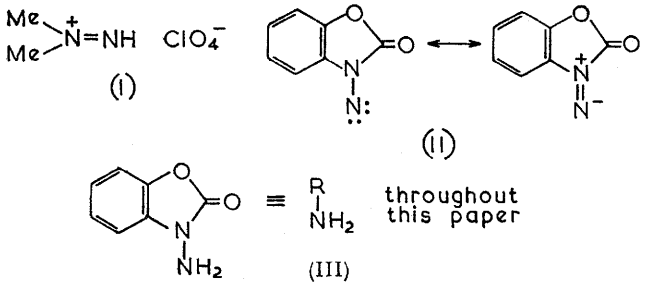
Reactive Intermediates. Part VII.[1] Oxidation of 3-Aminobenzoxazolin-2-one; Stereospecific Addition of the Amino-nitrene to Olefins

By **R. S. Atkinson** and **C. W. Rees,*** Department of Chemistry, The University, Leicester

Benzoxazolin-2-one with hydroxylamine-*O*-sulphonic acid gives the *N*-amino-derivative which is dehydrogenated smoothly by lead tetra-acetate to the amino-nitrene. This nitrene does not fragment to benzyne, carbon dioxide, and nitrogen. It adds to olefins to give aziridines, and the addition is stereospecific even at high dilution. It also adds exclusively 1,2 to conjugated dienes to give vinylaziridines. Thus the nitrene appears to be generated in a resonance-stabilised singlet state, which is probably the ground state. With the formally similar nitrene from *N*-amino-oxindole, however, rearrangement to 3-cinnolinol is much faster than reaction with olefins. The n.m.r. spectra of *N*-benzoxazolinonyl aziridines are complex and show that inversion at the aziridine nitrogen is greatly retarded.

OXIDATION of unsymmetrical disubstituted hydrazines results in a variety of reactions [2] including fragmentation, with [3] and without [4] recombination, ring insertion,[5] deamination,[6] and tetrazene formation.[7] Amino-nitrenes have been proposed as intermediates in many of these reaction and the isolation of the conjugate acid of such an amino-nitrene as a perchlorate salt (I) has been claimed [7].



In this paper we report the trapping by olefins of the nitrene (II) generated by the oxidation of 3-amino-benzoxazolin-2-one (III), and show that the adjacent ring nitrogen has a profound effect on the multiplicity and reactivity of the nitrene.

In contrast with carbenes, there are very few examples of the intermolecular trapping of nitrenes by olefins, to form aziridines.[8] Lwowski [9] has studied in detail the behaviour of ethoxycarbonylnitrene generated by the thermolysis and photolysis of ethoxycarbonyl azide and by treatment of the aryl sulphonate (IV) with base. The common nitrene intermediate is formed initially in the singlet state, but decays to the triplet as indicated by the decreasing stereospecificity of the addition to olefins at increasing dilution.

Oxidation of 3-*Aminobenzoxazolin*-2-*one* (III).—The oxidation of (III) to the nitrene (II) was of considerable interest for two reasons. The nitrene (II) could fragment to nitrogen, carbon dioxide, and benzyne, by analogy with the fragmentation of nitrenes (V) formed by lead

[1] Part VI, C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 765.

[2] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 174; P. A. Smith, 'Open Chain Nitrogen Compounds,' Benjamin, New York, 1965, vol. II, p. 136.

[3] C. G. Overberger and L. P. Herin, *J. Org. Chem.*, 1962, **27**, 2423, and references therein.

[4] D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, 1963, **85**, 1944.

[5] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.

[6] R. H. Poirier and F. Benington, *J. Org. Chem.*, 1954, **19**, 1157.

[7] W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, 1957, **79**, 572.

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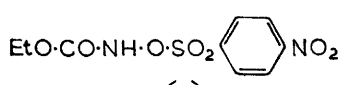
[9] W. Lwowski, *Angew. Chem. Internat. Edn.*, 1967, **6**, 897.

tetra-acetate oxidation of 1-aminobenzotriazoles.[10] Compound (III) would then be a potentially useful benzyne precursor. Alternatively the nitrene (II) might well be stable enough to be detected by physical



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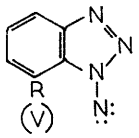


(V)

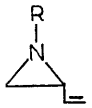
or chemical means. This would then give support for the intermediacy of the nitrenes (V) in the oxidation of 1-aminobenzotriazoles for which direct evidence was lacking, since these nitrenes fragment too fast to be detected. Indeed, all our attempts to trap such nitrenes intermolecularly or intramolecularly, by ring closure in such species as (V; R = Me, OMe, OH), have failed.

Amination of benzoxazolinone with hydroxylamine-*O*-sulphonic acid [11] was successful only when the sodium hydroxide, normally used, was replaced by sodium carbonate. Even then the yield was poor but starting material could be recovered and the procedure was simple. The *N*-amino-compound (III) formed, gave benzylidene and butylidene derivatives and was reconverted into benzoxazolinone by heating with *N*-nitrosodiphenylamine in benzene.

Oxidation of (III) alone with lead tetra-acetate was complex and no homogeneous product was isolated; no biphenylene, the product of oxidation of 1-aminobenzotriazole under the same conditions, was formed. (Benzoxazolinone itself, a possible primary product from deamination, was recovered in poor yield when subjected to the same conditions.) Oxidation in the presence of tetracyclone also gave none of the benzyne adduct, tetraphenylnaphthalene, but a yellow compound, the analysis and n.m.r. spectrum of which indicated that it was a 1 : 1-adduct of tetracyclone and the nitrene (II). Although the structure of this product was not immediately obvious it appeared likely that the nitrene intermediate was being intercepted by tetracyclone. This prompted a study of the oxidation of (III) in the presence of dienes.

Reaction of Nitrene (II) *with Dienes.*—Oxidation of (III) in buta-1,3-diene–methylene chloride with lead tetra-acetate gave the adduct (VI) in 71% yield. The n.m.r. spectrum of (VI) illustrates some complicated features observed with these aziridines. Firstly, inversion at the aziridine nitrogen is slow on the n.m.r. time scale and this leads to pronounced differences in chemical shift between protons *cis* and *trans* to the benzoxazolinone substituent (R). In particular aziridine ring protons *cis* are deshielded relative to those *trans* as a result of the effects of the aromatic ring and carbonyl group. Secondly, as a consequence of the slow inversion at nitrogen these aziridines often consist of a thermodynamic equilibrium mixture of invertomers, although in the case of (VI), only one invertomer is observed in the n.m.r. under normal operating conditions. Thirdly, in (VI) the chemical shift difference for the two protons *cis* to the benzoxazolinone ring is very small.* These features are responsible for the large differences in n.m.r. spectra of (VI) compared with 1-ethoxycarbonyl-2-vinylaziridine [13] and 2-vinylaziridine.[14]

The presence of the three olefinic protons in (VI) immediately excluded the possibility of 1,4-addition of the nitrene † to butadiene to give the 3-pyrroline (VII), and this was confirmed when authentic (VII) became available.[16] The i.r. spectrum of (VI) also supported the presence of an aziridine ring with bands at 3120, 3060, 1312, and 1160 cm.$^{-1}$.[17] Hydrogenation of (VI) over



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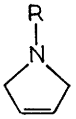

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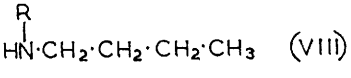

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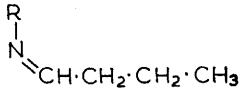
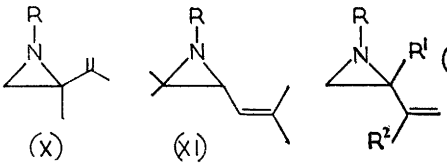


(IX)

Adams catalyst gave the ring-opened product (VIII) with absorption of 2 mol. of hydrogen. Ring-opening to (VIII) even accompanied the homogeneous hydrogenation of (VI) with tris(triphenylphosphine)chlororhodium, a reagent normally specific for double and triple bonds.[18] The structure of (VIII) was confirmed by its formation from the butylidene derivative (IX) by reduction with lithium aluminium hydride.

Adducts (X) and (XI) were also obtained by oxidation of (III) in the presence of 2,3-dimethylbuta-1,3-diene and 2,5-dimethylhexa-2,4-diene, respectively. With isoprene a mixture of the two aziridines (XII) and (XIIII) was obtained. The structure of all of these adducts follows



(X) (XI) (XII) R^1 = Me, R^2 = H (XIII) R^1 = H, R^2 = Me

from their n.m.r. spectra and, with the exception of (XI), their thermal rearrangement to 3-pyrrolines.[16] In (X) and (XII) peaks due to both invertomers are present in the n.m.r. spectra and comparison of the two provides an estimate of 11 : 1 for the ratio of (Xa) to (Xb) and of 1 : 1·4 for (XIIa) to (XIIb). It follows also from the

* The n.m.r. spectra of aziridines have been discussed.[12]

† The question of 1,2- *vs.* 1,4-addition of nitrenes has been raised.[15] The only well authenticated example of 1,4-addition (of cyanonitrene to cyclo-octatetraene) has been shown to proceed *via* the triplet.

[10] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.

[11] R. Gösl and A. Meuwsen, *Chem. Ber.*, 1959, **92**, 2521.

[12] S. J. Brois and G. P. Beardsley, *Tetrahedron Letters*, 1966, 5113.

[13] K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 1964, 3953.

[14] E. L. Stogryn and S. J. Brois, *J. Amer. Chem. Soc.*, 1967, **89**, 605.

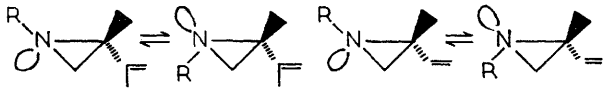
[15] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1968, **90**, 1527.

[16] R. S. Atkinson and C. W. Rees, following paper.

[17] H. L. Spell, *Analyt. Chem.*, 1967, **39**, 185.

[18] F. H. Jardine and G. Wilkinson, *J. Chem. Soc.* (*C*), 1967, 270.

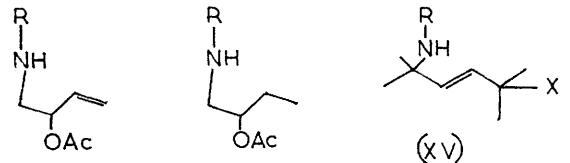
n.m.r. spectra that whereas the aziridine ring proton *cis* to the benzoxazolinone is deshielded relative to that which is *trans*, the reverse holds for aziridine ring methyl



(Xa) (Xb) (XIIa) (XIIb)

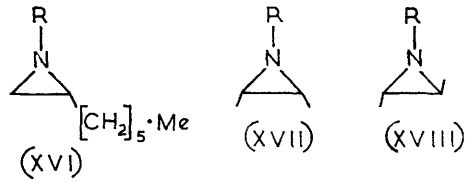
groups. Evidently the *cis* methyl group falls more within the shielding regions of the aromatic ring and carbonyl group, in contrast to the *cis* aziridine ring proton.

Vinylaziridines are particularly sensitive to acid, and basic alumina was necessary for chromatography. Cold acetic acid converted (VI) into the acetate (XIII). Hydrogenation of this acetate gave a mixture of (XIV) and (VIII), the latter by hydrogenolysis of the allylic acetate. Acid sensitivity is particularly marked in the case of (XI) which was rapidly attacked by the acetic acid generated from lead tetra-acetate used in its preparation, to give (XV; X = OAc). Similarly, percolation of a solution of (XI) over silica resulted in its conversion into the tertiary alcohol (XV; X = OH), and boiling in ethanol gave the corresponding ether (XV; X = OEt).



(XIII) (XIV) (XV)

Reaction of Nitrene (II) *with Mono-enes.*—Exclusive formation of 1,2-addition products in the trapping of the nitrene (II) with conjugated dienes led us to study the oxidation of (III) with lead tetra-acetate in the presence of simple olefins. With oct-1-ene the expected aziridine (XVI) was obtained in low yield. However, oxidation



(XVI) (XVII) (XVIII)

in the presence of *cis*- and *trans*-but-2-ene gave the corresponding aziridines (XVII), m.p. 88—89°, and (XVIII), m.p. 65—65·5°, respectively, in 60—70% yield. The additions were stereospecific. With 1·5 mol. of olefin at only 2 mole % concentration in methylene chloride, none of the other isomer was detected in each case; the best criterion for this was the substantial melting point depression observed in an artificial mixture of small amounts of each isomer in the other. The stereospecificity of the reactions was found, by this means, to be better (probably much better) than 95%. At this concentration the nitrene from ethoxycarbonyl azide showed extensive non-stereospecific addition.[9]

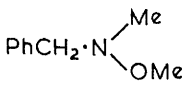
By extending Skell's postulate for carbenes[19] to nitrenes,[9] concerted and hence stereospecific addition should be observed with the singlet species, and stepwise non-stereospecific addition with the triplet. Thus we observe only singlet-state properties for the nitrene (II). Either the singlet to triplet decay is abnormally slow,* compared with that of ethoxycarbonylnitrene and cyanonitrene, or the singlet (S_0) state is the ground state. In the singlet state two pairs of electrons with opposite spins are presumably located on the exocyclic nitrogen atom in approximately sp^2 orbitals leaving an empty p orbital into which the lone pair on the adjacent nitrogen may be delocalised, as depicted in (II). This orbital overlap, which is not possible with the triplet, reverses the usual stability of the triplet and singlet states.[22]

The n.m.r. spectra of the dimethylaziridines (XVII) and (XVIII) have been briefly discussed.[23] (XVII) shows a complex multiplet for the aziridine ring protons which is possibly the coupling of each with both methyl groups ($X_3AA'X'_3$ system). The signal for the latter is a doublet although a small shoulder is visible on the higher-field arm at 100 Mc. (XVIII) shows a coalescence temperature (T_c) at *ca.* 150° where inversion of the benzoxazolinone substituent on the aziridine ring nitrogen becomes fast on the n.m.r. time scale. Theoretical reasons for the slow rate of inversion in substituted aziridines have been discussed; the electron-withdrawing inductive effect,[24] and the presence of lone pairs on the heteroatom substituent [25] are believed to be responsible. Both of these effects are present with the benzoxazolinone substituent where the value of T_c is higher than that reported for alkylaziridines (120°) [26] but below that for *N*-chloroaziridines (>180°),[27,28] where inversion is slow enough to allow isolation of the *N*-invertomers. That T_c for aziridines substituted by oxygen on the ring nitrogen is also likely to be high is suggested by the marked retardation of inversion rate for the hydroxylamine (XIX) compared with tertiary amines.[29] In view of the retarded inversion with benzoxazolinonylaziridines it is of interest that compounds (XX) and (XXI) have been reported [30] as showing no separation

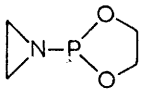
* The singlet to triplet decay of nitrenes has been shown to be influenced by solvent [20] and temperature.[21]

[19] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1956, **78**, 4496; R. C. Woodworth and P. S. Skell, *ibid.*, 1959, **81**, 3383.
[20] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1967, **89**, 3184.
[21] A. L. J. Beckwith and J. W. Redmond, *J. Amer. Chem. Soc.*, 1968, **90**, 1351; *Chem. Comm.*, 1967, 165.
[22] J. Hine, 'Divalent Carbon,' Ronald Press, New York, 1964, p. 45.
[23] R. S. Atkinson, *Chem. Comm.*, 1968, 676.
[24] M. Raban, *Chem. Comm.*, 1967, 1017.
[25] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.
[26] A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 5126.
[27] D. Felix and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1968, **7**, 224; S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 508.
[28] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 148.
[29] D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089.
[30] V. F. Bystrov, R. E. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Optics and Spectroscopy* 1965, **19**, 122.

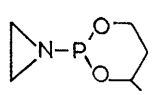
($\Delta\nu$) of *cis* and *trans* aziridine ring protons down to $-100°$ at 20·5 Mc./sec. Since high coalescence temperatures are not limited to aziridines substituted on nitrogen with first-row elements (*N*-bromoaziridine has



(XIX)

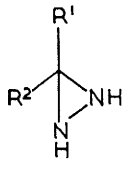


(XX)

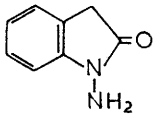


(XXI)

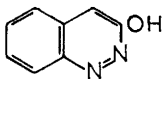
$T_c > 140°$ [28]), it seems likely that the results for (XX) and (XXI) are a combination of a small value for $\Delta\nu$ and a low operating frequency. Slow inversion (T_c 150°) is also shown by diaziridines (XXII) where the adjacent nitrogen is endocyclic rather than exocyclic.[31]



(XXII)



(XXIII)



(XXIV)

Oxidation of *N*-amino-oxindole (XXIII) in benzene with lead tetra-acetate gave 3-cinnolinol (XXIV) by ring insertion of the nitrene intermediate.[5] However, oxidation of (III) under the same conditions gave dimeric products, and none of the corresponding ring-expanded product. Conversely, oxidation of (XXIII) in the presence of a large excess of butadiene gave no aziridine but again a good yield of 3-cinnolinol (XXIV) (66%). Whether this intramolecular reaction stems from more rapid nucleophilic attack by the nitrene, in its dipolar form, on the carbonyl group, or from more rapid phenyl migration to the electron-deficient exocyclic nitrogen is not yet known. However the contrasting behaviour of (III) and (XXIII) towards lead tetra-acetate underlines the striking dependence upon structure of the reactions of formally similar amino-nitrenes.

EXPERIMENTAL

M.p.s were taken on a Kofler block. The purity of all products was checked on silica gel (Merck) plates, except where indicated, using different mixtures of benzene and ethyl acetate, and developing with iodine. The u.v., i.r., and n.m.r. spectra were measured with a Cary 14, a Perkin-Elmer 237, and Varian A 60 and HR 100 spectrometers, respectively. U.v. spectra were measured in ethanol, and i.r. spectra in Nujol mulls or thin films and the band intensities are indicated by s (strong), m (medium), and w (weak). The chemical shift of the AB systems present was taken as the arithemetical mean of the respective doublets. Column chromatography was performed using Light's 200/300 mesh silica and Spence H alumina. Light petroleum refers to the fraction b.p. 60—80°. Lead tetra-acetate was freed from acetic acid by pressing between filter papers, and keeping over sulphuric acid at atmospheric pressure.

3-Aminobenzoxazolin-2-one * (III).—Powdered benzoxazolin-2-one [32] (2·7 g.) and sodium carbonate (7·5 g.) were dissolved in water (50 ml.), and hydroxylamine-*O*-sulphonic acid [11] (2·26 g.) was added in small portions during 3 min., the temperature of the solution being maintained at 50—60°. The solution was stirred for a further 15 min. and the fine insoluble solid produced during this time separated. Crystallisation from methylene chloride–ethanol gave the *product* as colourless needles (0·67 g., 22%), m.p. 168—171° (Found: C, 56·2; H, 4·5: N, 18·6. $C_7H_6N_2O_2$ requires C, 56·0; H, 4·0; N, 18·7%), $\lambda_{max.}$ 229 (ε 9240) and 275 mμ (5020) with an inflection at 280 mμ (ε 4180), $\nu_{max.}$ 3314m, 3250w, 3180w, 1757s,br cm.$^{-1}$; *m/e* 150, 135, 105, 94, 77, 58. After 12 such procedures and removal of the product the combined filtrates were acidified and the separated solid crystallised from acetone–water (charcoal) to give benzoxazolin-2-one (20·5 g.).

Deamination of 3-Aminobenzoxazolin-2-one (III) *using N-Nitrosodiphenylamine.*—3-Aminobenzoxazolin-2-one (250 mg.) and *N*-nitrosodiphenylamine (460 mg.) were heated under reflux in benzene (12 ml.) for 10 hr. Benzene was removed under reduced pressure and the residue chromatographed over silica (30 g.). Benzene eluted diphenylamine, and benzene–ethyl acetate (3 : 1) eluted benzoxazolin-2-one (150 mg., 66%).

Benzylidene Derivative of 3-Aminobenzoxazolin-2-one.—3-Aminobenzoxazolin-2-one (200 mg.) and benzaldehyde (275 mg.) were heated in glacial acetic acid (7 ml.) for 2·5 hr. at 100°. The solution was cooled and the crystalline solid separated. Recrystallisation from ethanol gave the *product* (190 mg., 59%) as plates, m.p. 158—159° (Found: N, 11·7. $C_{14}H_{10}N_2O_2$ requires N, 11·8%), $\nu_{max.}$ 1771s, 1754s, 1612w cm.$^{-1}$; τ($CDCl_3$) 2·9—2·4 and 2·35—2·0 (9 aromatic H, multiplet), −0·08 (azomethine H, singlet); *m/e* 238, 135, 134, 106, 104, 103.

1-(Benzoxazolin-2-on-3-yl)-2-vinylaziridine (VI).—Buta-1,3-diene (10 g.) was dissolved in methylene chloride (30 ml.) at −60°. The solution was warmed to 0° and 3-aminobenzoxazolin-2-one (1 g.) was added, followed by lead tetra-acetate (3 g.) in small portions during 5 min. with vigorous magnetic stirring. After removal of the ice-bath and stirring for a further 30 min., the solution was filtered to remove insoluble lead salts and evaporated under reduced pressure to small bulk. This was chromatographed over alumina (70 g.) and continuous elution with benzene–ethyl acetate (10 : 1) gave a colourless oil (956 mg., 71%) which crystallised on standing. Recrystallisation (from methanol with cooling at −60°) gave the *vinylaziridine* (VI), m.p. 70·5—71° † (Found: C, 65·7; H, 4·9; N, 14·2. $C_{11}H_{10}N_2O_2$ requires C, 65·3; H, 5·0; N, 13·9%), $\nu_{max.}$ 3120m, 3060w, 1775s,br, 1312s, 1160s cm.$^{-1}$; n.m.r. (CCl_4) τ 7·71 (H3 *trans* to benzoxazolin-2-one; unsym. triplet, *J* 2·0 c./sec.), 6·71 (H3 *cis* to benzoxazolin-2-one and H2, multiplet); 4·85—4·6 and 4·6—4·35 (3 vinyl H, multiplet, 8 lines), 2·96 (4 aromatic H, singlet); *m/e* 202, 135, 134, 106, 68, 67.

3-(n-Butylamino)benzoxazolin-2-one (VIII).—1-(Benzoxazolin-2-on-3-yl)-2-vinylaziridine (80 mg.) in light petroleum (15 ml.) was hydrogenated at atmospheric pressure using Adams catalyst (15 mg.). Uptake was complete

* This compound was first prepared by Dr. C. D. Campbell in this Laboratory.

† The t.l.c. of this, and other vinyl aziridines, did not usually show a single spot after development with iodine because of decomposition on silica plates. Their purity was checked using alumina (Woelm) plates.

[31] A. Mannschreck, R. Radeglia, E. Grundemann, and R. Ohme, *Chem. Ber.*, 1967, **100**, 1778.

[32] W. G. Bywater, W. R. Coleman, O. Kamm, and H. H. Merritt, *J. Amer. Chem. Soc.*, 1945, **67**, 905.

within 45 min. and the catalyst was removed. Bulb-tube distillation of the residue after removal of the solvent gave the *product* (VIII) (70 mg., 86%), b.p. 170° (bath)/0·5 mm., as a mobile colourless oil (Found: C, 63·7; H, 7·1; N, 13·5. $C_{11}H_{14}N_2O_2$ requires C, 64·1; H, 6·8; N, 13·6%), $\nu_{max.}$ (*thin* film) 3313m, 2975s, 2948s, 2887m, 1780s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 9·35—8·3 (2 H-2, 2 H-3, 3 H-4, multiplet), 7·15—6·65 (2 H-1, multiplet), 5·22 (NH, triplet, *J* 5·0 c./sec.), 2·93 (4 aromatic H, singlet). After shaking with D_2O: 7·15—6·65 (2 H-1) and 5·22 (NH) gave 6·9 (2 H-1, triplet, *J* 7 c./sec.), and 5·28 (HOD, singlet), respectively.

1-(Benzoxazolin-2-on-3-yl)-2-vinylaziridine (50 mg.) was hydrogenated in the presence of tris(triphenylphosphine)-chlororhodium [33] (20 mg.) in benzene–ethanol (10 ml.; 1 : 1) for 4 hr. at room temperature and pressure. After removal of solvent, chromatography of the residue over alumina (5 g.) and elution with benzene–ethyl acetate (10 : 1) gave a colourless oil (27 mg., 53%) identical with the product (VIII) described above.

Butylidene Derivative of 3-*Aminobenzoxazolin*-2-*one* (IX).—3-Aminobenzoxazolin-2-one (0·6 g.) and butyraldehyde (0·7 g.) were heated under reflux for 3 hr. in ethanol (12 ml.). The solution was cooled, reduced in bulk, and crystallised by dropwise addition of water to give the *butylidene derivative* (IX) (609 mg., 74%), m.p. 55—57° (Found: C, 64·5; H, 5·9; N, 13·8. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%), $\nu_{max.}$ 1778sh, 1755s, 1730sh cm.$^{-1}$; n.m.r. ($CDCl_3$) τ 8·98 (3 H-4, triplet, *J* 7 c./sec.), 8·7—7·95 (2 H-3, multiplet), 7·55 (2 H-2, multiplet), 2·9—2·7 (4 aromatic H, multiplet), 0·95 (H-1, triplet, *J* 5 c./sec.).

Reduction of the Butylidene Derivative (IX).—The butylidene derivative of 3-aminobenzoxazolin-2-one (204 mg.) in sodium-dried ether (5 ml.) was treated with lithium aluminium hydride (12 mg.) in one portion. A vigorous reaction ensued and the mixture was heated under reflux for 30 min. After decomposing the complex with water (5 drops) the salts were filtered off and washed with chloroform. Drying of the filtrate (Na_2SO_4) and evaporation gave an oil which was chromatographed over silica (15 g.). Elution with benzene–ethyl acetate (25 : 1) gave starting material (30 mg.) and benzene–ethyl acetate (10 : 1) gave 3-(n-butylamino)-benzoxazolin-2-one (VIII) (71 mg., 40% on starting material consumed) as an oil with identical spectral properties to the product of hydrogenation of 1-(benzoxazolin-2-on-3-yl)-2-vinylaziridine (VI).

3-(2-*Acetoxybut*-3-*en*-1-*ylamino*)*benzoxazolin*-2-*one* (XIII).—1-(Benzoxazolin-2-on-3-yl)-2-vinylaziridine (VII) (535 mg.) was left to stand in acetic acid (1 ml.) overnight. The mixture was added to water and extracted with ether, the ether layer was washed with saturated sodium hydrogen carbonate solution and then with water, dried (Na_2SO_4), and evaporated. Chromatography of the residual oil over silica (48 g.) and elution with benzene–ethyl acetate (10 : 1) gave the *acetate* (372 mg., 53%) as an oil which crystallised on standing. Recrystallisation (from chloroform–light petroleum) gave needles, m.p. 80·5—82° (Found: C, 60·0; H, 5·5; N, 11·0. $C_{13}H_{14}N_2O_4$ requires C, 59·5; H, 5·4; N, 10·7%), $\nu_{max.}$ 3290w, 1770s,br, 1732s,sh cm.$^{-1}$; n.m.r. (CCl_4) τ 8·12 ($OCOCH_3$, singlet), 6·70 (2 H-4, triplet, *J* 5·5 c./sec.), 5·2—4·2 (2 H-1, 1 H-2, 1 H-3 and NH, multiplet), 2·96 (4 aromatic H, singlet).

3-(2-*Acetoxybut*-1-*ylamino*)*benzoxazolin*-2-*one* (XIV).—The olefin (XIII) (107 mg.) in ethyl acetate (8 ml.) was hydrogenated over Adams catalyst (21 mg.) at room temperature and pressure. Hydrogenation was rapid and complete within 15 min. The reaction mixture contained two products (t.l.c.) which were separated by chromatography over silica (10 g.) eluting with benzene–ethyl acetate (12 : 1). The first product (35 mg., 41%) was identical with a sample of 3-(n-butylamino)benzoxazolin-2-one prepared by catalytic reduction of 1-(benzoxazolin-2-on-3-yl)-2-vinylaziridine. The second product crystallised from chloroform–light petroleum to give the *acetate* (XIV) (57 mg., 53%) as colourless needles, m.p. 76·5—78° (Found: C, 59·4; H, 6·4; N, 10·8. $C_{13}H_{16}N_2O_4$ requires C, 59·1; H, 6·1; N, 10·6%), $\nu_{max.}$ 3260w, 1770s,br, 1735s,sh cm.$^{-1}$; n.m.r. (CCl_4) τ 9·09 (3 H-4; triplet, *J* 7 c./sec.), 8·41 [2 H-3; quartet (with further smaller splitting), *J* 7 c./sec.], 8·12 ($OCOCH_3$, singlet), 6·77 (2 H-1, triplet, *J* 5·5 c./sec.), 5·35—4·85 (H-2 and NH; multiplet), 2·95 (4 aromatic H, singlet). After shaking with D_2O: τ 6·77 (2 H-1) and 5·35—4·85 (H-2 and NH) gave 6·75 (2 H-1, doublet, *J* 5·5 c./sec.), and 5·45—4·85 (H-2, multiplet), respectively.

3-(2-*Isopropenyl*-2-*methylaziridin*-1-*yl*)*benzoxazolin*-2-*one* (X).—3-Aminobenzoxazolin-2-one (1 g.) was suspended in 2,3-dimethylbuta-1,3-diene (16 ml.) and lead tetra-acetate (3 g.) added in small solid portions during 5 min. with vigorous magnetic stirring. After stirring for a further 15 min. the lead salts were removed, washed with methylene chloride, and the combined solutions evaporated. Chromatography over alumina (75 g.) with benzene–ethyl acetate (10 : 1) gave a colourless oil, which crystallised on standing. Recrystallisation (from methanol with cooling at −60°) gave the *aziridine* (X) (648 mg., 42%), m.p. 38—39° (Found: C, 67·8; H, 6·0; N, 12·3. $C_{13}H_{14}N_2O_2$ requires C, 67·8; H, 6·2; N, 12·2%), $\nu_{max.}$ 3098w, 3065w, 3040w, 3020w, 1765s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 8·56 (aziridine ring CH_3; singlet), 8·13 (isopropenyl CH_3; doublet, *J* 1·5 c./sec.), 7·45 (aziridine ring H *trans* to benzoxazolin-2-one, doublet, *J* 2 c./sec.), 6·48 (aziridine ring H *cis* to benzoxazolin-2-one, doublet, *J* 2 c./sec.), 4·99 (isopropenyl H, quartet, *J* 1·5 c./sec.), 4·82 (isopropenyl H, singlet), 2·92 (4 aromatic H, singlet). In addition there were smaller peaks at 8·47 (singlet), 8·32 (singlet), 7·71 (doublet, *J* 3 c./sec.), 5·53 (doublet, *J* 3 c./sec.) attributed to resonances of the other invertomer, where the isopropenyl and benzoxazolin-2-one groups are *cis*. The ratio of the two invertomers was estimated as 11 : 1 from the combined integration values of the respective methyl peaks.

3-(2,2-*Dimethyl*-3-*isobutenylaziridin*-1-*yl*)*benzoxazolin*-2-*one* (XI).—3-Aminobenzoxazolin-2-one (1 g.) was suspended in methylene chloride (20 ml.) containing 2,5-dimethylhexa-2,4-diene (6 g.) and lead tetra-acetate (3 g.) was added to the rapidly stirred suspension in one portion, with cooling in cold water. Stirring was continued for 4 min. when the initially formed gum had solidified. The total solution was immediately added to the top of an alumina column (70 g.), made up in benzene, and chromatographed rapidly under pressure. Continuous elution with benzene gave 2,5-dimethylhexa-2,4-diene followed by a yellow band which crystallised from light petroleum to give the *aziridine* (XI) (610 mg., 35%), m.p. 92—95° (Found: C, 70·1; H, 6·8; N, 10·6. $C_{15}H_{18}N_2O_2$ requires C, 69·7; H, 7·0; N, 10·9%), $\nu_{max.}$ 1760s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 8·65 (2 aziridine ring CH_3, singlet), 8·15 (2 isobutenyl CH_3, broad singlet containing coupling *J* 1·5 c./sec.), 6·04 (aziridine ring H, doublet, *J* 8 c./sec.), 4·96 (isobutenyl H,

[33] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

double doublet, J 8 × 1·5 c./sec.), 2·93, 2·96 (4 aromatic H, 2 lines); *m/e* 258, 135, 124 (base peak), 109. The product was unstable to air and light but was stable in a dark stoppered tube.

In the above experiment, delay in chromatography resulted in a decreased yield of the aziridine (XI). The transformation product was eluted (benzene–ethyl acetate, 10 : 1) from the column as a pale yellow oil. Re-chromatography over basic alumina gave 3-(2-*acetoxy*-2,5-*dimethyl*-trans-*hex*-3-*en*-5-*ylamino*)*benzoxazolin*-2-*one* (XV; X = OAc) as a colourless oil, b.p. 160° (bath)/0·1 mm. (Found: C, 64·3; H, 7·1; N, 9·3. $C_{17}H_{22}N_2O_4$ requires C, 64·1; H, 7·0; N, 8·8%), $\nu_{max.}$ 3335w, 1770s,br, 1730s cm.$^{-1}$; n.m.r. (CCl_4) τ 8·66 (3 H-6 and 5-CH_3, singlet), 8·58 (3 H-1 and 2-CH_3, singlet), 8·11 (acetyl CH_3, singlet), 5·46 (NH, singlet), 4·27 (H-3 and H-4, singlet), 2·96 (4 aromatic H, singlet). Reaction of the vinylaziridine (XI) in cold acetic acid gave the above acetate as the major product.

Oxidation of 3-*Aminobenzoxazolin*-2-*one in the Presence of Isoprene*.—A rapidly stirred suspension of 3-aminobenzoxazolin-2-one (1 g.) in methylene chloride (15 ml.) containing isoprene (7 ml.) was treated with lead tetra-acetate (3 g.) in one portion, with cooling in cold water. After stirring for 15 min. lead salts were removed, benzene (10 ml.) was added, and the solution evaporated *in vacuo*. Chromatography over alumina (80 g.) and elution with benzene gave an oil (306 mg., 21%) which crystallised from hexane to give 3-(2-*methyl*-2-*vinylaziridin*-1-*yl*)*benzoxazolin*-2-*one* (XII), m.p. 44·5—45° (Found: C, 66·6; H, 5·7; N, 13·2. $C_{12}H_{12}N_2O_2$ requires C, 66·7; H, 5·6; N, 13·0%), $\nu_{max.}$ 3070w, 3040w, 1765s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 8·62 and 8·44 (2-CH_3 *cis* and *trans* to benzoxazolinone respectively; two singlets ratio 1 : 1·37), 7·6—7·4 [3 H *trans* to benzoxazolinone (2 invertomers), multiplet], 6·4—6·2 [3-H *cis* to benzoxazolinone (2 invertomers), multiplet], 5·0—3·9 (3 vinylic protons in both invertomers, multiplet), 2·98 and 2·96 (4 aromatic H in both invertomers, 2 lines).

Further elution of the column with benzene–ethyl acetate (10 : 1) gave a second oil (220 mg., 15%) which crystallised from light petroleum to give 3-(2-*isopropenylaziridin*-1-*yl*)-*benzoxazolin*-2-*one* (XIII), m.p. 74·75·5° (Found: C, 66·5; H, 5·7; N, 12·9. $C_{12}H_{12}N_2O_2$ requires C, 66·7; H, 5·6; N, 13·0%), $\nu_{max.}$ 1765s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 8·22 (isopropenyl CH_3, singlet), 7·60 (3-H *trans* to benzoxazolinone, doublet, J 4·7 c./sec.), 6·86 (3-H *cis* to benzoxazolinone, doublet, J 8·4 c./sec.), 6·64 (2-H *cis* to benzoxazolinone, double doublet, J 8·4 × 4·7 c./sec.), 4·96 and 4·83 (2 olefinic H, 2 broad singlets), 2·95 (4 aromatic H, singlet).

3-(2,5-*Dimethyl*-2-*hydroxy*-trans-*hex*-3-*en*-5-*ylamino*)-*benzoxazolin*-2-*one* (XV; X = OH).—3-(2,2-Dimethyl-3-isobutenylaziridin-1-yl)benzoxazolin-2-one (XI) (100 mg.) was dissolved in benzene–ethyl acetate (3 : 1) and passed through a column of silica (10 g.). Evaporation of solvent gave the *product* (XV; X = OH) (80 mg., 74%), which crystallised from chloroform–light petroleum as plates, m.p. 93—96° (Found: C, 65·2; H, 7·5; N, 10·4. $C_{15}H_{20}N_2O_3$ requires C, 65·2; H, 7·3; N, 10·1%), $\nu_{max.}$ 3450m,br, 3275m, 1765s,br cm.$^{-1}$; n.m.r. ($CHCl_3$) τ 8·77 (3 H-1 and 2-CH_3; singlet), 8·68 (3 H-6 and 5-CH_3; singlet), 8·25 (OH, singlet), 5·45 (NH, singlet), 4·46, 4·06 [H-3 and H-4, 2 doublets (AB system), J 16 c./sec.], 2·85 (4 aromatic H, singlet). After shaking with D_2O the 8·25 (OH) and 5·45 (NH) signals gave 5·41 (2 HOD, singlet).

3-(2,5-*Dimethyl*-2-*ethoxy*-trans-*hex*-3-*en*-5-*ylamino*)-*benzoxazolin*-2-*one* (XV; X = OEt).—3-(2,2-Dimethyl-3-isobutenylaziridin-1-yl)benzoxazolin-2-one (100 mg.) was heated under reflux with ethanol (5 ml.) for 10 min. Evaporation, chromatography over alumina, and combination of fractions showing a single spot at R_F 0·35 on t.l.c. in benzene–ethyl acetate (10 : 1) gave the *product* (XV; X = OEt) (85 mg.) as a colourless oil, b.p. 140° (bath)/0·1 mm. (Found: C, 67·2; H, 8·1; N, 9·4. $C_{17}H_{24}N_2O_3$ requires C, 67·1; H, 8·0; N, 9·2%), $\nu_{max.}$ 3310w and 1765s,br cm.$^{-1}$; n.m.r. (CCl_4) τ 9·01 (CH_3 of ethyl, triplet, J 7 c./sec.) superimposed on 8·87 (3 H-1 and 2-CH_3, singlet), 8·67 (3 H-6 and 5-CH_3, singlet), 6·90 (CH_2 of ethyl, quartet, J 7 c./sec.), 5·36 (NH, singlet), 4·65, 4·25 (H-3 and H-4, 2 doublets (AB pattern), J 16 c./sec.], 2·96 (4 aromatic H, singlet).

1-(*Benzoxazolin*-2-*on*-3-*yl*)-2-*hexylaziridine* (XVI).—Lead tetra-acetate (1·9 g.) was added in small portions to a rapidly stirred suspension of 3-aminobenzoxazolin-2-one (0·6 g.) in oct-1-ene (12 ml.) during 5 min. Stirring was continued for a further 30 min. and the lead salts were filtered off, a red tar remaining in the reaction flask. The red filtrate was evaporated under reduced pressure and chromatographed over alumina (30 g.) in benzene–ethyl acetate (20 : 1). After elution of residual oct-1-ene, the product was obtained as an oil which crystallised from methanol at −60°. Recrystallisation (from light petroleum at −60°) gave the *product* (XVI) as plates (110 mg., 10%), m.p. 38—41° (Found: C, 68·8; H, 8·2; N, 11·0. $C_{15}H_{20}N_2O_2$ requires C, 69·2; H, 7·7; N, 10·8%), $\nu_{max.}$ 1765s cm.$^{-1}$; n.m.r. (CCl_4) τ 9·25—8·75 (13 hexyl H, multiplet), 7·92 (H-3 *trans* to benzoxazolin-2-one, doublet, J 4·5 c./sec.), 7·35—6·8 (H-2 and H-3 *cis* to benzoxazolin-2-one, multiplet), 2·91 (4 aromatic H, singlet).

3-(2,3,-cis-*Dimethylaziridin*-1-*yl*)*benzoxazolin*-2-*one* (XVII).—*cis*-But-2-ene (12·85 g.) was dissolved in methylene dichloride (15 ml.) at −60°. The solution was warmed to 0° and 3-aminobenzoxazolin-2-one (1 g.) was added, followed by solid lead tetra-acetate (3·1 g.) in small portions during 3 min. with vigorous magnetic stirring. The cooling bath was removed and the excess of the butene was boiled off with gentle warming and stirring. Precipitated lead salts were separated, washed with methylene chloride, and the solution was evaporated to small volume under reduced pressure before chromatographing over alumina (70 g.). Elution with benzene–ethyl acetate (10 : 1) and crystallisation of the product from methanol (with cooling at −60°) gave colourless prisms of the *aziridine* (XVII) (820 mg., 60%), m.p. 88—89° (Found: C, 64·9; H, 5·7; N, 13·9. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%), $\lambda_{max.}$ 236 (ε 9100) and 277 mμ (5320), $\nu_{max.}$ 3086w, 3055m, 3020w, 3015w, 3000m, 1755s,br cm^{-1} The 100 Mc. n.m.r. spectrum (CCl_4) showed peaks at τ 8·63 (2 aziridine ring CH_3; doublet, J 5 c./sec. with shoulder on high field arm); 7·24—6·98 [2 aziridine ring H; multiplet (9 lines)], 3·01 and 2·99 (4 aromatic H; 2 lines).

The above experiment was repeated using 3-aminobenzoxazolin-2-one (0·4 g., 2·66 mmoles) in methylene chloride (15 ml.) containing *cis*-but-2-ene (200 mg., 3·57 mmoles, 2 moles %) with the addition of lead tetra-acetate (1·2 g.) in one portion. Precipitated lead salts were separated, benzene (5 ml.) was added, and the solution reduced in volume before chromatography over alumina (40 g.). Elution with benzene–ethyl acetate (10 : 1) gave a crystalline product (90 mg., 16%), m.p. 88—89·5°, identical with the above *cis*-aziridine (XVII). An mixture of the *trans*-isomer (5%) in the *cis*-isomer had a melting range of 83—88°.

3-(2,3-trans-*Dimethylaziridin*-1-*yl*)*benzoxazolin*-2-*one*

(XVIII).—This compound was prepared exactly as described for the *cis*-isomer (XVII) but with *trans*-but-2-ene instead of *cis*-but-2-ene. Elution with benzene–ethyl acetate (10 : 1) and crystallisation of the product from methanol (with cooling at −60°) gave colourless needles of the *product* (XVIII) (918 mg., 67%), m.p. 65—65·5° (Found: C, 64·7; H, 6·1; N, 13·2. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%), $\nu_{max.}$ 3059m, 3028w, 3000m,sh, 1765s,br cm.$^{-1}$, $\lambda_{max.}$ 237 (ε 8620) and 278 mμ (5070). The 100 Mc. n.m.r. spectrum (CCl_4) showed peaks at τ 8·72 (aziridine ring CH_3 *cis* to benzoxazolinone ring; doublet, *J* 5·6 c./sec.), 8·63 (aziridine ring CH_3 *trans* to benzoxazolinone ring; doublet, *J* 5·6 c./sec.), 7·75 (aziridine ring H *trans* to benzoxazolinone ring; quintet, *J* 5·6 c./sec.), 6·69 (aziridine ring H *cis* to benzoxazolinone ring, quintet, *J* 5·6 c./sec.), 2·97 (4 aromatic H, singlet). At 33° the 60 Mc. n.m.r. spectrum (dichlorobenzene) showed peaks at τ 8·87 (aziridine ring CH_3 *cis* to benzoxazolinone ring; doublet, *J* 6 c./sec.), 8·69 (aziridine ring CH_3 *trans* to benzoxazolinone ring, doublet, *J* 6 c./sec.), 7·75 (aziridine ring H *trans* to benzoxazolin-2-one; quintet, *J* 6 c./sec.), 6·90 (aziridine ring H *cis* to benzoxazolin-2-one; quintet, *J* 6 c./sec.); the benzoxazolin-2-one ring H absorption was obscured by the solvent.

At 120° the aziridine ring methyl signal had coalesced to a triplet (*J* 6 c./sec.) and the aziridine proton signals had broadened appreciably. At 160° the aziridine methyl signals showed a doublet (*J* 6 c./sec.) and the aziridine ring proton signals had disappeared (for diagram see ref. 23).

The above experiment was repeated using 3-aminobenzoxazolin-2-one (0·4 g., 2·66 mmoles) in methylene chloride (15 ml.) containing *trans*-but-2-ene (400 mg., 7·14 mmoles, 3·9 moles %) with the addition of lead tetra-acetate in one portion. Precipitated lead salts were separated, benzene (5 ml.) was added, and the solution reduced in volume before chromatography over alumina (40 g.). Elution with benzene–ethyl acetate (10 : 1) gave a crystalline product (275 mg., 50%), m.p. 64·5—65·5°, identical with the above *trans*-aziridine (XVIII). Infrared examination of this material showed complete absence of absorption at 760 cm.$^{-1}$, present in the spectrum of the *cis*-isomer. This band was clearly visible in an admixture (melting range 59—63°) of the *cis*-isomer (6·5%) in the *trans*-isomer.

Oxidation of 1-*Amino-oxindole* (XXIII) *in the Presence of Butadiene*.—1-Amino-oxindole was prepared by the method of Baumgarten *et al.*[5] except that the ' crude tin salt collected by filtration ' dissolved when added to water (200 ml.) and the product was obtained by careful neutralisation, and purified by chromatography over silica (elution with benzene–ethyl acetate, 2 : 1) and crystallisation from carbon tetrachloride; it had m.p. 124—126°.

1-Amino-oxindole (1 g.) was suspended in a stirred mixture of buta-1,3-diene (20 ml.) and methylene chloride (15 ml.) at −60°. Lead tetra-acetate (3·1 g.) was added in one portion at this temperature and the mixture allowed to warm to room temperature with vigorous stirring. Some yellow material separated. The solution was decanted and evaporated to small volume; addition of benzene gave cinnolin-3-ol (XXIV) (314 mg.), m.p. 197—201°. The yellow precipitate was triturated with 6N-sulphuric acid, filtered, and the solution was neutralised with sodium acetate and extracted with chloroform. The chloroform layer was washed with aqueous sodium hydrogen carbonate, and water, dried, and evaporated to give more cinnolin-3-ol (336 mg., 66% in all).

We thank Dr. C. D. Campbell for the initial experiments and the University of Leicester for a Research Fellowship (to R. S. A.) which together made this work possible

[8/1369 *Received, September 20th,* 1968]