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IODOCYCLISATIONS OF ALLYL- AMIDINES AND -UREAS

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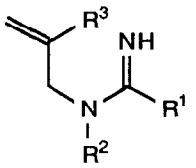
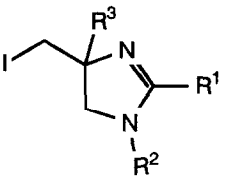
Summary: Iodocyclisation of allyl-amidines (**1**) and -ureas (**4**) gives imidazolines (**2**) and imidazolinones (**5**) respectively; in contrast, bromocyclisation of the amidine (**1a**) results in formation of the six-membered ring (**3**).

The continuing interest in halogen mediated cyclisations of nitrogen containing functional groups onto neighbouring carbon carbon double bonds[1-4] prompts us to report some of our own results in this area. In connection with our work on new methods of imidazole synthesis,[5] we chose to investigate the halocyclisation of allyl-amidines and -ureas as a route to imidazolines and imidazolinones, protected versions of vicinal diamines.

Although there are isolated reports of cyclisation of allyl amidines,[6,7] these reactions have not been investigated in detail. We now find that *N*-allyl-benzamidines and -trichloroacetamidines, easily prepared from the corresponding allylamines and benzonitrile or trichloroacetonitrile,[8,9] cyclise readily on treatment with iodine or *N*-iodosuccinimide (NIS). Thus treatment of *N*-allylbenzamidine (**1a**) with NIS in tetrahydrofuran (THF) gave the 4-iodomethyl-2-phenylimidazoline (**2a**) in 73% yield. The imidazoline (**2a**) readily loses HI to form the aromatic 4-methyl-2-phenylimidazole, although in the case of the imidazoline (**2b**), formed (76%) by iodocyclisation of the amidine (**1b**), this facile elimination is blocked. The iodocyclisation of the *N*-allyl trichloroacetamidines (**1c**), (**1d**), and (**1e**) was best effected using iodine and pyridine in THF rather than NIS, and resulted in the formation of the corresponding 2-trichloromethylimidazolines (**2c**) (88%), (**2d**) (86%), and (**2e**) (65%). Surprisingly when the halocyclisation of *N*-allylbenzamidine (**1a**) was carried out using *N*-bromosuccinimide the product was not the 4-bromomethylimidazoline corresponding to (**2a**), but rather the six-membered bromotetrahydropyrimidine (**3**) (88%), possibly indicating a change in reaction mechanism.



(1)



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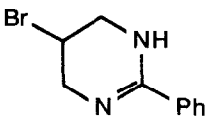
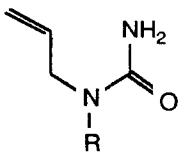


(3)

a, R^1 = Ph, R^2 = R^3 = H; **b**, R^1 = Ph, R^2 = H, R^3 = Me; **c**, R^1 = CCl_3, R^2 = R^3 = H;
d, R^1 = CCl_3, R^2= H, R^3 = Me; **e**, R^1 = CCl_3, R^2 = Me, R^3 = H.

In order to convert the allylureas (**4**), prepared by reaction of the corresponding allylamines with trimethylsilyl isocyanate, into the imidazolinones (**5**), prior silylation is necessary to prevent cyclisation occurring on oxygen.[3,4] Thus treatment of the urea (**4a**) with trimethylsilyl trifluoromethanesulphonate (2 equiv) and triethylamine (2.2 equiv) in dichloromethane, followed by reaction of the crude product with iodine in THF gave the 4-iodomethylimidazolin-2-one (**5a**) (83%). Similarly the allylurea (**4b**) gave the imidazolinone (**5b**) (71%).



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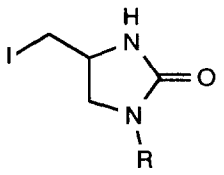

(5)

a, R = Me; **b**, R = CH_2Ph

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