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UNUSUAL INTERACTION OF N-PHENACYL-2-CHLORO-PYRIDINIUM YLIDE WITH NITRILES OF THE *trans*-1,3-BUTADIENE SERIES

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The reaction of N-aroylmethylpyridinium ylides, with electron-acceptor groups (CN, COOEt) in position 3, with unsaturated nitriles of the *trans*-1,3-butadiene series **2a,b** occurs as 1,3-dipolar cycloaddition to give substituted tetrahydroindolizines [1, 2]. In the absence of electron-acceptor substituents at position 3 pyridinium ylides react with activated alkenes under typical conditions to form Michael adducts which are stereoselectively transformed into *trans*-1,1-dicyanocyclopropanes with elimination of pyridine [3].

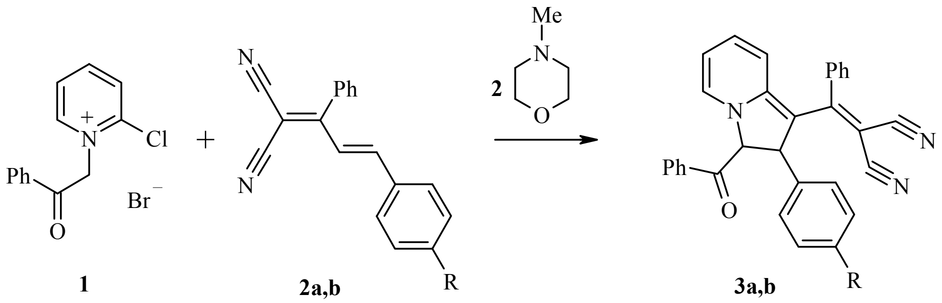
We have established that when N-phenacyl-2-chloropyridinium ylide reacts with *trans*-1,3-butadienes **2a,b** the corresponding 2,3-dihydroindolizines **3a,b** are formed.

N-Phenacyl-2-chloropyridinium ylide was not isolated but was generated *in situ* from N-phenacyl-2-chloropyridinium bromide **1**.

Clearly expressed signals for the H-2 and H-3 protons are observed in the ^{1}H NMR spectra of compounds **3a,b**. The ^3J coupling constants of these protons indicate that they are in the *cis* position.

The elemental analyses of compounds **3a,b** also indicate formation of 2,3-dihydroindolizines.

^{1}H NMR spectra of $CDCl_3$ solutions with TMS as internal standard were recorded on a Varian VRX-200 (200 MHz) instrument, and IR spectra of nujol mulls on an IKS-40 spectrometer.



a R = H, **b** R = Cl

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Butadienes **2a,b** were made by a known method [2].

Preparation of Compounds 3 (General Method). N-methylmorpholine (5.0 mmol) was added with stirring to a suspension of salt **1** (2.5 mmol) and the corresponding butadiene **2** (2.5 mmol) in methanol (10 ml). The mixture was stirred for 3 h. The precipitate formed was filtered off, washed with cold methanol and dried with hexane, and crystallized from acetonitrile.

3-Benzoyl-1-(2,2-dicyano-1-phenylvinyl)-2-phenyl-2,3-dihydroindolizine (3a). Yield 43%; mp 264°C (dec.). IR spectrum, ν, cm^{-1}: 2290 (CN), 2164 (CN), 1696 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.91 (2H, d, *J* = 8.3, H_{arom}); 7.72 (1H, t, *J* = 7.2, H_{arom}); 7.64-7.31 (10 H, m, H_{arom}); 7.26 (1H, s, H_{arom}); 7.10 (3H, m, H_{arom}); 6.50 (1H, t, *J* = 6.8, H-7); 5.76 (1H, d, *J* = 2.6 , H-3); 5.46 (1H, d, *J* = 9.2, H-8); 5.16 (1H, d, *J* = 2.6, H-2). Found, %: C 86.51; H 4.63; N 9.42. $C_{31}H_{21}N_3O$. Calculated, %: C 86.46; H 4.69; N 9.31.

3-Benzoyl-2-(4-chlorophenyl)-1-(2,2-dicyano-1-phenylvinyl)-2,3-dihydroindolizine (3b). Yield 41%; mp 242-244°C. IR spectrum, ν, cm^{-1}: 2292 (CN), 2164 (CN), 1694 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.88 (2H, d, *J* = 7.4, H_{arom}); 7.74 (1H, t, *J* = 7.6, H_{arom}); 7.64-7.32 (9H, m, H_{arom}); 7.26 (1H, s, H_{arom}); 7.20-7.00 (3H, m, H_{arom}); 6.52 (1H, t, *J* = 6.81, H_{arom}); 5.72 (1H, d, *J* = 2.6 , H-2); 5.47 (1H, d, *J* = 9.5, H-8); 5.14 (1H, d, *J* = 2.6, H-3). Found, %: C 76.60; H 4.19; N 8.71. $C_{31}H_{20}ClN_3O$. Calculated, %: C 76.62; H 4.15; N 8.65.

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