridine base.

We failed to obtain ylides from 2-picoline. The reaction of 4-dimethylaminopyridine with 1,3-indanedione and SeO_2 gave rise to ylide **IIe**; however the replacement of 1,3-indanedione by malononitrile led not to an ylide but to 4-dimethylaminopyridine pentacyanopropenide. The reaction of cyanoacetamide with pyridine and SeO_2 yielded pyridinium oxamate apparently due to the fast oxidation of the cyanoacetamide into oxamic acid.

Scheme.



Ia, Ib **IIa–IIe**

I, R = R' = H (**a**); R = Me, R' = H (**b**); **II**, R = R' = H, X = O (**a**); R = Me, R' = H, X = O (**b**); R = R' = H, X = $C(CN)_2$ (**c**); R = Me, R' = H, X = $C(CN)_2$ (**d**); R = H, R' = NMe_2, X = O (**e**).

Ylides **Ia, Ib, IIa–IIc** were previously described. The structure of newly prepared ylides **IId** and **IIe** was confirmed by ^{1}H NMR and mass spectra.

Synthesis of pyridinium ylides. *a.* To a solution of 1.3 g (0.0115 mol) of SeO$_2$ in 5 ml of pyridine or 3-picoline at 50–55°C was added dropwise within 30–40 min while stirring a solution of 0.5 g (0.0076 mol) of malononitrile in 5 ml of the same base. The reaction mixture was stirred for 20 min more, cooled, and dicyanomethylides **Ia** and **Ib** were filtered off.

b. A solution of 2.6 mmol of methylene active compound in a mixture of 2 ml of DMF and 2 ml of EtOH was added dropwise within 1 h to a solution of SeO$_2$ (0.71 g, 6.4 mmol) in 5 ml of pyridine base, 1 ml of DMF, and 1 ml of EtOH while stirring at 55–65°C. The reaction mixture was cooled, the precipitate was filtered off and washed with ethanol and then with ether. Ylides **IIa** and **IIb** were purified by recrystallization from ethanol, ylides **IIc** and **IId**, from DMF.

c. To a solution of 1.14 g (9.3 mmol) of 4-dimethylaminopyridine in ml of a mixture DMF–EtOH, 1:1, was added at stirring 0.94 g (8.5 mmol) of SeO$_2$ at 65°C. After 15 min a crystalline colorless precipitate separated. Then to the dispersion was added dropwise within 1 h a solution of 3.5 mmol of 1,3-indanedione in 4 ml of the same solvent. The reaction mixture was cooled, the precipitate was filtered off and washed with ethanol and then with ether. Ylide **IIe** was purified by recrystallization from ethanol.

Pyridinium dicyanomethylide (Ia). Yield 0.87 g (81%), mp 244–245°C (from acetonitrile) [1]. IR spectrum, cm^{-1}: 2187, 2147 (CN). ^{1}H NMR spectrum, δ, ppm: 7.8 m (3H, H$^{3-5}$), 8.55 d (2H, H^{2,6}, *J* 8.1 Hz). Mass spectrum, *m/z* 144 [*M* + H]$^+$.

3-Methylpyridinium dicyanomethylide (Ib). Yield 0.80 g (68%), mp 212–214°C (from acetonitrile) (publ.: mp 215–218°C [1]). IR spectrum, cm^{-1}: 2187, 2158 (CN). ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H, Me), 7.35 d (1H, H^4, *J* 7.8 Hz), 7.46 t (1H, H^5, J_1 6.5, J_2 7.6 Hz), 8.29 s (1H, H^2), 8.3 d (1H, H^6, *J* 7.6 Hz). Mass spectrum, *m/z* 158 [*M* + H]$^+$.

Pyridinium 2,3-dihydro-1,3-dioxo-1*H*-inden-2-ylide (IIa). Yield 0.42 g (73%), mp 225–227°C (from ethanol) (publ.: mp 257°C [3]). IR spectrum, cm^{-1}: 1622, 1584 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.45 m (2H$_{\text{arom}}$), 7.57 m (2H$_{\text{arom}}$), 7.7 m (2H, H^{3,5}), 7.8 t (1H, H^4, *J* 7.6 Hz), 10.22 d (2H, H^{2,6} *J* 5.9 Hz). Mass spectrum, *m/z* 224 [*M* + H]$^+$.

3-Methylpyridinium 2,3-dihydro-1,3-dioxo-1*H*-inden-2-ylide (IIb). Yield 0.49 g (80%), mp 205–207°C (from ethanol) (publ.: mp 225°C [3]). IR spectrum, cm^{-1}: 3060 (Me), 1651, 1620 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, Me), 7.45 m (2H$_{\text{arom}}$), 7.56 m (2H$_{\text{arom}}$), 7.61 m (2H, H^{4,5}), 9.97 d (1H, H^6, *J* 5.1 Hz), 9.99 s (1H, H^2). Mass spectrum, *m/z* 238 [*M* + H]$^+$.

Pyridinium 2,3-dihydro-1-dicyanomethylene-3-oxo-1*H*-inden-2-ylide (IIc). Yield 0.49 g (70%), mp 305–307°C (from DMF). IR spectrum, cm^{-1}: 2205 (CN), 1628 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.55 m (3H$_{\text{arom}}$), 8.12 d (1H$_{\text{arom}}$, *J* 7.1 Hz), 8.23 t (2H, H^{3,5}, J_1 7.5, J_2 6.9 Hz), 8.65 t (1H, H^4, J_1 7.8, J_2 8.1 Hz), 9.06 d (2H, H^{2,6}, *J* 6.6 Hz). Mass spectrum, *m/z* 272 [*M* + H]$^+$.

3-Methylpyridinium 2,3-dihydro-1-dicyanomethylene-3-oxo-1*H*-inden-2-ylide (IIc). Yield 0.51 g (70%), mp 280–282°C (from DMF). IR spectrum, cm^{-1}: 3064 (Me), 2200, 2187 (CN), 1650 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.5 s (3H, Me), 7.56 m (3H$_{\text{arom}}$), 8.11 m (2H, H^{4,5}), 8.49 d (1H$_{\text{arom}}$, *J* 8.1 Hz) 8.88 d (1H, H^6, *J* 6.1 Hz), 8.98 s (1H, H^2). Mass spectrum, *m/z* 286 [*M* + H]$^+$. Found, %: C 75.49; H 3.65; N 14.42. $C_{18}H_{11}N_3O$. Calculated, %: C 75.79; H 3.86; N 14.74. *M* 285.

4-Dimethylaminopyridinium 2,3-dihydro-1,3-dioxo-1*H*-inden-2-ylide (IIe). Yield 0.49 g (53%), mp 282–284°C (from ethanol). IR spectrum, cm^{-1}: 3050 (Me), 1622, 1644 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.18 s (6H, Me), 7.05 d (2H, H^{3,5}, *J* 6.8 Hz), 7.26 m (2H$_{\text{arom}}$), 7.36 m (2H$_{\text{arom}}$) 8.66 d (2H, H^{2,6}, *J* 6.8 Hz). Mass spectrum, *m/z* 267 [*M* + H]$^+$. Found,%: C 71.88; H 5.06; N 10.21. $C_{16}H_{14}N_2O_2$. Calculated, %: C 72.18; H 5.26; N 10.53. *M* 266.

IR spectra were recorded on a spectrophotometer Perkin Elmer Spectrum BX-II from KBr pellets. ^{1}H NMR spectra were registered on a spectrometer Bruker WM-250 at operating frequency 250 MHz in CDCl$_3$, mass spectra were measured on an instrument HP 1100 HPLC/MS in the mode of positive ions registering.

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