Pyridine Ring-opening in 2,7-Diazabiphenylene by Thiophosgene

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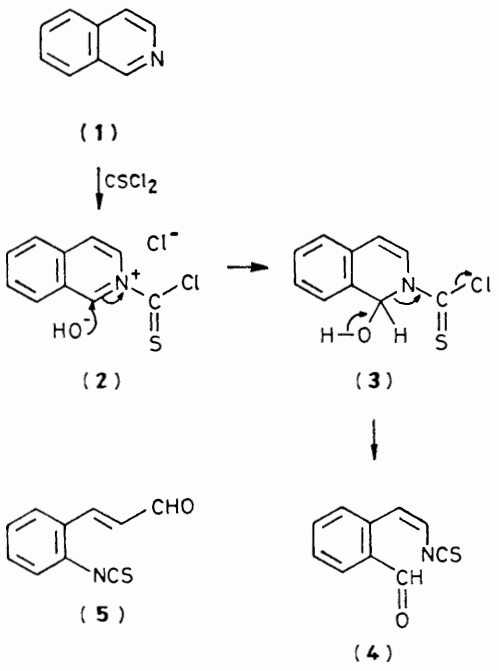
Treatment of 2,7-diazabiphenylene with thiophosgene in the presence of barium carbonate and water gives the cyclobutapyridine derivative (**8**) which was shown by ^{1}H n.m.r. spectroscopy to undergo spontaneous configurational change.

Previous study[1a] has shown that thiophosgene and barium carbonate in a two-phase water–dichloromethane system provides a general method of opening the rings of nitrogen heterocyclic compounds. Isoquinoline (**1**), for example, gives the formyl-isothiocyanate (**4**), a result rationalised by the quaternisation and nucleophilic addition sequence[1b] (**1**) → (**4**), and quinoline gives the cinnamaldehyde (**5**).

It is interesting to apply this reaction to pyridine analogues of biphenylene, particularly diazabiphenylenes such as (**6**), first, because derivatives of the cyclobutapyridine ring system are relatively rare,[2] and secondly because nucleophilic attack on unquaternised examples of diazabiphenylenes by hydroxide ion occurs at a ring junction position and opens the four-membered ring to give pyridyl-pyridones.[3]

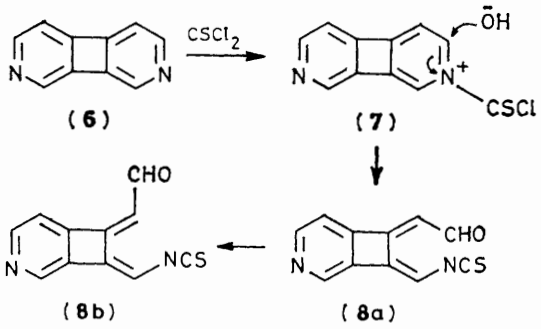
Treatment of a dilute (10 mg/ml) solution of 2,7-diazabiphenylene (**6**) in dichloromethane with a similar solution of thiophosgene (1 mol) at 0 °C in the presence of suspended barium carbonate (5 mol) and an equal volume of water gave



a single product in 60% yield (after filtration, evaporation of the organic phase, and vacuum sublimation), m.p. 157—158 °C (from benzene–cyclohexane).

The structure (**8**) expected from pyridine ring-opening without scission of the four-membered ring by the sequence (**6**) →(**8**) is assigned to this product on the basis of the following data. Micro-analysis and the mass spectrum (*M* 214) correspond to the formula $C_{11}H_6N_2OS$, and the i.r. spectrum (KBr) showed strong bands at 2060 (NCS) and 1666 cm^{-1} (conjugated CHO). The u.v. spectrum (MeOH) gave maxima at 233, 283, 309, and 345 nm with further structure revealed by inflections. The ^1H n.m.r. spectrum ($CDCl_3$, 60 MHz) showed δ 10.18 (d, *J* 5.4 Hz, =CH–C*H*O), 8.75 (m unresolved, pyridine α-protons), 7.57 (d, possibly dd, pyridine β-protons), 6.75 (d, *J* 5.4 Hz, =C*H*–CHO), and 6.60 (s, =CH–NCS).

The ^1H n.m.r. spectrum of the initial reaction product showed additional resonance at δ 10.5 (d, *J ca.* 7 Hz, =CH–C*H*O), and a more complex alkene region, attributable to the isomer (**8a**), which disappeared on standing or chromatography on silica. Since the *trans*-cinnamaldehyde (**5**) was similarly formed spontaneously from its *cis*-isomer while the unsaturated isothiocyanate (**4**) did not isomerise[1b] we infer that the final product has the configuration (**8b**).



The diene (**8**) is stable to air but discolours rapidly on exposure to light. 1,8-Diazabiphenylene reacts with thiophosgene under similar conditions but no distinct product could be isolated or detected by t.l.c.

It is interesting to note that whereas nucleophilic attack on the isoquinoline intermediate (**2**) occurs at C-1 the corresponding point of attack on the quaternised 2,7-diazabiphenylene (**7**) is C-3, in accordance with the positions of higher double-bond character in the naphthalene and biphenylene[4] π-systems. It is also noteworthy that the shifts of the pyridine-ring proton resonances in the cyclobutapyridines (**8**) are the usual pyridine values. The up-field shifts observed in 2,7-diazabiphenylene (**6**),[4] and other biphenylenes, are, therefore, associated with the biphenylene system rather than with the effect[5] of valence angle distortion at the ring-junction atoms which must remain in the ring-system of (**8**).

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References

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2 See for example, J. M. Riemann and W. S. Trahanovsky, *Tetrahedron Lett.*, 1977, 1867 and references therein; K. J. Gould, N. P. Hacker, J. F. W. McOmie, and D. H. Perry, *J. Chem. Soc., Perkin Trans.* 1, 1980, 1834; C. Kaneko, T. Naito, Y. Momose, H. Fujii, N. Nakayama, and I. Koizumi, *Chem. Pharm. Bull.*, 1982, **30**, (2), 519.

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5 For the effect of hybridisation changes at the ring-junction atoms of 1,6-diazabiphenylene and related compounds see J. A. H. MacBride, P. M. Wright, and B. J. Wakefield, *Tetrahedron Lett.*, 1981, 4545 and references therein.