One-step Synthesis of 3,5-Dihydro-2*H*-pyrrolo[3,4-*d*]oxazoles by Reaction of *p*-Nitrosophenols with 2-Aroylaziridines

By J. W. Lown * and M. H. Akhtar, Department of Chemistry, University of Alberta, Edmonton 7, Alberta

Reaction of 1-alkyl-2-aroyl-3-arylaziridines, bearing electron-releasing substituents in the 2- or 3-positions, with substituted *p*-nitrosophenols give 3,5-dihydro-2*H*-pyrrolo[3,4-*d*]oxazoles. The isolation of nitrones and aryl and aroyl imines as secondary products supports the interpretation of the reaction in terms of two consecutive 1,3-dipolar additions, in which the second regiospecific addition is autocatalytic and is followed by a Paal–Knorr condensation.

Separate regiospecific addition of ketoaldehydes to 2-aroylaziridines followed by Paal–Knorr condensation with primary amines confirms the proposed reaction scheme and gives excellent yields of 3,5-dihydro-2*H*-pyrrolo[3,4-*d*]-oxazoles and related compounds.

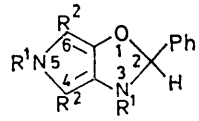
2-Aroylaziridines react with 1-nitroso-2-naphthol to produce both 2-aryl- and 2-aroyl-naphtho[1,2-*d*]oxazoles in good yield.[1] The reaction was interpreted as proceeding *via* initial 1,3-dipolar addition of an azomethine ylide (derived by thermal cleavage of the aziridine) to the nitrogen–oxygen bond in both orientations. Spontaneous 1,3-cleavage of the intermediate oxadiazolidines produced nitrones, which dehydrate and cyclise to give the observed products. The reactions of the azomethine ylides parallel those of the pyridinium ylides with

[1] J. W. Lown and J. P. Moser, *Canad. J. Chem.*, 1970, **48**, 2227.

nitrosonaphthols.[2,3] The total yield of the naphtho[1,2-*d*]oxazoles was *ca.* 80%, indicating one major, if not single, mode of cleavage of the oxadiazolidines.

2-Nitroso-1-naphthol behaves differently with 2-aroylaziridines than with pyridinium ylides, however, and affords 2-arylnaphtho[2,1-*d*]oxazoles, 2,2′-azodinaphthalene-1,1′-diol, and examples of the hitherto

(I) $R^1 = C_6H_{11}$, $R^2 = p$-MeC_6H
(II) $R^1 = C_6H_{11}$, $R^2 = p$-$MeO{\cdot}C_6H_4$
(III) $R^1 = Pr^i$, $R^2 = p$-$MeO{\cdot}C_6H_4$



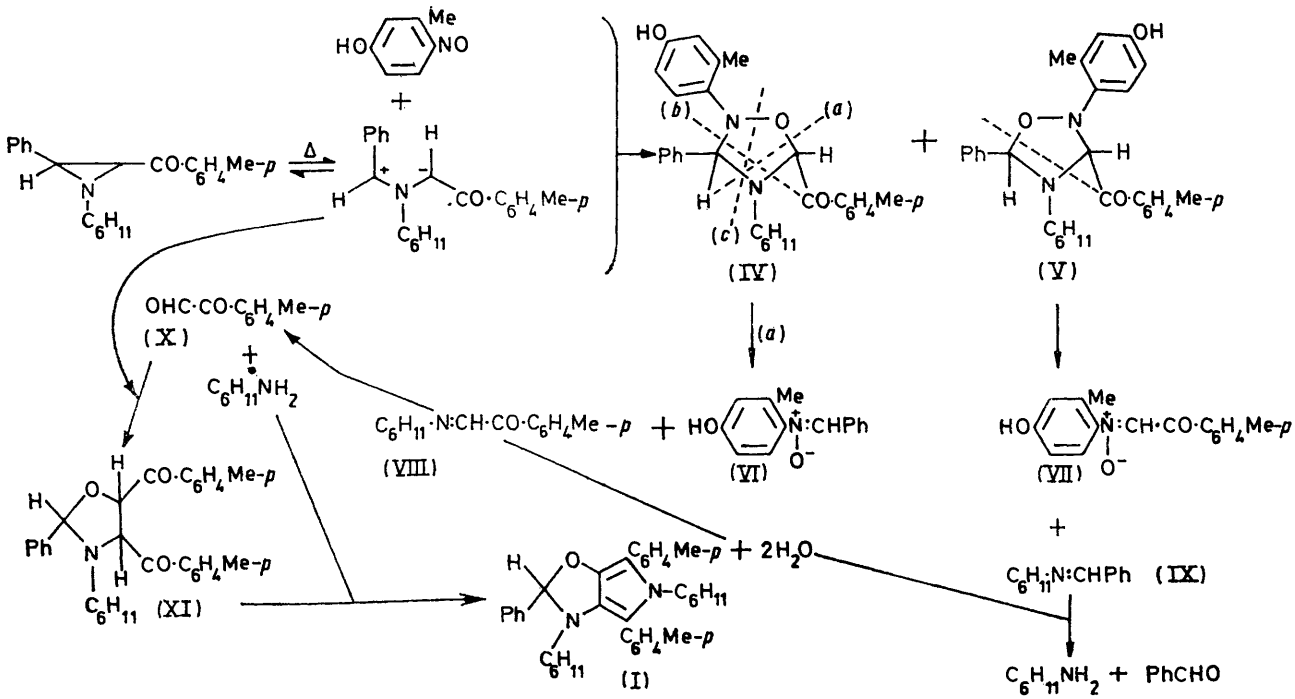
undescribed naphtho[2,1-*f*][1,3,5]oxadiazepine system,[4] whereas with pyridinium ylides only naphtho[2,1-*d*]-oxazoles are produced.[2] In the formation of the 2-arylnaphtho[2,1-*d*]oxazole, a similar 1,3-cleavage of the intermediate oxadiazolidine was required.

The reaction of 1-nitroso-2-naphthylamine with 2-aroylaziridines to give 3-arylbenzo[*f*]quinoxalines, cyclohexylimino-derivatives of 2-arylnaphtho[1,2-*d*]imidazoles, and a 2-arylnaphtho[1,2-*d*]imidazole, also requires two modes of cleavage of the oxadiazolidine.[5]

nitrones formed immediately cyclised with the *ortho*-hydroxy- or amino-groups to produce oxazole or imidazole residues respectively. It was considered that suitable positioning of the activating group in the nitroso-compound to prevent this cyclisation might permit isolation of a nitrone and thus support the postulated reaction schemes.

para-Nitrosophenols were suitable substrates and from their reactions with aziridines both Schiff bases and nitrones were isolated, thus providing evidence of the selective trapping of another intermediate. A general synthetic scheme for fused bicyclic heterocycles has been devised.

Treatment of 3-methyl-4-nitrosophenol with one equiv. of 1-cyclohexyl-2-phenyl-3-*p*-toluoylaziridine in benzene under reflux for 24 h gave the dihydropyrrolo-[3,4-*d*]oxazole (I) in 29% yield. Similarly, treatment of 2-methyl-4-nitrosophenol or *p*-nitrosophenol with 1-cyclohexyl-2-phenyl-3-*p*-toluoylaziridine produced the oxazole (I) in comparable yield, while treatment of 3-methyl-4-nitrosophenol with 2-*p*-anisoyl-1-cyclohexyl-3-phenylaziridine under similar conditions afforded compound (II).



SCHEME

It was desirable to obtain more direct supporting evidence for the proposed modes of cleavage of the oxadiazolidine intermediate by detecting the secondary fragments. These included Schiff bases, which had not been isolated directly owing to their ready hydrolysis by the water produced in these reactions. Also the

The synthesis may be extended to include other *N*-substituents, *e.g.* 2-*p*-anisoyl-1-isopropyl-3-phenylaziridine with 4-nitrosophenol gives the dihydro-*NN*′-diisopropylpyrrolo[3,4-*d*]oxazole (III) in which the two *N*-isopropyl substituents may be distinguished by n.m.r. spectroscopy. The signal for the methine protons of

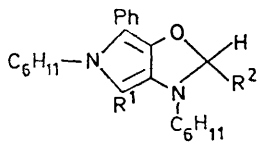
[2] F. Krohnke, *Angew. Chem. Internat. Edn.*, 1962, **2**, 380.
[3] K. Gerlach and F. Krohnke, *Chem. Ber.*, 1962, **95**, 1124.
[4] J. W. Lown and J. P. Moser, *Tetrahedron Letters*, 1970, 3019.
[5] J. W. Lown and M. H. Akhtar, *Canad. J. Chem.*, 1971, **49**, 1610.

the 5-isopropyl group appears at lower field, owing to the ring current in the pyrrole ring.[6]

The formation of the pyrrolo-oxazoles (I)—(III) is rationalised (see Scheme) by involving initial cycloaddition of the azomethine ylide (derived from thermal cleavage of the aziridine) to the nitroso-group to form the intermediate oxadiazolidines (IV) and (V) followed by 1,3-cleavage to give respectively the nitrone (VI) and the aroyl-amine (VIII) and the nitrone (VII) and benzylidenecyclohexylamine (IX).

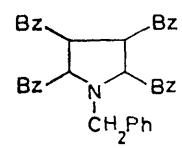
As in other 1,3-dipolar additions,[1,4,5] the secondary products, the Schiff bases (VIII) and (IX), usually undergo rapid hydrolysis by water (released in the subsequent condensation) forming the ketoaldehyde (X) and benzaldehyde respectively together with 2 mol. equiv. of cyclohexylamine, which are involved in the subsequent condensation. The ketoaldehyde (X) undergoes a regiospecific 1,3-dipolar addition with the azomethine ylide derived from the aziridine to form the oxazolidine (XI). We and others have shown that aromatic and aliphatic aldehydes, provided they are activated by polarising groups, will readily undergo such cycloadditions with aziridines [7] with such regiospecificity.[8] The oxazolidine (XI) is a 1,4-dicarbonyl compound ideally suited to the subsequent Paal–Knorr condensation [9] with cyclohexylamine to form the pyrrolo-oxazole (I). Since 2 mol. equiv. of water are released in the last condensation step, water becomes available to hydrolyse the imine (VIII) and further promote the succeeding steps so that the overall reaction is autocatalytic. In fact water is visibly present in the mixture after a few hours in benzene.

The proposed Scheme is supported independently by the reaction of phenylglyoxal with 2-*p*-anisoyl-1-cyclohexyl-3-phenylaziridine in benzene, which produced the dihydropyrrolo[3,4-*d*]oxazole (XII) in 63% yield. Similarly reaction of phenylglyoxal with 2,3-dibenzoyl-1-cyclohexylaziridine in benzene afforded the 2-benzoyl-3,5-dicyclohexyl-3,5-dihydro-4,5-diphenyl-2*H*-pyrrolo-[3,4-*d*]oxazole (XIII) in 55% yield. In these two cases apparently the final Paal–Knorr condensation step with cyclohexylamine (generated *in situ* by hydrolysis of some of the aziridine) is too rapid to allow isolation of the intermediates analogous to the oxazolidine (XI).

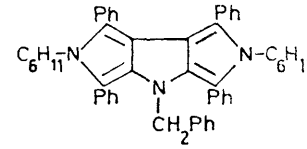


(XII) R^1 = *p*-MeO·C_6H_4, R^2 = Ph
(XIII) R^1 = Ph, R^2 = Bz

However, reaction of *trans*-1,2-dibenzoylethylene with 2,3-dibenzoyl-1-benzylaziridine in toluene gave the 2,3,4,5-tetrabenzoyl-1-benzylpyrrolidine (XIV) in 65% yield with undetermined stereochemistry. Treatment of (XIV) with cyclohexylamine in methanol at room temperature gave the tetraphenyldipyrrolo[3,4-*b*:3′,4′-*d*]-pyrrole (XV) smoothly in 87% yield.



(XIV)



(XV)

The Scheme explains why formation of the pyrrolo-oxazole (I) and similar compounds is independent of the structure of the nitroso-compound, provided that the nitroso-bond is sufficiently activated to permit initial cycloaddition. Therefore, 2-*p*-anisoyl-1-cyclohexyl-3-phenylaziridine upon treatment with 2-methyl-4-nitrosophenol, 3-methyl-4-nitrosophenol, or *p*-nitrosophenol gave the same pyrrolo-oxazole (II).

When reaction of 2-methyl-4-nitrosophenol or nitrosophenol with 2-anisoyl-1-cyclohexyl-3-phenylaziridine was carried out in acetonitrile it was possible to isolate, besides (II), both cyclohexylamines (VIII) and (XVI) in a ratio of 3 : 2. The rate of hydrolysis of (VIII) and (XVI) appears to be diminished under these conditions.

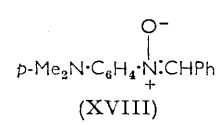
C_6H_{11}·N:CH·CO·C_6H_4·OMe-*p* (XVI)

OHC·CO·C_6H_4·OMe-*p* (XVII)

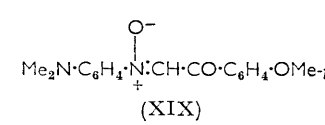
This experiment also indicates that the imine (XVI) is less dipolarophilic than the activated aldehyde (XVII), a conclusion which is in agreement with previous findings.[10]

In general, the yield of the pyrrolo-oxazole (I) and similar compounds is not increased by the addition of an excess of aziridine, indicating that the rate of production of (I) is controlled by the rate of generation of the ketoaldehyde (X). Treatment of 1-cyclohexyl-2-*p*-nitrobenzoyl-3-phenylaziridine with nitrosophenols did not give rise to dihydropyrrolo[3,4-*d*]oxazoles.

The nitrones (VI) and (VII) were detected spectroscopically but attempts to separate the dark crystalline solids were unsuccessful. However when *p*-*NN*-dimethylaminonitrosobenzene was treated with 2-*p*-anisoyl-1-cyclohexyl-3-phenylaziridine in benzene both nitrones (XVIII) and (XIX) [analogous to (VI) and (VII) respectively] were isolated together with the dihydropyrrolo[3,4-*d*]oxazole (II). The *N*-oxide (XVIII)



(XVIII)



(XIX)

[6] P. B. Woller and N. H. Cromwell, *J. Org. Chem.*, 1971, **35**, 888.

[7] (*a*) F. Texier and R. Carrie, *Compt. rend.*, 1969, *C*, **269**, 709; (*b*) G. Dallas, J. W. Lown, and J. P. Moser, *J. Chem. Soc.* (*C*), 1970, 2383; (*c*) H. W. Heine and R. P. Henzel, *J. Org. Chem.*, 1969, **34**, 171; (*d*) R. Huisgen, V. Martin-Ramos, and W. Scheer, *Tetrahedron Letters*, 1971, 477.

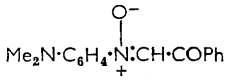
[8] A. Hassner, *J. Org. Chem.*, 1968, **33**, 2684.

[9] (*a*) C. Paal, *Ber.*, 1884, **17**, 2756; (*b*) L. Knorr, *ibid.*, p. 2863.

[10] J. W. Lown, J. P. Moser, and R. Westwood, *Canad. J. Chem.*, 1969, **47**, 4335.

was identified by comparison with an authentic sample,[11b] while (XIX) was synthesised independently by reaction of *p*-methoxyphenacylpyridinium bromide and *NN*-dimethyl-*p*-nitrosoaniline in ethanol in the presence of sodium hydroxide at low temperature.

Also, reaction of *p-NN*-dimethylaminonitrosobenzene with 2,3-dibenzoyl-1-cyclohexylaziridine in toluene gave the nitrone (XX) and the dihydropyrrolo[3,4-*d*]oxazole (XIII) consistent with the scheme. The structure of the *N*-oxide (XX) was similarly proven by comparison with an authentic sample.[11b]



(XX)

Previous reactions between *p-NN*-dialkylaminonitrosobenzene and 2-aroylaziridines bearing an electron-withdrawing group in the 3-position gave exclusively Schiff bases *via* cleavage mode (*c*) of the oxadiazolidine (IV) (see Scheme). This sensitivity of the mode of cleavage parallels the behaviour of 1-nitroso-2-naphthylamine with aziridines.[5]

The relatively low yield of the dihydropyrrolo[3,4-*d*]-oxazoles (*ca.* 35%) from the nitrosophenols may be attributed in part to the complexity of the overall reaction, but also may be due to the susceptibility of aziridines to undergo nucleophilic attack by water (especially in acetonitrile) leading to some cleavage to the aldehyde as has been observed previously.[12]

Another factor tending to limit the yield of the pyrrolo-oxazole (I) in this reaction is the regiochemistry of the initial addition leading to compounds (III) and (IV). Previous work on the cycloadditions of nitroso-compounds [1,4,5,13] has shown that such additions are not regiospecific but proceed almost equally in the two possible orientations. Indeed in the present case one would expect, from considerations of the location of charges in the dipole, that the orientation leading to oxadiazolidine (V) would be favoured over that giving (IV). The larger proportion of benzylidenecyclohexylamine (IX) isolated compared with the imine (VIII) in acetonitrile suggests a bias in favour of the isomer (V). It may be argued that some of the benzylidenecyclohexylamine arises from cleavage mode (*b*) of (IV), but there is no evidence by way of isolated products or fragments that this mode operates in this reaction. On the contrary the isolation of the nitrones (XVIII)—(XX) favours mode (*a*).

This orientation factor may explain the lack of production of any dihydropyrrolo[3,4-*d*]oxazole by the reaction of 2-benzoyl-1-cyclohexyl-3-phenylaziridine with activated nitroso-compounds. In contrast, 2,3-dibenzoyl-1-cyclohexylaziridine [in which by symmetry only one orientation of addition giving (IV) is possible] readily reacts with 2-methyl-4-nitrosophenol to give the dihydropyrrolo[3,4-*d*]oxazole (XIII). The same compound (XIII) is obtained by the reaction of phenylglyoxal with 1-cyclohexyl-2,3-dibenzoylaziridine.

In conclusion, 3,5-dihydro-2*H*-pyrrolo[3,4-*d*]oxazoles may now be obtained in excellent yield by direct reaction of ketoaldehydes and similarly activated dipolarophiles with azomethine ylides.

EXPERIMENTAL

M.p.s were determined with a Fisher–Johns apparatus. I.r. spectra were recorded with a Perkin-Elmer model 421 spectrophotometer. N.m.r. spectra were recorded with Varian A60 and A100 spectrometers for *ca.* 5—10% (w/v) solutions; line positions are reported in p.p.m. from tetramethylsilane. Mass spectra were determined with an A.E.I. MS12 double-focusing high-resolution mass spectrometer (ionisation energy usually 70 eV). Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15,000. Kieselgel DF-5 (Camag, Switzerland) and Eastman Kodak precoated silica sheets were used for t.l.c. Microanalyses were carried out by Mrs. D. Mahlow of this department. Grade 1 alumina (B.D.H.) was used for chromatography.

General Preparation of 2-*Aroylaziridines*.—The aziridines were prepared by the Gabriel synthesis as described in the literature.[14]

General Procedure for the Reaction of 2-*Arylaziridines with* p-*Nitrosophenols*.—Representative examples of the preparation of 2,3-dihydropyrrolo[3,4-*d*]oxazoles are described.

Reaction of 1-*Cyclohexyl*-2-*phenyl*-3-p-*toluoylaziridine with* 2-*Methyl*-4-*nitrosophenol*.—A solution of the aziridine (1·61 g, 5 mmol) and the nitrosophenol (0·69 g, 5 mmol) in dry benzene (50 ml) was heated under reflux for 24 h. Removal of the solvent *in vacuo* gave a red oil which was chromatographed on alumina (80 g). Elution with benzene–hexane (50 : 50) gave an orange oil (0·384 g, 29%), which on trituration with methanol gave orange 3,5-*dicyclohexyl*-3,5-*dihydro*-2-*phenyl*-4,6-*di*-p-*tolyl*-2H-*pyrrolo*[3,4-d]*oxazole* (I), m.p. 158—159° [Found: C, 83·3; H, 8·1; N, 5·4%; *M* (mass spectrum), 530·3317. $C_{37}H_{42}N_2O$ requires C, 83·5; H, 8·0; N, 5·3%; *M*, 530·3297], δ ($CDCl_3$) 0·42—2·19 (20H, m, cyclohexyl CH_2), 2·33 and 2·57 (3H, each, s, Me), 2·66br (1H, s, cyclohexyl CH), 3·63—4·30br (1H, s, cyclohexyl CH), and 6·70—7·53 (14H, m, ArH and 2-H).

Reaction of 1-*Cyclohexyl*-2-*phenyl*-3-p-*toluoylaziridine with* 3-*Methyl*-4-*nitrosophenol*.—A solution of the aziridine (1·59 g, 5 mmol) and the nitrosophenol (0·71 g, 5 mmol) in dry benzene (50 ml) was similarly heated under reflux for 24 h. Removal of the solvent *in vacuo* gave a red oil, which was chromatographed on alumina (80 g). Elution with benzene–hexane (50 : 50) gave one main fraction as an orange oil, which on trituration with methanol gave the oxazole (I) as an orange solid (0·374 g, 28·5%), m.p. and mixed m.p. 159—160°; the n.m.r. and i.r. spectra were superimposable with those obtained from the material from the foregoing preparation.

Reaction of 2-p-*Anisoyl*-1-*cyclohexyl*-3-*phenylaziridine with* 3-*Methyl*-4-*nitrosophenol*.—A solution of the aziridine (3·35 g, 10 mmol) and the nitrosophenol (1·38 g, 10 mmol)

[11] (*a*) F. Krohnke, *Ber.*, 1938, **71**, 2583; (*b*) F. Krohnke and E. Borner, *ibid.*, 1936, **69**, 2006.
[12] J. W. Lown and M. H. Akhtar, unpublished results.
[13] G. Kresze, J. Firl, and H. Braun, *Tetrahedron*, 1969, **25**, 4481.
[14] N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson, and J. H. Anglin, *J. Amer. Chem. Soc.*, 1951, **73**, 1044.

in dry benzene (100 ml) was heated under reflux for 24 h. Work-up as before gave 3,5-*dicyclohexyl*-3,5-*dihydro*-4,6-*bis*-(p-*methoxyphenyl*)-2-*phenyl*-2H-*pyrrolo*[3,4-d]*oxazole* (II) (0·987 g, 35%), m.p. 151—153° [Found: C, 79·3; H, 7·8; N, 4·8%; *M* (mass spectrum) 562·3185. $C_{37}H_{42}N_2O_3$ requires C, 79·0; H, 7·5; N, 5·0%; *M*, 562·3195], δ ($CDCl_3$) 0·47—2·45 (20H, m, cyclohexyl CH_2), 2·72br (1H, s, cyclohexyl CH), 3·72 (3H, s, OMe), 3·90 (3H, s, OMe), 3·75—4·24br (1H, s, cyclohexyl CH), and 6·52—7·73 (14H, m, ArH and 2-H).

Similar reactions of 2-*p*-anisoyl-1-cyclohexyl-3-phenylaziridine with (*a*) 2-methyl-4-nitrosophenol and (*b*) 4-nitrosophenol gave compound (II) in 34 and 31% yields, respectively.

Reaction of 2-p-*Anisoyl*-1-*cyclohexyl*-3-*phenylaziridine with* 2-*Methyl*-4-*nitrosophenol in Acetonitrile.*—A solution of the aziridine (3·35 g, 10 mmol) and the nitrosophenol (1·35 g, 10 mmol) in acetonitrile (100 ml) was heated under reflux for 24 h. Removal of the solvent *in vacuo* gave a dark oil, which was chromatographed on alumina (150 g). Elution with benzene–hexane (50 : 50) gave an oil (2·07 g), trituration of which with methanol deposited orange crystals of (II) (0·627 g, 22·3%), m.p. 149—151°; the n.m.r. and i.r. spectra were identical with those of the products obtained before. The methanolic filtrate was evaporated to dryness *in vacuo* to give an oil, which did not crystallise. The n.m.r. spectrum showed the presence of the imines (VIII) and (XVI) (3 : 2) (19·5 and 14% of the overall yield, respectively). Distillation of the oil *in vacuo* gave a pure sample of cyclohexyliminomethyl *p*-tolyl ketone (VIII), which had n.m.r. and i.r. spectra identical with those of an authentic sample.[15]

Reaction of 2-p-*Anisoyl*-1-*cyclohexyl*-3-*phenylaziridine with Phenylglyoxal in Benzene.*—A solution of the aziridine (1·68 g, 5 mmol) and phenylglyoxal (0·67 g, 5 mmol) in dry benzene (50 ml) was heated under reflux for 24 h. Removal of the solvent gave an oil, which was chromatographed on alumina (80 g). Elution with benzene–hexane (50 : 50) gave an orange oil (0·843 g, 63%), which on trituration with methanol gave yellow 3,5-*dicyclohexyl*-3,5-*dihydro*-4-(p-*methoxyphenyl*)-2,6-*diphenyl*-2H-*pyrrolo*[3,4-d]*oxazole* (XII), m.p. 140—142° [Found: C, 81·0; H, 7·4; N, 5·4%; *M* (mass spectrum), 532·3080. $C_{36}H_{40}N_2O_2$ requires C, 81·0; H, 7·6; N, 5·3%; *M*, 532·3090], δ ($CDCl_3$) 0·46—2·20 (20H, m, cyclohexyl CH_2), 2·73br (1H, s, cyclohexyl CH), 3·88 (3H, s, OMe), 3·77—4·25br (1H, s, cyclohexyl CH), and 6·80—7·74 (15H, m, ArH and 2-H).

Reaction of 2,3-*Dibenzoyl*-1-*benzylaziridine with* trans-1,2-*Dibenzoylethylene.*—A solution of the *trans*-aziridine[16] (0·85 g, 2·5 mmol) and 1,2-dibenzoylethylene (0·60 g, 2·5 mmol) in dry toluene (20 ml) was heated under reflux for 24 h. Removal of the solvent *in vacuo* gave a red oil, trituration of which with methanol deposited the white 2,3,4,5-*tetrabenzoyl*-1-*benzylpyrrolidine* (XIV) (0·945 g, 65%), m.p. 172—173·5° [Found: C, 80·9; H, 5·3; N, 2·6%; base peak (mass spectrum) (*M* − C_7H_5O), 472·1925. $C_{39}H_{31}NO_4$ requires C, 80·9; H, 5·3; N, 2·6%; base peak, 472·1913], δ ($CDCl_3$) 3·80 (2H, ABq, *J* 14·5 Hz, PhC*H*$_2$), 5·16 (4H, ABq, *J* 5·5 Hz, 2-, 3-, 4-, and 5-H), and 7·11—8·15 (25H, m, ArH), $\nu_{max.}$ ($CHCl_3$) 1720—1670 cm^{-1} (C=O).

Reaction of 2,3,4,5-*Tetrabenzoyl*-1-*benzylpyrrolidine with Cyclohexylamine.*—A solution of the pyrrolidine (0·578 g, 1 mmol) and cyclohexylamine (0·401 g, 4 mmol) in methanol (40 ml) was left at room temperature overnight. Evaporation gave a red oil, which crystallised from benzene–hexane to give yellow 1-*benzyl*-2,6-*dicyclohexyl*-4,6-*dihydro*-1,3,5,7-*tetraphenyl*-2H-*dipyrrolo*[3,4-b:3′,4′-d]*pyrrole* (XV) (0·605 g, 87%), m.p. 140—141·5° [Found: C, 86·9; H, 7·1; N, 5·8%; *M* (mass spectrum), 703·3907. $C_{51}H_{49}N_3$ requires C, 87·0; H, 7·0; N, 6·0%; *M*, 703·3927], δ ($CDCl_3$) 0·83—2·4 (20H, m, cyclohexyl CH_2), 2·57—3·45br (2H, s, 2 × cyclohexyl CH), 5·15 (2H, s, PhCH_2), and 7·21—8·15 (25H, ArH).

Reaction of 2,3-*Dibenzoyl*-1-*cyclohexylaziridine with* 2-*Methyl*-4-*nitrosophenol.*—A solution of the aziridine (3·33 g, 10 mmol) and the nitrosophenyl (1·37 g, 10 mmol) was heated under reflux in dry toluene (100 ml) for 24 h. Removal of the solvent gave a dark red oil, which was chromatographed on alumina (150 g). Elution with benzene–hexane (60 : 40) gave 2-*benzoyl*-3,5-*dicyclohexyl*-3,5-*dihydro*-4,6-*diphenyl*-2H-*pyrrolo*[3,4-d]*oxazole* (XIII) as an orange oil (0·743 g, 28%) [Found: C, 81·0; H, 7·3; N, 5·4%; *M* (mass spectrum), 530·2946. $C_{36}H_{38}N_2O_2$ requires C, 81·5; H, 7·2; N, 5·3%; *M*, 530·2933], δ ($CDCl_3$) 0·56—2·46 (20H, m, cyclohexyl CH_2), 2·94—3·45br (1H, s, cyclohexyl CH), 3·57—4·34br (1H, s, cyclohexyl CH), and 7·14—8·24 (16H, m, ArH and 2-H), $\nu_{max.}$ ($CHCl_3$) 1676 cm^{-1} (C=O).

Reaction of 2,3-*Dibenzoyl*-1-*cyclohexylaziridine with Phenylglyoxal.*—A solution of the aziridine (1·67 g, 5 mmol) and phenylglyoxal (0·68 g, 5 mmol) was heated under reflux in dry toluene (50 ml) for 24 h. Work-up as before gave the pyrrolo-oxazole (XIII) as an orange oil (0·74 g, 55%). The n.m.r. and i.r. spectra of this oil were superimposable with those of the product obtained from the reaction of 2,3-dibenzoyl-1-cyclohexylaziridine and 2-methyl-4-nitrosophenol in benzene described above.

Reaction of 2-p-*Anisoyl*-1-*isopropyl*-3-*phenylaziridine with* 4-*Nitrosophenol.*—A solution of the aziridine (2·96 g, 10 mmol) and the nitrosophenol (1·26 g, 10 mmol) in dry benzene (50 ml) was heated under reflux for 24 h. Work-up in the usual way gave 3,5-*dihydro*-3,5-*di-isopropyl*-4,6-*bis*-(p-*methoxyphenyl*)-2-*phenyl*-2H-*pyrrolo*[3,4-d]*oxazole* (III) as an orange oil (0·473 g, 20·0%) [Found: C, 77·2; H, 6·9; N, 5·6%; *M* (mass spectrum), 482·2577. $C_{31}H_{34}N_2O_3$ requires C, 77·1; H, 7·1; N, 5·8%; *M*, 482·2569], δ ($CDCl_3$) 0·63 (6H, d, *J* 6·5 Hz, *Me*$_2$CH), 1·43 (6H, d, *J* 6·5 Hz, *Me*$_2$CH), 3·23—3·52 (1H, m, Me$_2$C*H*), 3·65 (3H, s, OMe), 3·85 (3H, s, OMe), 4·43—4·74 (1H, m, Me$_2$C*H*), and 6·87—7·84 (14H, m, ArH and 2-H).

Reaction of 2,3-*Dibenzoyl*-1-*cyclohexylaziridine with* NN-*Dimethyl*-4-*nitrosoaniline in Toluene.*—A solution of the aziridine (3·33 g, 10 mmol) and the nitrosoaniline (1·50 g, 10 mmol) in dry toluene (100 ml) was heated under reflux for 24 h. Removal of the solvent *in vacuo* gave an oil, which on dilution with methanol and chilling deposited red N-*benzoylmethylene*-4-*dimethylaminoaniline* N-*oxide* (XX) (0·158 g, 11%), m.p. and mixed m.p. 108—110° (lit.,[11b] 110—111°).

The filtrate was concentrated to a small volume and chromatographed on alumina (120 g). Elution with benzene–hexane (75 : 25) gave the pyrrolo-oxazole (XIII) as an orange oil (0·092 g, 6·2%). The n.m.r. and i.r. spectra of this oil were superimposable with those of the product obtained before.

Reaction of 2-p-*Anisoyl*-1-*cyclohexyl*-3-*phenylaziridine with* NN-*Dimethyl*-4-*nitrosoaniline.*—A solution of the aziridine

[15] E. D. Bergmann, E. Zimkin, and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 168.

[16] A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, *J. Amer. Chem. Soc.*, 1965, **87**, 1050.

(3·38 g, 10 mmol) and the nitroso-compound (1·52 g, 10 mmol) in dry benzene (100 ml) was heated under reflux for 24 h. Removal of the solvent gave a red oil. Dilution of the oil with a small amount of methanol (*ca.* 10 ml) precipitated brown *N*-benzylidene-4-dimethylaminoaniline *N*-oxide (0·308 g, 13%), m.p. and mixed m.p. 139—141° (lit.,[11a] 144°). The filtrate was concentrated to a small volume and chromatographed on alumina (120 g). Elution with benzene–hexane (50 : 50) gave an orange oil of the pyrroloxazole (II) (0·318 g, 11·3%), which crystallised on trituration with methanol, m.p. 151—152·5°. The i.r. and n.m.r. spectra of this compound were identical with those of the product obtained before. Further elution with benzene–chloroform (80 : 20) gave N-(p-*anisoyl*)*methylene*-4-*dimethylaminoaniline* N-*oxide* (XIX) (0·201 g, 7%), which did not crystallise. The i.r. and n.m.r. spectra of this oil were superimposable with those of an authentic sample prepared by the reaction of *p*-methoxyphenacylpyridinium bromide and *NN*-dimethyl-4-nitrosoaniline in ethanolic solution at −5° in the presence of 1N-NaOH according to a literature procedure [11b] [Found: *M* (mass spectrum), 298·1311. $C_{17}H_{18}N_2O_3$ requires *M*, 298·1317], δ ($CDCl_3$) 2·97 (6H, s, Me_2N), 3·80 (3H, s, OMe), 6·51—8·01 (8H, m, ArH), and 8·22 (1H, s, vinyl H), $\nu_{max.}$ ($CHCl_3$) 1618 cm^{-1} (C=O).

This research was supported by the National Research Council of Canada and the Chemistry Department of the University of Alberta.

[1/2247 *Received*, 26*th November*, 1971]