Tetrahedron Letters,Vol.30,No.36,pp 4885-4888,1989   0040-4039/89 $3.00 + .00
Printed in Great Britain   Pergamon Press plc

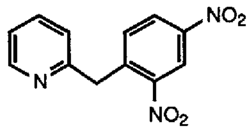
TAUTOMERISM OF 2-(2,4-DINITROBENZYL)PYRIDINE

by Rory A. More O'Ferrall* and Anne P. Quirke

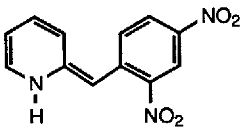
Department of Chemistry, University College, Belfield, Dublin 4, Ireland.

ABSRACT; The Equilibrium constants for imine-enamine and *aci*-nitro tautomerism of 2-(2,4-dinitrobenzyl)pyridine have been determined as 7.5×10^{-9} and $\sim 3 \times 10^{-14}$ respectively.

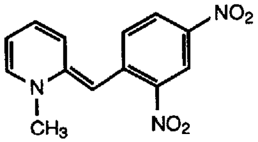
2-(2,4-Dinitrobenzyl)pyridine **1** is a well known photochromic compound first prepared by Tschitschibabin.[1] Its buff-coloured crystals become intensely blue in sunlight and slowly revert to their originial colour in the dark. In solution the blue colour fades rapidly but may be regenerated by flash photolysis. A spectrum has been measured (λ_{max} = 550nm)[2] and its similarity to that of the N-methyl enamine **3** identifies the blue species as the enamine tautomer **2**.[3] Nanosecond flash photolysis further shows that formation of the enamine is preceded by appearance and decay of another short-lived species (τ = 100ns, λ_{max} = 420nm) which is probably the *aci*-tautomer **4** formed via an intramolecular proton shift between the methylene and nitro groups of **1**.[4]



1

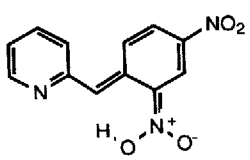


2

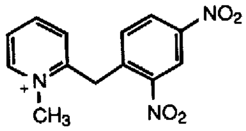


3

As an extension of these measurements we have determined equilibrium constants K_T for the imine-enamine and *aci*-nitro tautomerism of **1**. Rate constants for conversion of the enamine tautomer **2** to imine **1** were measured by Wettermark[5] following flash photolysis of **1** in aqueous acetic acid buffers of buffer ratio ($[AcO^-]/[AcOH]$) =

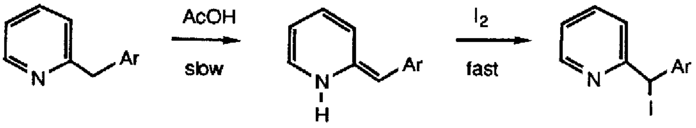


4



5

1.19. Analogy with rate measurements for enolisation of ketones and formation of enamines from phenacylpyridines and quinolines[6] suggested that the rate constant for the reverse reaction might be obtained by trapping the enamine with iodine following rate determining formation from the imine. Combination of these forward and reverse rate constants would yield the imine-enamine tautomeric constant.



SCHEME 1

Reaction of iodine with excess 2-(2,4-dinitrobenzyl)pyridine showed characteristic zero order kinetics* and as expected became reversible at low pH. Plots of first order rate constants against buffer acid concentration in acetic acid buffers at various buffer ratios are shown in the Figure. Combining an apparent rate constant, $2.60 \times 10^{-4} M^{-1} s^{-1}$, for buffer acid catalysis, corrected for protonation of the substrate (pK_a 4.1), with the corresponding value of 3.48×10^4 determined by Wettermark and corrected for ionisation of the enamine ($pK_a = 6.0$, see below) yields a tautomeric constant in aqueous solution at 25° $K_T = [2]/[1] = 7.5 \times 10^{-9}$ ($pK_T = -\log K_T = 8.10$).

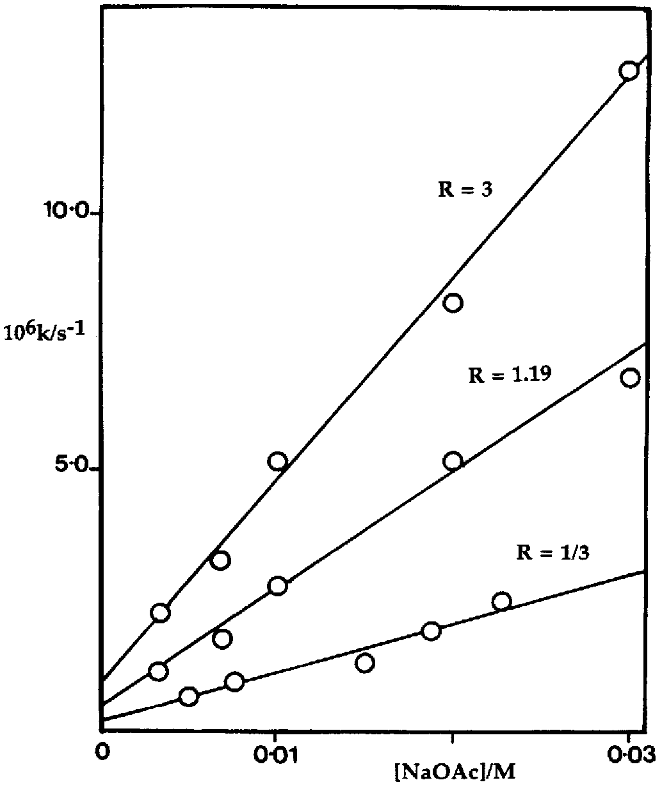


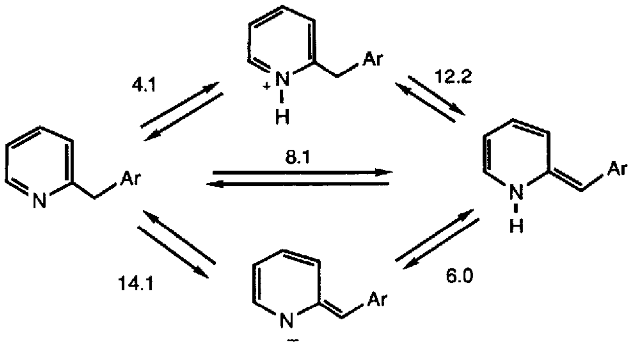
FIGURE - Iodination of 2-(2,4-dinitrobenzyl)pyridine in acetic acid buffers (buffer ratio R = [AcOH]/[AcO$^-$])

---

* The iodinated product was not isolated but the bromo analogue has been reported.[7]

This value of K_T is corroborated by measurement of $pK_a = 11.4$ for ionisation of the N-methylated imine **5** to form the N-methyl enamine **3** in aqueous sodium hydroxide. Assuming that the N-methyl derivative satisfactorily models the N-H enamine the difference between this pK_a and that for ionisation of the protonated imine (4.1) gives an independent measure of the tautomeric constant. The value obtained, $pK_T = 7.3$, is as close to the directly measured value (8.1) as expected of the 'methyl for hydrogen' approximation made.

The $pK_T = 8.1$ for enamine formation from **1** may be compared with corresponding values of $pK_T = 11.9$ for 2-benzylpyridine and 14.0 for 2-picoline.[8] The relative magnitudes of these constants is consistent with the expectation that the enamine tautomer is stabilised by through conjugation of the nitrogen atom with the aromatic ring of the benzyl structures, particularly when these are substituted with nitro groups as in **2**. A pK_a was also measured for ionisation of 2-(2,4-dinitrobenzyl)pyridine in aqueous sodium hydroxide. The value obtained (14.1) and the acid dissociation constant (4.1) may be combined with pK_T to give the corresponding pK_as of the enamine tautomer, and these constants are summarised in Scheme 2.



SCHEME 2

A value of pK_T for formation of the *aci*-tautomer **4** could not be obtained directly. However, the corresponding pK_Ts for 2-nitrotoluene and 2,4-dinitrotoluene may be deduced from measurements of pK_as for ionisation of their nitro- and *aci*-tautomers to yield a common nitronate anion. The pK_a for the nitro tautomer was measured directly by Terrier,[9] and that for the *aci*-tautomer was obtained by Wettermark[10] from the pH profile for tautomerisation of the photochemically generated *aci*-species. The values are listed in the Table, and an approximate pK_T for 2-(2,4-dinitrobenzyl)pyridine may be inferred by noting that although there is a large difference in pK_as between the nitro forms of 2-nitro- and 2,4-dinitrotoluene the difference in pK_as between their *aci*-forms is small. Assuming that this is also true of the nitro and *aci*-forms of **1** the pK_a of the *aci*-form may be obtained as a small extrapolation from that for 2,4-dinitrotoluene by supposing that a rough proportionality exists between nitro- and *aci*-pKas.*

Combining the *aci*-pK_a so obtained (0.6) with the directly measured value of 14.1 for the 2-(2,4-dinitrobenzyl)pyridine imine **1** gives $pK_T = 13.5$. The accessibility of such a small tautomeric constant and of the

---

*An equivalent approximation is that the nitro-pK_as and pK_T s are proportional.

TABLE

Compound	pK_T	pK_a(nitro)[a]	pK_a(*aci*)[b]
2-nitrotoluene	21.3	25	3.7
2,4-dinitrotoluene	14.9	16	1.1
2-(2,4-dinitrobenzyl)pyridine	(13.5)	14.1	(0.6)

[a] Ref 8 and this work [b] Determined from the pH profile for tautomerisation of the photochemically generated *aci*-nitro species.[9]

even smaller values (pK_T = 14.9 and 21.3) for 2,4-dinitro- and 2-nitro-toluenes is remarkable. With respect to the photochromism, the value for 2-(2,4-dinitrobenzyl)pyridine confirms that the *aci*-tautomer is indeed less stable than the enamine ($[4]/[2] \sim 10^{-5}$), and this is consistent with the suggested photochemical mechanism for formation of the enamine[4] with the *aci*-tautomer as a short-lived intermediate.

REFERENCES

1. A.E. Tschitchibabin, B.M. Kuindishi and S.W. Benewolenskaja, *Ber.*, 1925, **58**, 1580.

2. D. Ben-Hur and R. Hardwick, *J. Chem. Phys.*, 1972, **57**, 2240; J.A. Sousa and J. Weinstein *J. Chem. Phys.*, 1962, **27**, 3155.

3. E. Klemn and D. Klemn, *J. prakt. Chemie*, 1979, **321**, 415.

4. E. Klemn and D. Klemn, *J. prakt. Chemie*, 1979, **321**, 407; E. Klemn, D. Klemn, A. Graness and T. Kleinschmidt, *Chem. Phys. Lett.*, 1978, **55**, 113.

5. G. Wettermark and R. Ricci, *J. Chem. Phys.*, 1963, **39**, 1218.

6. A.R.E. Carey, G. Fukata, R.A. More O'Ferrall and M.G. Murphy, *JCS Perkin Trans II*, 1985, 1711; B. Murray, Ph.D. Thesis, University College Dublin, 1988.

7. E. Klemm, D. Klemm, J. Kleinschmidt and A. Graness, *Z. phys. Chemie, Leipzig,*, 1981, **262**, 621.

8. R.A. Cox, R. Stewart, M.J. Cook, A.R. Katritzky and R.P. Tack, *JCS Perkin Trans II*, 1973, 1080.

9. J. Lelievre, P.G. Farrell and F. Terrier, *JCS Perkin Trans II*, 1986, 333.

10. G. Wettermark, E. Black and L. Dogliotti, *Photochem. and Photobiol.*, 1965, **4**, 229; G. Wettermark and R. Ricci, *J. Chem.Phys.*, 1963, **39**, 1218.

(Received in UK 17 July 1989)