DIRECT HETARYLATION OF QUINOXALINE BY N-ACETYL HETEROAROMATIC RADICALS *in situ*

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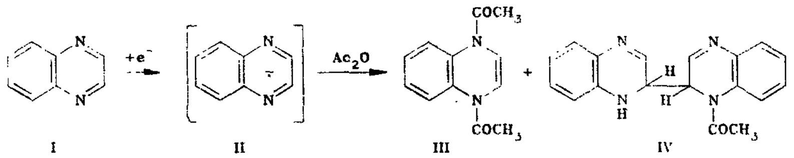
543.422

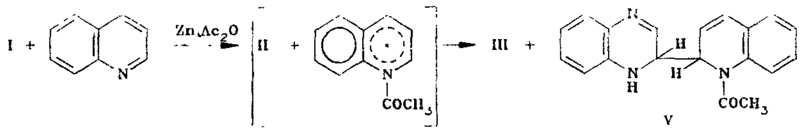
Pyridine bases in acetic anhydride form N-acetyl heteroaromatic cations, readily reduced by zinc dust to the corresponding N-acetyl radicals. The latter are used *in situ* for the production of symmetrical bis-heterocycles [1] or for free-radical hetarylation of nucleophilic organic compounds [2].

We have found that this reaction can also be used for heterylation of π-deficient N-heteroaromatic compounds, after preliminarily converting them to radical anions. For this it is necessary that such compounds be significantly less basic and more readily reduced in comparison with pyridines.

Actually, quinoxaline I does not form an intermediate N-acetyl cation in acetic anhydride in the presence of zinc dust but is reduced, like pyrazine [3], to the radical anion II, which not only is acylated further to 1,4-diacetyl-1,4-dihydroquinoxaline (III) (10% yield) but also dimerizes, followed by partial acylation, forming 1-acetyl-2-(1,2-dihydroquinoxalyl-2)-1,2,-dihydroquinoxaline (IV) (65% yield).



The radical anion of quinoxaline II proved to be a rather nucleophilic substrate for its hetarylation by N-acetylheteroaromatic radicals. Thus, in the reaction of quinoxaline with quinoline under the same conditions, in addition to compound III (8% yield) we obtained 1-acetyl-2-(1,2-dihydroquinoxalyl-2)-1,2-dihydroquinoline (V).



Analogously, in the reaction with isoquinoline we obtained compound III (10% yield) and 2-acetyl-1-(1,2-dihydroquinoxalyl-2)-1,2-dihydroisoquinoline (VI).

Compound III, mp 250°C (from DMFA). IR spectrum (in nujol): 1660 cm^{-1} (C=O). PMR spectrum (in CF$_3$COOH): 2.41 (s, 6H); 7.0-7.5 (m, 4H); 6.6-7.0 ppm (m, 2H). M$^+$ 216. Dimer IV, mp 265-267°C (from ethanol). IR spectrum (in CHCl$_3$): 1590 (C=N), 1660 (C=O), 3340 cm^{-1} (NH). PMR spectrum (in CDCl$_3$): 2.30 (s, 3H); 5.18 (d, 1H, 2'-H, J = 2.6 Hz); 5.24 (d, 1H, 2-H, J = 3 Hz); 6.8-7.6 (m, 8H); 7.70 (d, 2H, 3-H and 3'-H, J = 3 Hz); 14.0 ppm (n, s, 1H, NH). M$^+$ 304. Dimer V, yield 54%, mp 206-208°C (from CCl$_4$). Dimer VI, yield 50%, mp 193-194°C (from CCl$_4$). M$^+$ of V and VI 303. The IR spectra of V and VI are analogous to the spectrum of the dimer IV plus a band at 1620 cm^{-1} (C=C). In the PMR spectra (in CDCl$_3$) of the dimer V and VI, in addition to the signals of the protons of the CH$_3$CO group and the protons of monoazine fragments are observed: 5.16 (d, 1H, 2'-H) in V; 5.00 (s, 1H, 1'-H) in VI; 6.20 and 6.45 (d, 2H, CH=CH, J = 7 Hz) and 6.8-7.2 ppm (M, 4H, arom.) in V and VI.

Elementary analysis of all the compounds corresponds to that calculated.

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REACTIONS OF TETRACYANOETHYLATED KETONES WITH HYDROCHLORIC AND HYDROBROMIC ACIDS.

SYNTHESIS OF 2-CHLORO(BROMO)-3,4-DICYANOPYRIDINES

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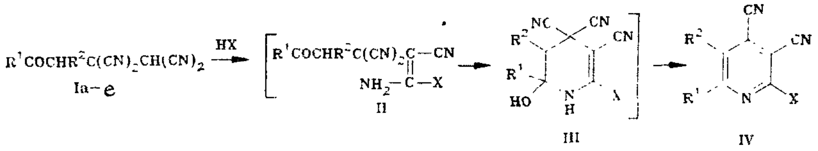
We have discovered that tetracyanoethylated ketones Ia–e [1, 2] react with concentrated aqueous solutions of hydrochloric and hydrobromic acids for 6-120 h at room temperature in an excess of acid, forming 5,6-dialkyl-2-halo-3,4-dicyanopyridines (IVa-e). With hydrobromic acid, the pyridines IV were isolated only with the ketones Ib, e. All the ketones I react with hydrochloric acid. The reaction probably proceeds according to the scheme:



I—IV a $R^1=CH_3$, $R^2=H$; b $R^1=R^2=CH_3$; c $R^1{-}R^2=-(CH_2)_4-$; d $R^1{-}R^2=-(CH_2)_3-$; e $R^1=C_2H_5$, $R^2=H$; X=Cl, Br

The structure of the pyridines IV was confirmed by the IR, ^{13}C NMR, and mass spectra, as well as by chemical conversions. The yield in percent; melting point, °C; and IR spectroscopic data, cm^{-1} (suspension in liquid petrolatum) are cited below for each substance. 5,6-Dimethyl-2-chloro-3,4-dicyanopyridine: 84; 72-74; 2250 (C≡N), 1560, 1538 (arom. ring); 5,6-dimethyl-2-bromo-3,4-dicyanopyridine: 61; 103-104; 2248 (C≡N), 1565, 1537 (arom. ring); 6-methyl-2-chloro-3,4-dicyanopyridine: 73; 98-100; 2242 (C≡N), 1560, 1540 (arom. ring); 5,6-tetramethylene-2-chloro-3,4-dicyanopyridine: 62; 95-96; 2245 (C≡N), 1558, 1540 (arom. ring); 5,6-trimethylene-2-chloro-3,4-dicyanopyridine: 70; 77-79; 2250 (C≡N), 1580, 1553 (arom. ring). All the pyridine derivatives obtained have satisfactory analytical characteristics.

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