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1-VINYLPYRROLES

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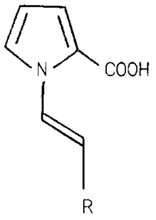
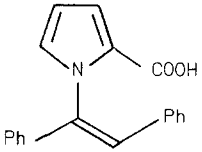
Although alkylations of pyrrole salts are well documented[1] few reactions with epoxides are known. Potassium pyrrole and ethylene oxide yield 1-(2-hydroxyethyl)pyrrole[2], whereas pyrrole magnesium chloride and the epoxide give a mixture of the 2- and 3-substituted isomers[3]. 2-Cyano-5-nitropyrrole and ethylene oxide undergo a cyclisation reaction to produce 1-imino-5-nitro-3,4-dihydropyrrolo [2,1-*c*] - [1,4] oxazine[4] and 2-acyl-5-nitropyrroles and this epoxide yield 5-acyl-2,3-dihydropyrrolo [2,1-*b*] oxazoles[5] *via* intramolecular nucleophilic substitution of the nitro group. We now report some reactions of potassium methyl pyrrole-2-carboxylate with epoxides which yield 1-vinylpyrroles under mild conditions[6].

Potassium methyl pyrrole-2-carboxylate and styrene oxide in dry DMF under nitrogen at room temperature (18h) yielded *trans*-1-styrylpyrrole-2-carboxylic acid (1;R=Ph) m.p. 178-179°. The configuration of this acid was shown by ^{1}H n.m.r. (CH=CH, J= 14Hz) and UV spectra (λmax 302 nm, εmax 20,900) and by photochemical isomerisation by irradation at 350 nm to yield *cis*-1-styrylpyrrole-2-carboxylic acid, m.p. 131-133° (CH=CH, J= 8.5Hz; λmax 270nm, εmax 12,900).



(1)



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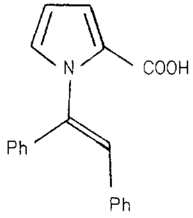
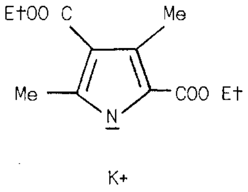


(3)

In similar reactions with the pyrrole anion ethylene oxide yielded 1-vinylpyrrole-2-carboxylic acid (2;R=H) m:p. 137-138°, propylene oxide gave *trans*-1-(2-methylvinyl)-pyrrole-2-carboxylic acid (1;R-Me) m.p. 152-153° (CH=CH, J=14Hz λmax 267 nm, εmax 12,100), *cis*-stilbene oxide produced 1-(*trans*-1,2-diphenylvinyl)pyrrole-2-carboxylic acid (2) m.p. 193-194° (λmax 299 nm, εmax 25,00), and *trans*-stilbene oxide yielded the *cis*-1,2-diphenylpyrrole isomer (3) m.p. 164-165° (λmax 292 nm, εmax 9,800).



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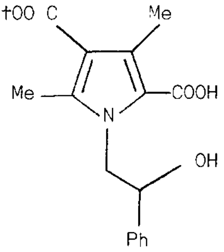

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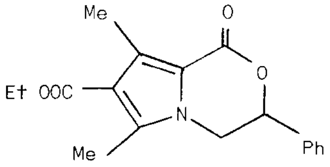
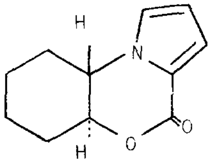


(6)

Under moist conditions the pyrrole anion and styrene oxide yielded 1-(2-hyroxy-2-phenylethyl)pyrrole-2-carboxylic acid, m.p. 161-163° (νc=o 1670 cm^{-1}), which yielded 1H-3-phenyl-3,4-dihydropyrrolo[2,1-*c*]-[1,4] oxazin-1-one, m.p. 111-112° (νc=o 1710 cm^{-1}), on treatment with polyphosphoric acid. The potassium salt of Knorr's pyrrole (4) and styrene oxide also yielded a pyrrole alcohol acid (5) m.p. 153-154° ($\nu_{c=o}$ 1700 and 1670 cm^{-1}) which cyclised (PPA) to yield the lactone (8) m.p. 180-181° ($\nu_{c=o}$ 1700 cm^{-1}).

This selective hydrolysis of the 2-ester group suggests the involvement of a neighbouring-group effect, possibly lactone formation,[7] assisting both the hydrolysis and elimination reactions. This view is supported by the isolation of the lactone (7) m.p. 128-129° ($\nu_{c=o}$ 1700 cm^{-1}) from the reaction of the pyrrole anion and cyclohexene oxide. It is interesting to note that the stereochemistry in this instance is unfavourable for an elimination reaction to occur.



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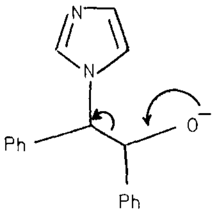

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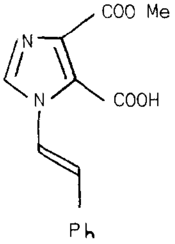

(9)

Experiments in other systems complement these results. Thus potassium imidazole and styrene oxide yielded 1-(2-hydroxy-2-phenylethyl) imidazole, m.p. 151-152°, which proved difficult to eliminate. *Cis*- and *trans*-stilbene oxides gave the corresponding *threo*-, m.p. 171-172°, and *erythro*-alcohols, m.p. 171-172° (mixed m.p. depressed) at room temperature. Reaction of the stilbene oxides with potassium imidazole at 100° or treatment of the alcohols with sodium hydride resulted in the elimination (8) of benzaldehyde to yield 1-benzylimidazole. Potassium benzimidazole and styrene oxide yielded 1-(2-hydroxy-2-phenylethyl) benzimidazole, m.p. 106-107°.

The presence of an ester group in the imidazole favoured olefin formation and potassium dimethyl imidazole-4,5-dicarboxylate and styrene oxide gave the 1-styryl acid ester (9), m.p. 164-165°, (CH=CH, J=15Hz; νc=o 1725 cm^{-1}).

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