Synthesis of Pyridines by Thermolysis of 4a,7a-Dihydrocyclopenta[*e*][1,2]oxazines

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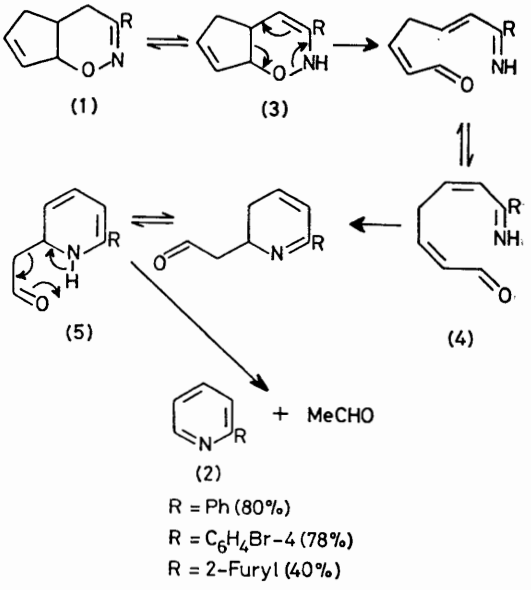
Summary The dihydro-oxazines (**1**) are converted into pyridines (**2**) when they are heated at 200 °C, whereas the benzo-derivative (**7**) gives 2-naphthyl phenyl ketone; a mechanism is proposed which involves electrocyclic opening of the oxazine rings.

CYCLOPENTADIENE reacts with α-halogenoketoximes in the presence of sodium carbonate to give, in high yield, adducts having the structure (**1**).[1] We find that the oxazine derivatives (**1**) can be converted into 2-arylpyridines (**2**) when they are heated† at 200 °C; acetaldehyde is also detected as a product of the reaction. The sequence thus represents a simple two-stage preparation of 2-arylpyridines from cyclopentadiene.

The rearrangement may take place by electrocyclic ring-opening of the tautomers (**3**) (Scheme). The unsaturated imines (**4**) can then cyclise in the manner shown, and acetaldehyde can be eliminated from the dihydropyridines (**5**) in a retro-ene process. An alternative mechanism involving the initial homolysis of the N–O bond was ruled out because the dihydroisoxazole (**6**)[2] proved to be stable when heated at 200—250 °C.

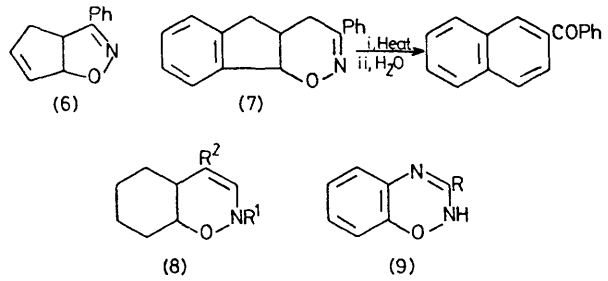
Indene also gives a cycloadduct (**7**) (26%), m.p. 140—143 °C, with α-chloroacetophenone oxime in the presence of



SCHEME

† The oxazines were heated in the melt for 15 min at 200 °C; the pyridines were then distilled out and were characterized as their picrates.

sodium carbonate.‡ Pyrolysis of the adduct (**7**) at 200 °C and separation of the products by chromatography on silica gave 2-naphthyl phenyl ketone (32%). The isolation of this ketone is in accord with the mechanism shown in the Scheme because the extra benzene ring in (**7**) prevents the cyclisation of the unsaturated imine intermediate, which instead is hydrolysed and dehydrated during the isolation procedure.



(6) (7) (8) (9)

These reactions are closely analogous to two other ring-cleavage reactions which have previously been reported; the mild thermal ring-opening of 2-alkyldihydro-oxazine derivatives such as (**8**),[3] and the thermolysis of 1,2,4-benzoxadiazines (**9**).[4]

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‡ We suggested earlier (ref. 1) that the oxazines (**1**) might be formed by cycloaddition of cyclopentadiene to the carbon–carbon double bonds of nitroso-alkene intermediates, followed by a [3,3] shift. In view of the fact that indene also forms an adduct, this mechanism now seems less likely than a direct cycloaddition in which cyclopentadiene acts as a monoene, and the nitroso-alkenes as dienes. Some azo-alkenes have also recently been observed to add to simple alkenes (S. Sommer, *Tetrahedron Letters*, 1977, 117).

[1] R. Faragher and T. L. Gilchrist, *J.C.S. Chem. Comm.*, 1976, 581.
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[3] P. Gygax, T. K. Das Gupta, and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 2205.
[4] T. L. Gilchrist, C. J. Harris, M. E. Peek, and C. W. Rees, *J.C.S. Chem. Comm.*, 1975, 962.