Asymmetric Induction in Addition of *N*-Nitrenes to Alkenes: 2-(Chiral)-substituted Benzimidazole-derived *N*-Nitrene Additions to Alkenes

Robert S. Atkinson and Gary Tughan
Department of Chemistry, University of Leicester, Leicester LE1 7RH

Oxidation of the optically active 1-aminobenzimidazoles (**5**)—(**7**) with lead tetra-acetate in the presence of various prochiral alkenes yields mixtures of the diastereoisomeric aziridines with little asymmetric induction (Table). Oxidation of the racemic 1-amino-2-(1,2,2-trimethylpropyl)-1*H*-benzimidazole (**12**) in the presence of α-methylene-γ-butyrolactone (**1**) yields the stereoisomeric aziridines (**16**) in a 5.5:1 ratio, and oxidation in the presence of γ,γ-dimethyl-α-methylene-γ-butyrolactone (**18**) gives the aziridine (**19**) stereospecifically. The stereochemistry of (**19**) was determined by *X*-ray crystallography.

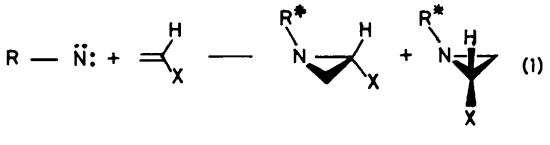
A rationalisation for the stereospecificity of addition of the intermediate *N*-nitrene, produced by oxidation of (**12**) to the lactone (**18**), is given in terms of competitive reaction *via* two different transition states both of which lead to the same sense of chiral induction (Scheme 5).

Significant asymmetric induction is also found in the addition of the nitrene derived from oxidation of (**12**) to (*E*)-but-2-ene (5.2:1 ratio of stereoisomers) and styrene (5.6:1 ratio of stereoisomers).

The epoxidation of double bonds by peracids is a widely used method in synthesis. Invariably the epoxide is prepared only to be ring-opened and the derived product further manipulated. Since epoxide ring-opening can be regio- and stereo-specific, the overall transformation is a versatile and controlled functionalisation of the original double bond. *Complete* stereocontrol in this functionalisation, however, can be claimed only when epoxidation of prochiral double bonds is facially specific: in the ideal and simplest case, epoxidation of a prochiral alkene could be directed to produce either enantiomer of the chiral epoxide. Whilst this goal seems at present some way off (even using microbiological assistance [1]), Sharpless *et al.*[2] have introduced a titanium alkoxide tartrate catalyst for epoxidation of allylic alcohols to α-hydroxy epoxides in high enantiomeric excess. The frequency with which this method is now used in (chiral) synthesis is a testimony both to its reliability and also to the need for such a method.

By contrast, the nitrogen analogue of epoxidation—'aziridination'—is hardly used as a general synthetic method although aziridines themselves have the same desirable feature as epoxides as synthetic relay intermediates, *viz.* susceptibility to ring-opening in a controlled way. Aziridination can, of course, be accomplished by nitrene insertion into (addition to) π-bonds although the intermolecular version of this reaction is possible with relatively few nitrenes.[3] The characteristic reactivity of this latter nitrene class does not, in any case, commend them for use in synthesis of aziridines; their highly reactive nature often results in competitive insertion into σ- and π-bonds and their discrimination in reacting with different π-bonds is poor. Moreover, insertion into π-bonds at low concentrations of the latter may be complicated by intervention of the triplet state of the nitrene and consequent non-stereospecific formation of aziridines.

In principle, one could conceive of using the substituent R of a nitrene R–N to advantage in cycloaddition to a prochiral alkene.



If R* is chiral, the two aziridines are diastereoisomeric [equation (1)]; if R*–N can be generated in optically active form and if discrimination between the two faces of the double bond is sufficient, a single optically active aziridine will be produced.

There is, however, little by way of precedent for the conversion given in equation (1). The reactions of free carbenes and nitrenes are usually interpreted as involving early transition states and consequently a reduction in the free energy difference between the two diastereoisomeric transition states would be expected. In practice, significant asymmetric induction in the reactions of free carbenes or nitrenes has not been reported although the reactions of chiral *carbenoids* can show high levels of such induction.[4]

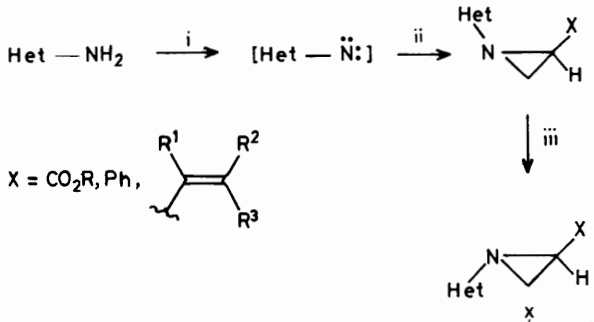
There is a family of *N*-nitrenes whose members show almost complementary behaviour to that more commonly associated with nitrenes as reactive intermediates.[5] Thus this family of *N*-nitrenes, which invariably has the nitrogen N-2 (attached to the nitrene N-1) as part of a heterocyclic ring, (a) have singlet ground states and consequently always insert stereospecifically into π-bonds, (b) do not insert into σ-bonds, (c) show selectivity in competitive insertion into different π-bonds, (d) insert into π-bonds substituted either by electron-donating or electron-withdrawing groups (or both), and (e) show stereospecific formation of a single pyramid at the aziridine ring nitrogen in their addition to mono substituted alkenes ('*syn*-selectivity').[6,*]

The single nitrogen pyramid formed in (e) is, unexpectedly, that with the heterocyclic group and the substituent (from the alkene) *cis* although the barrier to inversion at nitrogen in the aziridine dictates that this kinetically formed pyramid is converted into the thermodynamically preferred *trans*-isomer on warming above ~0 °C (Scheme 1).

To account for this '*syn*-selectivity', an attractive *secondary interaction* between the heterocycle and the alkene substituent in the transition state for nitrene addition was proposed.[6] This is illustrated in Figure 1 for the particular case of phthalimido-nitrene addition to methyl acrylate.

In this transition-state geometry (TSG), the αβ-unsaturated

* Throughout this paper, the stereochemistry of the aziridine ring is classified as either *cis* ('*syn*') or *trans* ('*anti*').



Scheme 1. *Reagents and conditions:* i, LTA, < -20 °C; ii, $\overset{X}{=\!\!/}$, < 20 °C; iii, > 0 °C

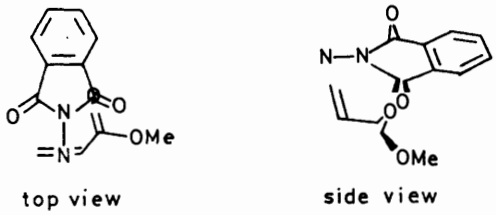


Figure 1.

ester is shown to be reacting *via* its s-*cis* conformation. We have found that whereas the α-methylene-γ-butyrolactone (**1**) reacts normally with *N*-nitrenes (see below) no aziridine was isolated or detected when the butenolide (**2**), in which the ester is fixed in the s-*trans* conformation, was used as a trap.

(**1**) (**2**)

Further evidence for the TSG shown in Figure 1 derives from studies on intramolecular *N*-nitrene additions which support an orthogonal approach of the N–N bond of the nitrene to the C=C bond of the alkene.[7]

The TSG illustrated in Figure 1 leads directly to the single nitrogen pyramid which is the kinetically formed product of the nitrene addition to methyl acrylate. Other monosubstituted alkenes, *e.g.* styrene and butadiene, react similarly with phthalimido and other heterocyclic *N*-nitrenes in this family: in every case examined, the heterocycle and alkene substituent are *cis* in the kinetically formed product.

Although the precise nature of the attractive interaction between the heterocycle and the alkene substituent cannot at present be specified, the compact nature of the proposed transition state involved (Figure 1) suggested to us that it might be possible to bring about asymmetric induction in addition of these *N*-nitrenes to alkenes. Two heterocycles which appeared to be particularly well suited to test this possibility were the *N*-aminoquinazolinone (**3**) and *N*-aminobenzimidazole (**4**)

(**3**) (**4**)

since both have positions α to the *N*-amino function to which a chiral substituent R* could be attached. Thus, using a TSG for benzimidazolyl nitrene addition to an α,β unsaturated ester analogous to that shown in Figure 1 would result in asymmetric induction if the chiral substituent at position 2, R*, were able to bring about discrimination in the addition of the nitrene between two faces of a (prochiral) alkene. These two diastereoisomeric transition states are illustrated in Figure 2, from which it is clear that the sense of chiral induction, *i.e.* which face of the prochiral αβ-unsaturated ester is attacked, will depend on the better 'fit' of the chiral substituent with the OR function of the ester. Implicit in the TSG depicted in Figure 2 is the assumption

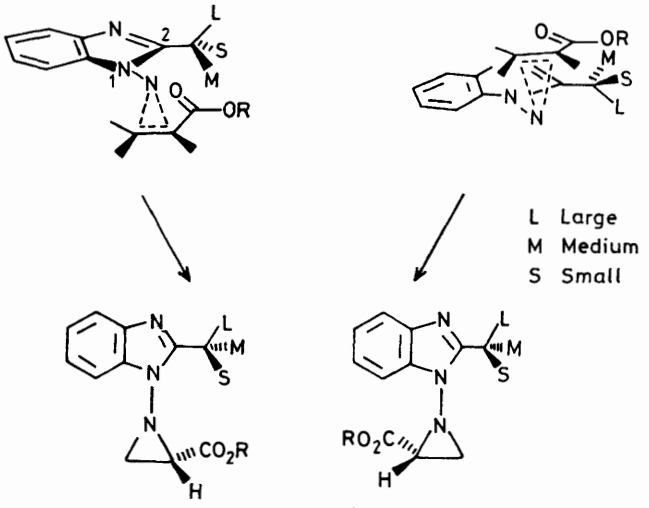


Figure 2.

that it is the 2-position of the benzimidazole ring which interacts secondarily with the ester and not the alternative position α to the N-1 ring nitrogen.

We elected to study first aziridination using *N*-nitrenes derived from oxidation of *N*-aminobenzimidazoles bearing chiral substituents in the 2-position: addition of the nitrenes derived by oxidation of similarly substituted *N*-aminoquinazolinones to prochiral alkenes are reported in the following papers.

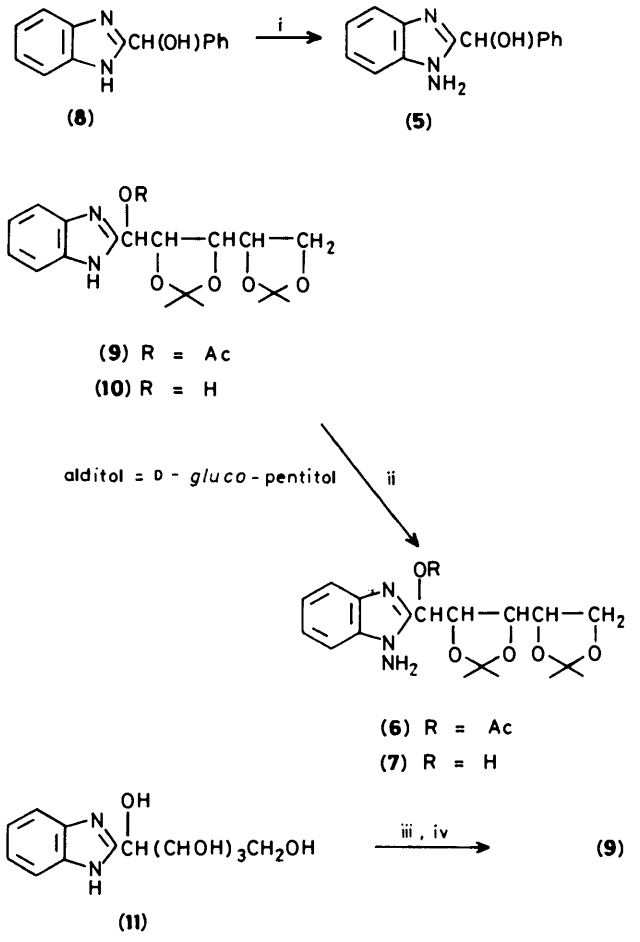
Our initial experiments † were carried out using the *N*-aminobenzimidazoles (**5**), (**6**), and (**7**), prepared in each case by amination of the corresponding benzimidazoles (**8**), (**9**), and (**10**).

The benzimidazoles (**9**) and (**10**) were obtained by reaction of D-gluconic acid and *o*-phenylenediamine using the Phillips method for formation of the benzimidazole ring system (**11**),[8] followed by acetalisation and acetylation.

Reactions of the nitrenes derived from (**5**), (**6**), and (**7**) with various prochiral alkenes, *e.g.* methyl acrylate, 2,3-dimethylbutadiene, and styrene, gave good yields of the corresponding aziridines and the addition did, in most cases, proceed with some asymmetric induction. From examination of the crude reaction mixture by n.m.r. spectroscopy at high field (400 MHz), the presence of the two diastereoisomers was easily distinguishable in every case. The degree of asymmetric induction, however, was disappointingly low (Table) and in no case were the two (non-crystalline) diastereoisomers separable by chromatography.

We supposed that the level of induction might be enhanced if R* at the 2-position of the benzimidazole was selected for the maximum disparity in size between its constituent groups, and

† Details of earlier preliminary experiments in this area (R. S. Atkinson, J. R. Malpass, and K. L. Woodthorpe) are given in the thesis of K. L. Woodthorpe, Leicester University, 1983.



Reagents: i, NH_2OSO_3H, KOH; ii, $NH_2OSO_2C_6H_2Me_3$-2,4,6, $CHCl_3$; iii, $(HOCH_2)_2$, H^+; iv, Ac_2O–pyridine

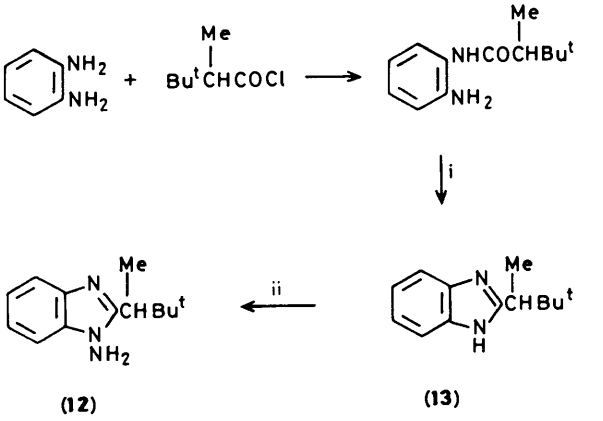
Table. Ratio of aziridine diastereoisomers from oxidation of *N*-aminobenzimidazoles (**5**), (**6**), and (**7**) in the presence of alkenes (from 400 MHz spectra of the crude reaction products)

	N-Aminobenzimidazole		
Alkene	(5)	(6)	(7)
Methyl acrylate	2.0:1	1.1:1	3.6:1
2,3-Dimethylbutadiene	1.4:1	1.2:1	1.4:1
Styrene		1.7:1	1.05:1

thus we elected to synthesize the amine (**12**) since, in this case, simple steric interactions would be likely to control which face of the prochiral alkene was vulnerable to attack by the nitrene (Figure 2).

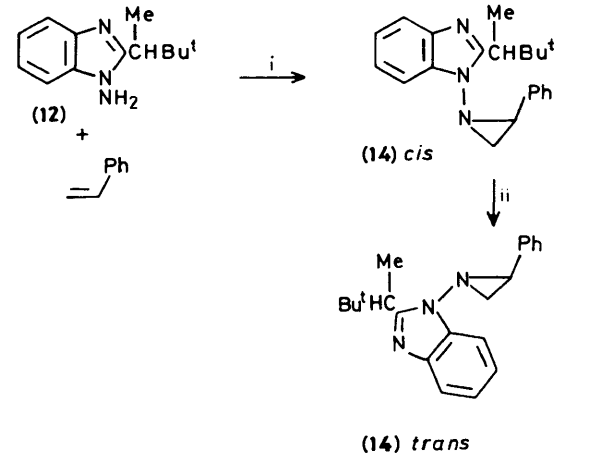
This *N*-aminobenzimidazole (**12**) proved to be more difficult to make than others reported in this paper. Reaction of 2,3,3-trimethylbutyric acid with *o*-phenylenediamine in hydrochloric acid—the Phillips method[8]—gave none of the benzimidazole (**13**). This heterocycle was eventually obtained by the route shown in Scheme 2 which may be of general applicability for 2-substituted benzimidazole synthesis when the Phillips method fails.

The most inefficient step in Scheme 2 was the amination of compound (**13**): the crude amination product (**12**) (~ 50% yield) was freed from the accompanying unchanged benzimidazole (**13**) only after careful chromatography and with considerable loss, although the amine (**12**) when pure is crystalline and stable.



Scheme 2. *Reagents:* i, $POCl_3$–pyridine; ii, $NH_2OSO_2C_6H_2Me_3$-2,4,6, CH_2Cl_2

Oxidation of the *N*-aminobenzimidazole (**12**) in styrene at −20 °C and examination of the solution by n.m.r. without any intermediate warming of the solution showed clearly that only the *cis*-invertomer of the aziridine (**14**) was present. Allowing the solution to warm to ambient temperature resulted in complete inversion to the *trans*-form of (**14**).*

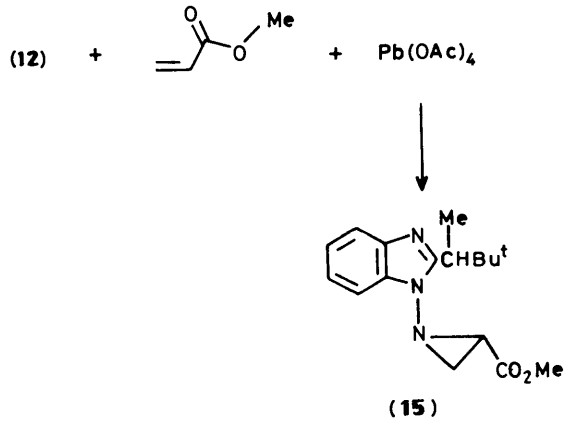


Reagent and conditions: i, LTA, −20 °C; ii, +20 °C

It is clear therefore that this benzimidazole (**12**) shows the same '*syn*-selectivity' as other heterocycles in this family[6] and hence that conditions for bringing about asymmetric induction are present.

Oxidation of amine (**12**) was carried out at room temperature with methyl acrylate as the trap. From examination of the crude reaction mixture by n.m.r. spectroscopy at 400 MHz, the ratio of stereoisomeric aziridines (**15**) present was 2.1:1 (Scheme 3). With the exception of the benzimidazole aromatic ring protons, all the protons in the n.m.r. spectrum of the mixture of stereoisomers of compound (**15**) have non-identical chemical shifts and hence allow multiple checks on the ratio of stereoisomers present. Although, from this point of view, the case of the product (**15**) was particularly favourable, measurement of stereoisomer ratios in this (and the following) paper was never a problem. This was the case even though the spectra of some aziridines (see below) were complicated by the presence of both invertomers at the aziridine ring nitrogen.

* That '*syn*-specificity' obtains in addition of simple benzimidazoles to monosubstituted alkenes was previously demonstrated in the thesis by H. L. Woodthorpe (see above).



Scheme 3.

There is good evidence that the preferred conformation for methyl esters is that in which the Me–O bond is *cis* to the C=O bond.[9] If this conformation is assumed to be also the preferred one for methyl acrylate (as drawn in Scheme 3), then it seemed to us that this might account for the poor level of asymmetric induction in the formation of ester (**15**). This can best be seen by taking into account the TSG for nitrene addition to the acrylate (*cf.* Figure 2). A model for this addition is depicted in Figure 3 in

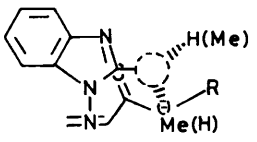


Figure 3.

which the t-butyl substituent is represented by the dotted circle (*not* to any scale) projecting *towards* the viewer and the other two substituents of the chiral group R* (H and Me) are therefore directed towards the acrylate which lies in a plane below that of the benzimidazole as shown. Inspection of Figure 3 suggests that the R group of the ester is 'sandwiched' between the H and the Me or R*. It is not clear, therefore, which position will be assumed by the methyl and which by the hydrogen (the relative configuration of chiral centres in the major stereoisomer produced is not known). Significant induction, therefore, would not be expected since, according to this model, it is ultimately whether the two sites for this methyl and hydrogen are differentiated enough which determines which face of the (prochiral) acrylate is attached by the nitrene.

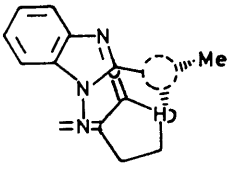
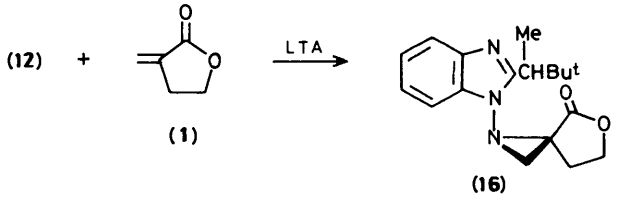


Figure 4.

Oxidation of *N*-aminobenzimidazole (**12**) in the presence of α-methylene-γ-butyrolactone (**1**) was carried out since it appeared that, with this trap, the two preferred sites for the hydrogen and methyl group were clearly identifiable (Figure 4).

The two stereoisomers of the aziridine product (**16**) were formed in a 5.5:1 ratio and the major stereoisomer was obtained pure by crystallisation from chloroform–light petroleum. Repeated crystallisation of more of this major stereoisomer from the mother liquors eventually left a ~1.5:1 mixture of stereoisomers with the aziridine ring protons from the minor stereoisomer resonating at δ 3.68 and 3.35 (d, *J* 1.6 Hz) and the methyl substituent CH*Me*(Bu^t) resonating at δ 1.46 (d, *J* 7 Hz). The fact that enrichment of the minor stereoisomer was possible showed that these species were not conformational isomers (including invertomers: see below).



The major stereoisomer of (**16**) exists as a mixture of two invertomers at nitrogen (ratio 2.2:1). The major invertomer is assigned structure (**16a**) in which the lactone carbonyl oxygen and benzimidazole are *cis*. This assignment is based on the pronounced shielding of one proton of the methylene group of the lactone ring adjacent to the spiro-centre in the *minor* invertomer (**16b**) (Figure 5). Similar shielding effects in analogous *N*-heterocyclic aziridines have been previously reported.[10]

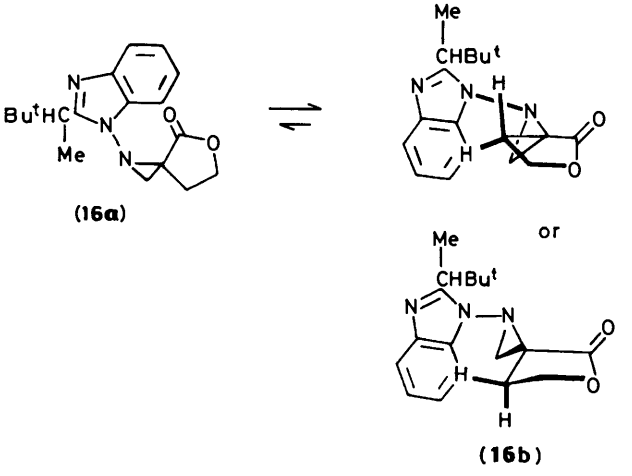


Figure 5.

Whilst the major invertomer (**16a**) shows sharp signals for all protons in its n.m.r. spectrum including two aziridine ring doublets δ 3.7 (d, *J* 1.2 Hz) and 3.19 (d, *J* 1.2 Hz), most signals from the minor invertomer (**16b**) are significantly broadened in $CDCl_3$. This broadening is less for some signals in pyridine but is still present, particularly for the aziridine ring protons.

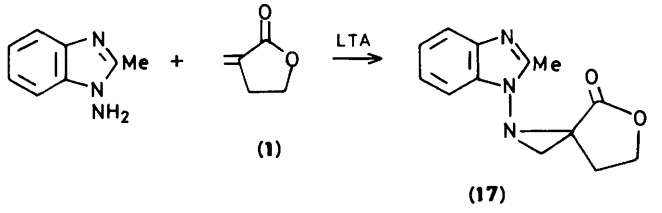
On heating in pyridine, the (separated) t-butyl signals from the two invertomers of (**16**) coalesce to give an approximate Δ*G* of ~19 kcal mol^{-1} for the barrier separating the two nitrogen pyramids. This value is in reasonable agreement with the expected inversion barrier (~21 kcal mol^{-1}) in these *N*-heterocyclic aziridines.[11]

What is the reason for the broadening of the signals in the n.m.r. spectrum of the minor invertomer? We believe that this must be the result of hindred *rotation* in this invertomer around the N–N bond.* Measurement of the spectrum at lower temperatures might have been expected to reveal eventually spectra from the individual rotamers. Although this was not observed for the case of this minor invertomer of (**16**),† the same

* There is evidence for a similar hindered rotation around the N–N bond in N(quinazolinone)-substituted aziridines (see ref. 12).

† This is possibly because of complications from rotation around the benzimidazole (C-2)–CH(Bu^t)Me bond within one rotamer becoming slow on the n.m.r. time-scale at lower temperature.

broadened signals are observed for the minor invertomer in the analogous spiro aziridine (**17**) which lacks the chiral 2-substituent [and hence the stereoisomerism present in (**16**)]. The broadened aziridine ring protons in this minor invertomer do separate into 2 pairs of signals (of non-equal intensity) on cooling to −70 °C in CD_2Cl_2: the aziridine ring protons in the major invertomer also separate into two pairs of signals (of non-equal intensity) at this low temperature.

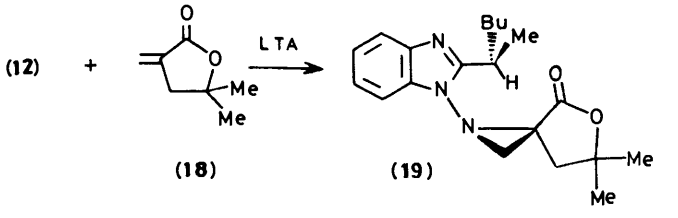


(1) (17)

The fact that the *major* invertomer of (**16**) shows no broadening of its proton signals down to −60 °C does not necessarily imply that the barrier to N–N bond rotation within this invertomer is significantly lower but may indicate that the rotamer equilibrium is wholly on one side.[12]

The significant improvement in asymmetric induction in the formation of lactone (**16**) by comparison with ester (**15**) did appear to provide support for the TSG models in Figures 3 and 4. To demonstrate *complete* asymmetric induction, the *N*-aminobenzimidazole (**12**) was oxidised in the presence of 4,4-dimethyl-2-methylenebutyrolactone (**18**). This modification of the butyrolactone (**15**) was chosen on the reasonable assumption that the *minor* stereoisomer in the formation of (**16**) (ratio of major:minor; 5:1) was the result of addition *via* a TSG resembling that in Figure 4 but with methyl and hydrogen positions reversed.* It was expected that the strategically placed *gem*-dimethyl group of (**18**) would direct the methyl and hydrogen substituents referred to above to occupy exclusively their respective sites as indicated in Figure 4.

In the event, oxidation of the *N*-aminobenzimidazole (**12**) in the presence of the substituted butyrolactone (**18**) gave a single crystalline stereoisomer of the product (**19**).



(18) (19)

There was no evidence from the n.m.r. spectrum of the crude reaction mixture for any of the other stereoisomer: the aziridine ring protons from this (absent) stereoisomer can reasonably be expected to appear in chemical-shift positions close to those of the corresponding protons in the minor stereoisomer of (**16**).

After crystallisation from ethanol, the aziridine (**19**) was isolated in 69% yield as a crystalline solid. The relative configuration at the two chiral centres in this stereoisomer was determined by *X*-ray crystallography and found to be as shown in structure (**19**).[13] This relative configuration is that which would be produced directly from a TSG for the reaction analogous to that shown in Figure 4.

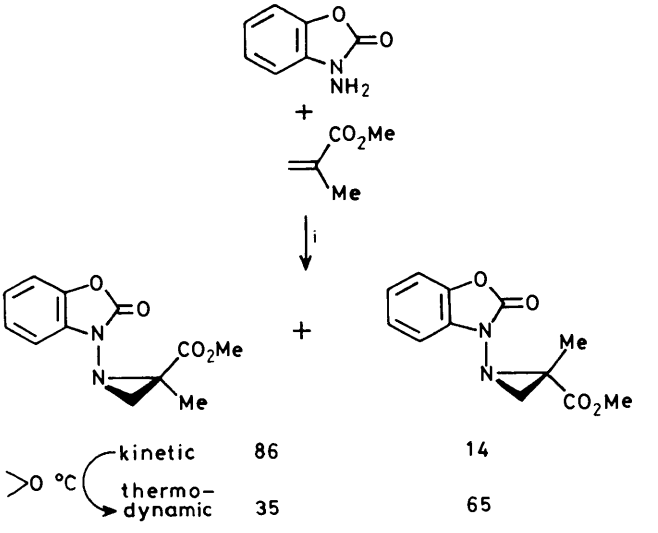
Spiroaziridine (**19**) shows an n.m.r. spectrum with similar features to those present in the spectrum of the parent spirolactone (**16**): both invertomers of (**19**) are present (ratio ~2:1) and peaks from the minor invertomer are broadened at room temperature.

The rate of inversion at the ring nitrogen in these *N*-benzimidazolyl-substituted aziridines is negligible below −20 °C (Scheme 1) and effectively fast at room temperature in solution. The *X*-ray structure determination carried out at room temperature showed the crystal to contain only the invertomer with the lactone carbonyl and benzimidazole *cis*. Inclusion of the aziridine ring into a crystal lattice has been previously shown to retard the rate of nitrogen inversion.[14] It occurred to us that if the crystalline compound (**19**) were dissolved in $CDCl_3$ below −30 °C and its n.m.r. spectrum recorded without any warming of the solution and if the material had all crystallised as a single invertomer (a 'second-order asymmetric transformation')[15] then this would be obvious in the spectrum obtained. Moreover, signals from the other invertomer would appear after raising the temperature of the solution to ambient.

In the event, the recrystallised material which had dissolved at −30 °C in $CDCl_3$ contained *both* invertomers in the ratio 3.5:1 (spectrum run at −40 °C).† Significantly, however, warming the sample to room temperature and then re-recording the spectrum at −40 °C showed a change in invertomer ratio to 2.1:1 which is the 'thermodynamic' equilibrium value (at room temperature; 2.0:1). This behaviour is consistent with an invertomer relationship between the two species of (**19**) which are present in solution with an energy barrier of the expected magnitude separating them.

In the introduction to this paper it was pointed out that addition of this family of *N*-nitrenes to methyl acrylate gives stereospecifically that aziridine invertomer (as the kinetically formed product) in which the heterocycle and ester groups are *cis* (Scheme 1). This '*syn*-stereospecificity', however, does not extend to all heterocycles when a *disubstituted alkene*, *e.g.* methyl methacrylate, is substituted for methyl acrylate although the *selectivity* usually favours a *cis*-relationship between the ester and heterocycle. For example, addition of dihydrobenzoxazolone *N*-nitrene to methyl methacrylate gives an 86:14 ratio of aziridine invertomers as the kinetically formed product (Scheme 4)[6] which changes to a thermodynamically controlled ratio of 35:65 on warming.

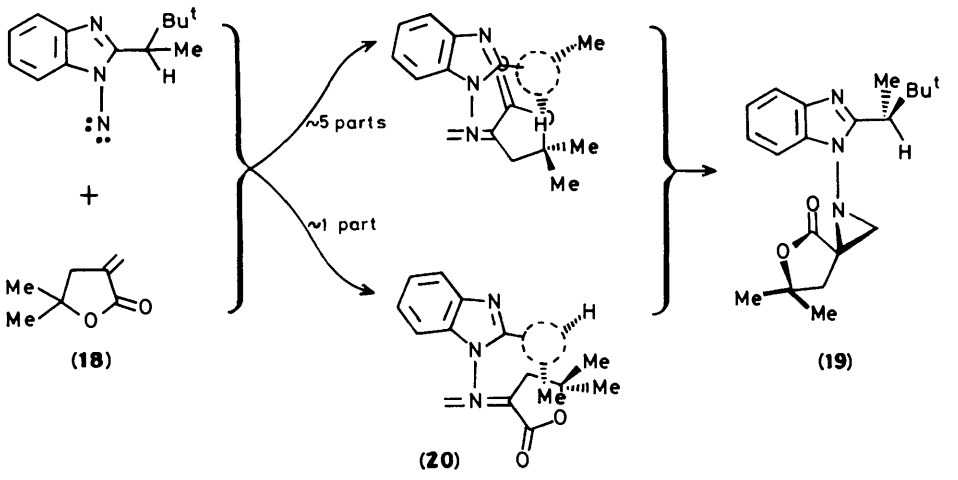
In view of the similarity between *N*-aminodihydrobenzoxazole and *N*-aminobenzimidazole, it seemed possible



Scheme 4. *Reagents and conditions:* i, LTA, −20 °C

* This is equivalent to addition to the opposite face of the lactone shown undergoing addition in Figure 4.

† The crystal selected for the *X*-ray structure determination was evidently a single one of the major invertomer.



Scheme 5.

that addition of the nitrene derived from oxidation of amine (**12**) to butyrolactones might be proceeding, at least in part, *via* a TSG different from that in Figure 4. This, presumably, would be similar to that shown in Figure 6 in which the secondary interaction is between the 3-methylene group of the lactone ring and the 2-position of the benzimidazole.

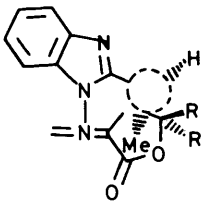


Figure 6.

In practice, this possibility was tested by examination of the *kinetically* formed products of the (**12**)-derived *N*-nitrene additions to butyrolactones (**1**) and (**18**), *i.e.* carrying out the oxidations at a temperature at which the rate of inversion at the aziridine ring nitrogen is negligible.

These experiments have led to some surprising results. Thus oxidation of amine (**12**) in $CDCl_3$ in the presence of (**1**) at −20 °C and examination of the n.m.r. spectrum of the total reaction mixture at −30 °C without any intermediate warming of the solution reveals that *both* invertomers of the major stereoisomer of the aziridine (**16**) are undoubtedly present in a ratio ~5:1, with the major invertomer, as expected, having the lactone carbonyl and benzimidazole *cis*. Warming of the sample to ambient and rerecording of the spectrum at −30 °C results in a growth of the minor invertomer to a thermodynamic ratio of 2.2:1.

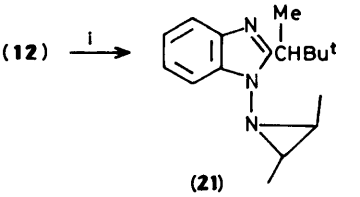
Addition of the nitrene derived from (**12**), therefore, to both faces of the double bond of lactone (**1**) must be occurring mainly *via* TSGs represented by Figures 4 and 6 (R = H). Note that, in Figure 6, a configurational change is necessary at the chiral centre by comparison with Figure 4 if both TSGs are to produce the *same* stereoisomer.*

A similar oxidation of the *N*-aminobenzimidazole (**12**) in the presence of the lactone (**18**) at −20 °C and examination of the spectrum of the product by n.m.r. spectroscopy (at −40 °C) without any intermediate warming of the solution showed that the ratio of kinetically formed invertomers in this case was ~5.3:1 and, predictably, this changed to 2.0:1 (the thermodynamic ratio) after warming the sample to ambient and then rerecording the spectrum at −40 °C.

Addition in this case also, therefore, must be taking place at least to a small extent (1 part in 5) *via* a TSG having the secondary interaction and site occupancy of Me and H shown in Figure 6 (R = Me). The two pathways which lead stereospecifically in this case to (**19**) are shown diagramatically in Scheme 5.*

Support for the site preference of the Me and H as in Figure 6 (R = Me) is available from examination of models of transition state (**20**) (Scheme 5) in which the less encumbered site for the methyl does appear to be that shown.

Trapping of the nitrene derived from amine (**12**) by (*E*)-but-2-ene was found to give a stereoisomer ratio of 5.2:1 from examination of the n.m.r. spectrum of the crude reaction product. The major oily aziridine stereoisomer (**21**) (60%) was freed from the minor isomer by flash chromatography; the relative configuration at the two chiral centres remains to be determined.



Reagents: i, LTA, but-2-ene

Similarly, oxidation of (**12**) in the presence of styrene at room temperature was found to give a 5.6:1 ratio of aziridines (**14**). The major stereoisomer, of as yet unknown relative configuration, was freed from the minor one by chromatography and was isolated in 45% yield. The same ratio of aziridine stereoisomers (**14**) was obtained by oxidation of the *N*-aminobenzimidazole (**12**) with phenyl iodosodiacetate [(diacetoxyiodo)benzene] in dichloromethane and in the presence of

* Since the amine (**12**) is racemic, Figures 3, 4, and 6 represent in each case only one of the two enantiomeric TSGs which together lead to the racemic aziridine. Similarly in Scheme 5 there will be two enantiomeric TSGs to those drawn, which lead to the enantiomer of aziridine (**19**) shown.

styrene at room temperature; the major isomer in this case was isolated in 61% yield. The identity of these ratios is good evidence for the same *N*-nitrene species being an intermediate in both oxidations.

From the examples given in this paper, it is apparent that significant asymmetric induction can be realised in the addition of the *N*-nitrene derived from oxidation of amine (**12**) to a variety of alkenes. This is the first step in a procedure whose objective is the conversion of these alkenes into optically active derivatised adducts. A more efficient synthesis of compound (**12**) in optically active form is just one of the problems which must be solved before such an objective can be achieved.

Experimental

Light petroleum refers to the fraction with b.p. 60—80 °C throughout. α-Methylene-γ-lactone (**1**) (Aldrich) was used as supplied. Silica chromatography was carried out using MN-Kiesegel 60 (CAMLAB). N.m.r. spectra were run at 90 MHz in $CDCl_3$ and i.r. spectra as Nujol mulls unless otherwise indicated. For other general experimental details see refs. 7 and 16.

1-*Amino*-2-(α-*hydroxybenzyl*)-1H-*benzimidazole* (**5**).—2-(α-Hydroxybenzyl)-1*H*-benzimidazole (**8**)[8] (12 g) was heated in a mixture of water (72 ml) and ethanol (40 ml) to 60 °C. Solid potassium hydroxide (17.6 g) was added to the stirred mixture at this temperature, followed by hydroxyamine-*O*-sulphonic acid (14.5 g) while the temperature was kept at 55—65 °C. The mixture was stirred for a further 20 min at 60 °C, then cooled, and the solid was separated. This solid was heated in boiling acetonitrile and the insoluble potassium sulphate was separated. Ice-cooling of the acetonitrile gave the N-*aminobenzimidazole* (**5**) (4.6 g) as a solid, m.p. 157—160 °C (from acetonitrile) (Found: C, 70.25; H, 5.6; N, 17.45. $C_{14}H_{13}N_3O$ requires C, 70.25; H, 5.5; N, 17.55%); δ 7.25 (m, 9 × ArH and OH), 6.16 [s, C*H*(OH)], and 4.49 (br s, NH_2); $\nu_{max.}$ 3 420m, 3 265m, 3 195w, 1 630m, and 1 610 cm^{-1}.

2-(D-gluco-1-*Acetoxy*-2,3:4,5-*di-isopropylidenedioxypentyl*)-1H-*benzimidazole* (**9**).—2-(D-*gluco*-1,2,3,4,5-Pentahydroxypentyl)-1*H*-benzimidazole (**11**)[17] (6 g) was dissolved in dry acetone (120 ml) containing 1% hydrogen chloride. The homogeneous mixture was set aside for 36 h at room temperature then poured into aqueous sodium carbonate (1M; 30 ml). Extraction with ether (2 × 50 ml), drying of the combined ether layers, and evaporation gave a syrup, to which pyridine (66 ml) and acetic anhydride (22 ml) were added, and the mixture was set aside for 2 h at room temperature. After the mixture had been poured into water and set aside for a further 10 min, extraction with ether (70 ml), removal of acetic acid from the extract by cautious washing with aqueous sodium carbonate, drying, and evaporation gave a residual oil, which solidified on addition to ice–water. Crystallisation from ethanol–water gave the *benzimidazole* (**9**) (4.8 g) as crystals, m.p. 181 °C (from ethanol–water) (Found: C, 61.3; H, 6.65; N, 7.1. $C_{20}H_{26}N_2O_6$ requires C, 61.55; H, 6.7; N, 7.2%); δ* 9.70 (br s, NH), 7.73 (m, 1 × ArH), 7.26 (m, 3 × ArH), 6.30 (d, *J* 3 Hz, 1′-H), 4.49 (dd, *J* 7 and 3 Hz, 2′-H), 3.96 (m, 3′- and 4′-H and 5′-H_2), 2.10 (s, MeCO), and 1.36 (4 s, 4 × Me); $\nu_{max.}$ 2 750m, 2 520m, and 1 750s cm^{-1}; *m/z* 390 (M^+), 375, 273, 190, 150, 148, 60, 58, and 43.

Amination of (**9**).—A solution of *O*-(mesitylsulphonyl)-hydroxylamine[18] (0.382 g) in dichloromethane (10 ml) was washed once with ice-cold water and was then added dropwise to a stirred, ice-cooled solution of compound (**9**) (0.66 g) in dichloromethane (40 ml) in which solid sodium hydrogencarbonate (1 g) was suspended. After the addition the mixture was stirred at room temperature for a further 1.5 h and was then extracted with aqueous sodium hydroxide (3M; 20 ml). The organic layer was separated and extracted successively with more aqueous sodium hydroxide (3M; 3 × 20 ml), then with water (2 × 20 ml), dried, and evaporated to yield the aminated product (**6**) (0.081 g), m.p. 130—131 °C (from ether); δ 7.65 (m, 1 × ArH), 7.25 (3 × ArH), 6.35 (d, *J* 6 Hz, 1′-H), 4.80 (s, NH_2), 4.65 (dd, *J* 6 and 12 Hz, 2′-H), 3.90 (m, 3′- and 4′-H, and 5′-H_2), 2.10 (s, MeCO), 1.35 (s, 2 × Me), and 1.00 (2 s, 2 × Me); $\nu_{max.}$ 3 310m, 3 180m, and 1 735s cm^{-1}; *m/z* 405 (M^+), 273, 205, 190, 162, 147, 143, and 101.

1-*Amino*-2-(D-gluco-1-*hydroxy*-2,3:4,5-*di-isopropylidenedioxypentyl*)-1H-*benzimidazole* (**7**).—The acetylated benzimidazole (**9**) (3.01 g) was heated under reflux for 2 h with aqueous sodium hydroxide (5M; 50 ml). After cooling, the solution was extracted with ether; the extract was dried and the solvent was removed to yield a white foam (2.19 g), which was dissolved in a mixture of water (10 ml) and ethanol (10 ml) at 60 °C and aminated with potassium hydroxide (2.03 g) and hydroxylamine-*O*-sulphonic acid (1.75 g) as described for the preparation of compound (**5**) above. Ice-cooling of the acetonitrile gave the N-*aminobenzimidazole* (**7**) (0.4 g) as crystals, m.p. 213—214 °C (from acetonitrile) (Found: C, 59.55; H, 6.9; H, 11.4. $C_{18}H_{25}N_3O_5$ requires C, 59.5; H, 6.95; N, 11.55%); δ 7.45 (m, 2 × ArH), 7.13 (m, 2 × ArH), 5.93 (s, NH_2), 5.73 (d, *J* 6 Hz, OH), 5.10 (dd, *J* 6 and 3 Hz, 1′-H), 4.36 (m, 2′-H), 3.90 (m, 3′- and 4′-H, and 5′-H_2), and 1.20 (4 s, 4 × Me); $\nu_{max.}$ 3 360s, 3 340w, 3 280w, and 1 635w cm^{-1}; *m/z* 363 (M^+), 349, 163, 148, 143, 86, 60, 58, and 43.

Synthesis of 1-*Amino*-2-(1,2,2-*trimethylpropyl*)-1H-*benzimidazole* (**12**).—2,3,3-Trimethylbutanoic acid was prepared from t-butylacetic acid (3,3-dimethylbutanoic acid) by a modification of the literature method.[19] Thus dry tetrahydrofuran (68 ml) and redistilled di-isopropylamine (12.66 ml, 0.0903 mol) were added to a flame-dried and dry-nitrogen-flushed 3-necked flask under nitrogen. The flask was cooled to −78 °C and a solution of n-butyl-lithium (0.0903 mol) was added to the stirred mixture, during 20 min, from a dropping funnel, and then the mixture was stirred at −78 °C for a further 30 min. t-Butylacetic acid (Aldrich) (5.0 g, 0.043 mol) was then added to the solution at −78 °C during 5 min *via* a syringe through a septum cap and the mixture was stirred for 3 h at room temperature. After the mixture had been recooled to −78 °C, iodomethane (2.68 ml, 0.43 mol) was added briskly at this temperature and then the solution was allowed to warm to room temperature, at which point a white precipitate was formed. The mixture was stirred for a further 1.5 h at room temperature and was then neutralised with ice-cooled–hydrochloric acid (10%) and extracted with light petroleum (2 × 100 ml). The combined organic layers were washed successively with hydrochloric acid (10%; 3 × 100 ml), water (3 × 100 ml), and brine (3 × 100 ml), dried, and the solvent was removed under reduced pressure.

The crude product from this procedure was contaminated only with t-butylacetic acid (~5%) and was used directly for the procedure below, δ 11.30 (br s, CO_2H), 2.27 (q, *J* 7 Hz, Bu^{t}C*H*Me), 1.12 (d, *J* 7 Hz, Bu^{t}CH*Me*), and 1.03 (s, Bu^t).

2-(1,2,2-*Trimethylpropyl*)-1H-*benzimidazole* (**13**). The 2,3,3-trimethylbutanoic acid prepared above (17.55 g, 0.135 mol) and thionyl chloride (5 mol equiv.) were heated at 40—50 °C for 1.5 h after which gas evolution had ceased. Excess of thionyl chloride was removed under reduced pressure and the residual

* Primed constants refer to the alditol side-chain.

acid chloride was diluted with dry dichloromethane (~200 ml) and added dropwise during 45 min *via* a dropping funnel equipped with a drying tube to a briskly stirred solution of *o*-phenylenediamine (0.297 mol) in dry dichloromethane (500 ml). After the addition was complete, the mixture was set aside overnight, the insoluble hydrochloride salt was separated, and the dichloromethane solution was washed successively with aqueous sodium hydrogencarbonate (2 × 100 ml) and water (100 ml), dried, and evaporated under reduced pressure. Crystallisation (ethyl acetate) of the solid residue gave the monoamide (12.1 g, 41%) as crystals, m.p. 173—178 °C (with sublimation).

This amide (9.04 g) was dissolved in dry pyridine (30 ml) and phosphoryl trichloride (7.6 g) was added. The resulting mixture was heated at 80 °C (bath temperature) for 20 min, then cooled, poured onto ice, acidified with concentrated hydrochloric acid, then cautiously made alkaline with concentrated ammonia which precipitated an off-white solid. This solid was separated and washed thoroughly with cold water. Crystallisation from ethanol–water gave the *benzimidazole* (**13**) as crystals (4.65 g, 56%), m.p. 209—211 °C (Found: C, 77.05; H, 8.95; N, 13.75. $C_{13}H_{18}N_2$ requires C, 77.2; H, 8.95; N, 13.85%); δ 7.8 (br s, NH), 7.6—7.0 (m, 4 × ArH), 2.88 (q, *J* 7 Hz, C*H*Me), 1.38 (d, *J* 7 Hz, CH*Me*), and 1.00 (s, Bu^t); $\nu_{max.}$ 2 740br s, 2 630br m, and 1 620w cm^{-1}; *m/z* 202 (M^+), 187, 147, 146 (100%), 145, 132, 92, and 65.

Amination of the benzimidazole (**13**). The benzimidazole prepared as above (1.81 g) was suspended in dichloromethane (100 ml) and the mixture was cooled to 0 °C. O-(Mesitylsulphonyl)hydroxylamine[18] (2.31 g, 1.2 mol equiv.) in dichloromethane (20 ml) was added dropwise to the stirred mixture during 5 min and the resulting solution was stirred for 2 h, washed with saturated aqueous sodium carbonate (50 ml), dried, and evaporated. The residual solid (1.77 g) was found (n.m.r.) to be a *ca.* 1:1 mixture of the required *N*-aminobenzimidazole (**12**) and the starting benzimidazole (**13**), and the bulk of the latter was separated by trituration of the solid with ethyl acetate–light petroleum (1:2) and filtration. The filtrate, which contained the bulk of the aminated material, was evaporated and the residue was chromatographed over silica with light petroleum–ethyl acetate (1:3). The N-*aminobenzimidazole* (**12**) was obtained as crystals (0.243 g, 13%), m.p. 173—174 °C (from acetonitrile) (Found: C, 71.75; H, 8.8; N, 19.3. $C_{13}H_{19}N_3$ requires C, 71.85; H, 8.8; N, 19.35%); δ 7.65 (m, 1 × ArH), 7.38—7.05 (m, 3 × ArH), 4.52 (s, NH_2), 3.42 (q, *J* 7 Hz, C*H*Me), 1.35 (d, *J* 7 Hz, CH*Me*), and 1.00 (s, Bu^t); $\nu_{max.}$ 3 310s, 3 120m, and 1 625w cm^{-1}; *m/z* 217 (M^+), 202, 161 (100%), 160, 147, 146, 145, 143, 119, and 77.

General Procedure for Oxidation of N-*Aminobenzimidazoles with Lead Tetra-acetate in the Presence of Alkenes.*—The powdered *N*-aminobenzimidazole (1 mol equiv.) was intimately mixed in the solid state with powdered (acetic acid-free) lead tetra-acetate (LTA) (1.1 mol equiv.) (**CAUTION**: this procedure was never carried out on > 500 mg total solid). This mixture was then added continuously in very small amounts during 15 min at room temperature to a vigorously stirred solution of the alkene (2—10 mol equiv.) in dry dichloromethane (1 ml/100 mg of the *N*-aminobenzimidazole). The mixture was then stirred for a further 30 min at room temperature, the insoluble lead diacetate was separated, then washed with dichloromethane, and the total filtrate was washed successively with aqueous sodium hydrogen carbonate and water, dried, and evaporated.

Procedure for Oxidation of N-*Aminobenzimidazoles with Phenyl Iodosodiacetate* [*(Diacetoxyiodo)benzene*] in the Presence *of Alkenes.*—The powdered *N*-aminobenzimidazole (1 mol equiv.) was intimately mixed with solid dry phenyl iodosodiacetate (1.1 mol equiv.), the mixture was suspended in dry dichloromethane (1 ml/100 mg of the *N*-aminobenzimidazole) containing the alkene (2—10 mol equiv.), and the suspension was stirred at room temperature overnight. The reaction mixture was washed successively with aqueous sodium hydrogen carbonate and water, dried, and evaporated.

Oxidation of (**12**) *in the Presence of Methyl Acrylate.*—Oxidation of the amine (**12**) (76 mg) with LTA (171 mg) in dichloromethane (0.8 ml) containing methyl acrylate (302 mg) was carried out using the general procedure given above. The aziridine (**15**) was obtained as a light yellow oil (75 mg, 71%). Chromatography over silica with light petroleum–ethyl acetate (1.5:1) failed to separate the two stereoisomers, which n.m.r. showed were present in a 2.1:1 ratio: δ (400 MHz) major stereoisomer 7.85—7.19 (m, 4 × ArH), 3.88 (s, CO_2Me), 3.70 (dd, *J* 7.6 and 5 Hz, C*H*CO_2Me), 3.33 (q, *J* 7.2 Hz, C*H*Me), 3.08 (dd, *J* 7.6 and 1.2 Hz, aziridine ring C*H*H *cis* to benzimidazole), 2.99 (dd, *J* 5 and 1.2 Hz, aziridine ring CH*H trans* to benzimidazole), 1.40 (d, *J* 7.2 Hz, CH*Me*), and 1.00 (s, Bu^t); minor stereoisomer 7.85—7.19 (m, 4 × ArH), 3.88 (s, CO_2Me), 3.38 (dd, *J* 7.8 and 5.0 Hz, C*H*CO_2Me), 3.25 (q, *J* 7.2 Hz, C*H*Me), 3.23 (dd, *J* 7.8 and 1.2 Hz, aziridine ring C*H*H *cis* to benzimidazole), 3.04 (dd, *J* 5.0 and 1.2 Hz, aziridine ring CH*H trans* to benzimidazole), 1.41 (d, *J* 7.2 Hz, CH*Me*), and 1.00 (s, Bu^t); $\nu_{max.}$ 1 750s, cm^{-1}; *m/z* 301 (M^+), 286, 245, 145, 130, 129, 117 (100%), and 103.

Oxidation of (**12**) *with* LTA *in the Presence of Styrene.*—Oxidation of the amine (**12**) (53 mg) with LTA (115 mg) in dichloromethane (0.6 ml) containing styrene (102 mg) was carried out as above. Chromatography of the crude product (a 5.6:1 ratio of stereoisomers) over alumina separated the aziridines from a more polar impurity, and crystallisation from ethanol gave the major *aziridine* stereoisomer (**14**) as a solid (35 mg, 45%), m.p. 152—154 °C (from acetonitrile) (Found: C, 78.9; H, 7.9; N, 13.15. $C_{21}H_{25}N_3$ requires C, 78.95; H, 7.9; N, 13.15%); δ (400 MHz) major stereoisomer 7.80—7.10 (m, 9 × ArH), 3.95 (dd, *J* 8.0 and 5.2 Hz, C*H*Ph), 3.34 (q, *J* 7.2 Hz, C*H*Me), 3.06 (dd, *J* 8.0 and 1.4 Hz, aziridine ring C*H*H *cis* to benzimidazole), 2.81 (dd, *J* 5.2 and 1.4 Hz, aziridine ring CH*H trans* to benzimidazole), 1.43 (d, *J* 7.2 Hz, CH*Me*), and 1.02 (s, Bu^t); the following peaks were visible from the minor stereoisomer; 7.80—7.10 (m, 9 × ArH), 3.55 (dd, *J* 8 and 4.9 Hz, C*H*Ph), 3.22 (q, *J* 7.2 Hz, C*H*Me), 2.85 (dd, *J* 5.4 and 1.6 Hz, aziridine ring C*H*H *trans* to benzimidazole), 1.39 (d, *J* 7.2 Hz, CH*Me*), and 0.88 (s, Bu^t); $\nu_{max.}$ 1 605w, 735s, and 705s cm^{-1}; *m/z* 319 (M^+), 145, 144, 130, 117 (100%), 91, and 77.

Oxidation of (**12**) *with Phenyl Iodosodiacetate in the Presence of Styrene.*—Oxidation of the amine (**12**) (100 mg) with phenyl iodosodiacetate (156 mg) in dichloromethane (1 ml) containing styrene (479 mg) was carried out according to the procedure described above. The 400 MHz spectrum of the crude reaction product showed that the ratio of stereoisomers present was 5.6:1, and the major stereoisomer was isolated, by crystallisation from acetonitrile (89 mg, 61%), as a solid, m.p. 152—154 °C, identical in all respects with the major stereoisomer isolated from the previous experiment.

Oxidation of (**12**) *with LTA in the Presence of Styrene at* −20 *to* −25 °C: *Formation of* cis-*Aziridine* (**14**).—The general procedure above was followed except that deuteriochloroform was used as the solvent and the temperature was maintained between −20 and −25 °C (bath temperature) throughout the reaction. Lead diacetate was separated at ambient temperature of < −30 °C, and the n.m.r. spectrum was recorded at −40 °C without any intermediate warming of the solution. The *cis*-invertomer of the aziridine (**14**) which is produced under these

conditions has δ (300 MHz) 7.95—7.10 (m, 9 × ArH), 3.83 (dd, *J* 7.0 and 6.6 Hz, C*H*Ph), 3.52 (dd, *J* 6.6 and 2.5 Hz, aziridine ring C*H*H *cis* to benzimidazole), 3.34 (dd, *J* 7.1 and 2.5 Hz, aziridine ring CH*H trans* to benzimidazole), 2.57 (q, *J* 7.0 Hz, C*H*Me), 0.86 (s, Bu^t), and 0.22 (d, *J* 7.0 Hz, CH*Me*). After allowing the solution to warm to room temperature and then rerecording at −40 °C, the spectrum was identical with that of the pure *trans*-invertomer of aziridine (**14**).

Oxidation of (**12**) *with LTA in the Presence of α-Methylene-γ-butyrolactone* (**1**).—Oxidation of the amine (**12**) (74 mg) with LTA (166 mg) in dichloromethane (0.8 ml) containing α-methylene-γ-butyrolactone (**1**) (100 mg) was carried out using the general procedure given above. Chromatography of the product over alumina and elution with light petroleum –ethyl acetate (1.5:1) separated the two stereoisomeric aziridines (**16**) from a more polar by-product; crystallisation from chloroform–light petroleum yielded the major stereoisomer of the *aziridine* (**16**) as a solid (35 mg, 33%), m.p. 189—191 °C (Found: C, 68.45; H, 7.25; N, 13.2. $C_{18}H_{23}N_3O_2$ requires C, 69.0; H, 7.4; N, 13.4%); $\nu_{max.}$ 1 775s cm^{-1}; δ (400 MHz) major stereoisomer, major invertomer (lactone carbonyl *cis* to benzimidazole) 7.73—7.08 (m, 4 × ArH), 4.66—4.56 (m, CH_2O_2C), 3.71 (d, *J* 1.2 Hz, aziridine ring H *cis* to benzimidazole), 3.19 (d, *J* 1.2 Hz, aziridine ring H *trans* to benzimidazole), 2.78 (ddd, *J* 15, 9, and 6 Hz, C*H*HCH_2O_2C), 2.69 (ddd, *J* 15, 9, and 5 Hz, CH*H*CH_2O_2C), 2.48 (q, *J* 7.1 Hz, C*H*Me), 1.32 (d, *J* 7.1 Hz, CH*Me*), and 0.95 (s, Bu^t); minor invertomer (lactone carbonyl *trans* to benzimidazole) 7.73—7.08 (m, 4 × ArH), 4.46 (ddd, *J* 9.4, 9.4, and 5.3 Hz, C*H*HO_2C), 4.29 (ddd, *J* 9.4, 9.2, and 6.4 Hz, CH*H*O_2C), 3.87 (br s, aziridine ring H *cis* to benzimidazole), 3.40 (br s, C*H*Me), 3.02 (br s, aziridine ring H *trans* to benzimidazole), 2.73 (m, C*H*HCH_2O_2C), 2.21 (br s, CH*H*-CH_2O_2C), 1.34 (d, *J* 7.1 Hz, CH*Me*), and 0.92 (s, Bu^t). The ratio of major:minor invertomers was 2:1 in $CDCl_3$ and 3.4:1 in pyridine. A sample containing a 1.5:1 ratio of major:minor stereoisomers was obtained by repeated crystallisation and removal of the major stereoisomer from chloroform–light petroleum followed by evaporation of the latter. From the n.m.r. spectrum of this sample, the following assignments of signals from the minor stereoisomer can be made: δ 3.68 (d, *J* 1.6 Hz, aziridine ring H *cis* to benzimidazole), 3.35 (d, *J* 1.6 Hz, aziridine ring H *trans* to benzimidazole), 1.46 (d, *J* 7.2 Hz, CH*Me*), and 0.97 (s, Bu^t); other signals from this minor stereoisomer were obscured by those from the major stereoisomer.

The ratio of major:minor stereoisomers in the n.m.r. spectrum of the crude oxidation product was 5.5 (±0.5):1 from comparison of the integration values from their respective aziridine ring-proton signals.

Oxidation of (**12**) *with LTA in the Presence of α-Methylene-γ-butyrolactone* (**1**) *at Low Temperature: Kinetically formed Ratio of Aziridines* (**16**).—The oxidation of compound (**12**) with LTA in the presence of lactone (**1**) was carried out at between −20 and −25 °C as described above for the oxidation of the same compound in the presence of styrene. From comparison of the spectra obtained on the filtered (< −30 °C) deuteriochloroform solution at −40 °C before and after warming to room temperature, and, in particular, from integration of signals at δ 3.40 (aziridine ring H *trans* to benzimidazole in major invertomer) and 3.27 (C*H*Me in minor invertomer), in the spectrum obtained before warming, the kinetically formed ratio of *cis*- (**16a**) to *trans*-aziridine (**16b**) produced was ~5:1.

Oxidation of (**12**) *with Phenyl Iodosodiacetate in the Presence of Lactone* (**1**).—The oxidation of compound (**12**) (170 mg) with phenyl iodosodiacetate (278 mg) in dichloromethane (1.5 ml) containing lactone (**1**) (154 mg) was carried out using the procedure described earlier. The ratio of aziridine stereoisomers (**16**) in the crude product (5.5:1) was identical with that obtained in the analogous oxidation using LTA above, and the major stereoisomer was obtained as a solid (122 mg, 50%), m.p. 189—191 °C, by cryatallisation from chloroform–light petroleum.

Oxidation of (**12**) *with LTA in the Presence of Lactone* (**18**).—The general oxidation procedure was followed using the *N*-aminobenzimidazole (**12**) (65 mg) and LTA (146 mg) in dichloromethane (0.5 ml) containing lactone (**18**)[20] (65 mg). Chromatography over alumina and elution with dichloromethane gave the *aziridine* (**19**) as crystals (70 mg, 69%), m.p. 136—137 °C (from ethanol) (Found: M^+, 341.2107. $C_{20}H_{27}N_3O_2$ requires *M*, 341.2103); $\nu_{max.}$ 1 755s cm^{-1}; δ (400 MHz) major invertomer (**19**) 7.81—7.14 (m, 4 × ArH), 3.74 (d, *J* 0.9 Hz, aziridine ring H *cis* to benzimidazole), 3.27 (d, *J* 0.9 Hz, aziridine ring H *trans* to benzimidazole), 2.84 (d, *J* 14 Hz, C*H*HCMe$_2$), 2.64 (q, *J* 7.2 Hz, C*H*Me), 2.42 (d, *J* 14 Hz, CH*H*Me$_2$), 1.70 and 1.55 (2 s, CH_2CMe_2), 1.38 (d, *J* 7.0 Hz, CH*Me*), and 1.02 (s, Bu^t); minor invertomer 7.81—7.14 (m, 4 × ArH), 4.01 (br s, aziridine ring H *cis* to benzimidazole), 3.62 (br q, *J* 7.0 Hz, C*H*Me), 3.05 (br s, aziridine ring H *trans* to benzimidazole), 2.51 (d, *J* 14 Hz, C*H*HCMe$_2$), 2.12 (d, *J* 14 Hz, CH*H*CMe$_2$), 1.70 and 1.57 (2 s, CH_2CMe_2), 1.38 (d, *J* 7.0 Hz, CH*Me*), and 1.00 (s, Bu^t). The ratio of invertomers was 2.0 (±0.4):1 from averaging of the values obtained by integration comparison of the respective signals from aziridine and lactone ring protons.

Oxidation of (**12**) *with LTA in the Presence of Lactone* (**18**) *at Low Temperature; Kinetically formed Ratio of Aziridines* (**19**).—Oxidation of compound (**12**) with LTA in the presence of lactone (**18**) was carried out between −20 and −25 °C as described for the oxidation of the same substrate in the presence of styrene. From comparison of the spectra obtained on the filtered (< −30 °C) deuteriochloroform solution at −40 °C before and after warming to room temperature, and in particular from integration of signals at δ 3.48 (aziridine ring H *trans* to benzimidazole in major invertomer) and 4.28 (aziridine ring H *cis* to benzimidazole in minor invertomer) in the spectrum obtained before warming, the kinetically formed ratio of *cis* (**19**) to *trans*-aziridine (**19**) produced was 5.3:1.

Oxidation of (**12**) *with LTA in the Presence of* (E)-*But*-2-*ene*.—Oxidation of compound (**12**) (88 mg) with LTA (189 mg) was carried out using the general procedure but the dichloromethane (1 ml) containing (*E*)-but-2-ene (200 mg) was cooled in ice–water during the reaction. Chromatography of the product over alumina and elution with light petroleum–ethyl acetate (5:1) gave the major stereoisomer of (**21**) (16 mg, 60%) as an oil (Found: M^+, 271.2064. $C_{17}H_{25}N_3$ requires *M*, 271.2048); δ (300 MHz) major stereoisomer 7.80—7.10 (m, 4 × ArH), 3.08 (q, *J* 7.2 Hz, 2-C*H*Me), 2.99 (dq, *J* 5.7 and 5.3 Hz, aziridine ring H *cis* to benzimidazole), 2.51 (dq, *J* 5.9 and 5.2 Hz, aziridine ring H *trans* to benzimidazole), 1.56 (d, *J* 5.7 Hz, aziridine ring Me *trans* to benzimidazole), 1.46 (d, *J* 7.2 Hz, CH*Me*), 1.06 (d, *J* 5.9 Hz, aziridine ring Me *cis* to benzimidazole), and 0.99 (s, Bu^t). Assignable signals for the minor stereoisomer are δ 2.64 (dq, *J* 5.8 and 5.3 Hz, aziridine ring H *cis* to benzimidazole), 1.57 (d, *J* 5.6 Hz, aziridine ring Me *trans* to benzimidazole), 1.43 (d, *J* 7.1 Hz, CH*Me*), 1.17 (d, *J* 5.8 Hz, aziridine ring Me *cis* to benzimidazole), and 1.03 (s, Bu^t).

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