The 1,3-Dipolar Addition of 2-Aroyl-aziridines to 1-Nitrosonaphth-2-ol: Novel Syntheses of Substituted Naphtho[1,2-*d*]oxazoles

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Summary A series of 2-aroyl-aziridines underwent 1,3-dipolar additions in both orientations to the nitrogen–oxygen bond of 1-nitrosonaphth-2-ol; spontaneous cleavage of the intermediate oxadiazolidine to a nitrone and cyclisation of the latter afforded both 2-aryl- and 2-aroyl-naphtho[1,2-*d*]oxazoles in good yield: the interpretation of the reaction received confirmation by independent, unambiguous synthesis of a 2-aroyl-naphtho[1,2-*d*]oxazole.

REACTIONS involving the thermal and photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon–carbon multiple bonds are firmly established.[1] We have reported the additions of 2-aroyl- and 2-alkoxycarbonyl-aziridines to the following hetero-multiple bonds as dipolarophiles (i) the C=S bond of aryl isothiocyanates with the formation of 4-aroyl-5-arylamino-4-thiazolines,[2] (ii) the C=N bond of imines and sulphonylimines with the formation of imidazolidines,[3] (iii) the C=O bond of diphenylcyclopropenone which ultimately affords 4-aroyl-4-oxazolines,[4] and (iv) the C=N bond of cyclopropenimines to form imidazolines and imidazolidines.[5]

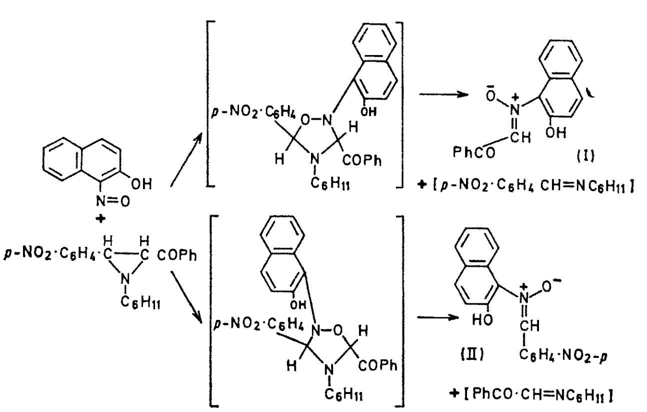
2-Aryl-naphtho[1,2-d]*oxazoles*†

	R^1	R^2	M.p.	Yield (%)	Molecular ion
(IIIa)	H	NO_2	240°	35·5	290
(IIIb)	NO_2	H	237—239°	32	290
(IIIc)	H	H	125—130°	40	245

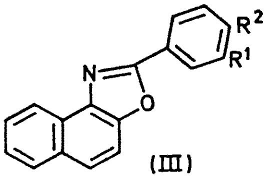
2-Aroyl-naphtho[1,2-d]*oxazoles*†

	R	M.p.	Yield (%)	I.r. (C=O)	Molecular ion
(IVa)	H	124°	41·5	1658 cm^{-1}	273
(IVb)	Me	114°	32·3	1652	287
(IVc)	OMe	124—125°	41·5	1651	303
(IVd)	NO_2	223—225°	31·5	1663	318

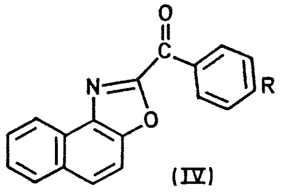
We report the synthesis of both 2-aryl- and 2-aroylnaphtho[1,2-*d*]oxazoles by the addition of a series of 2-aroyl-aziridines to 1-nitrosonaphth-2-ol *via* initial 1,3-dipolar addition in both orientations to the N=O double bond. Treatment of 2-benzoyl-1-cyclohexyl-3-*p*-nitrophenylaziridine[6] with 1 equiv. of 1-nitrosonaphth-2-ol in refluxing benzene afforded the insoluble 2-(4-nitrophenyl)-naphtho[1,2-*d*]oxazole (IIIa) (35·5%), m.p. 240°; ν_{max} (KBr disc) 1532 cm^{-1} (NO_2); M^+ 290·0694, calc. 290·0691. Concentration of the filtrate and chromatographic separation afforded pale-green 2-benzoylnaphtho[1,2-*d*]oxazole (IVa) (38·5%), m.p. 123°; ν_{max} ($CHCl_3$) 1660 cm^{-1} (C=O); λ_{max} (CH_2Cl_2) 264 (log ϵ 4·19), 356 (4·19) nm; M^+ 273·0788, calc. 273·0790. In view of the strong analogies quoted above we interpret the reaction as proceeding by thermal cleavage of the aziridine to an azomethine ylide, followed by 1,3-dipolar addition to the N=O bond in both orientations and 1,3-cleavage of the intermediate oxadiazolidine to give initially nitrones (I) and (II).



The oxadiazolidine which results from the 1,3-dipolar addition of a nitrile ylide to nitrosobenzene similarly cannot be isolated and undergoes a 1,3-cleavage to give a nitrone and benzonitrile.[7] The isolation of an oxadiazolidine has been reported only once in the literature and it was shown to be unstable.[8] The neighbouring hydroxyl groups in (I) and (II) cyclise to the polarised azomethine bond and loss of water produces (IV; R = H) and (III; R^1 = H,R^2=NO_2) respectively. This interpretation of the reaction and the structure of (IVa) receives confirmation



(III)



(IV)

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† Satisfactory analytical data were obtained on all new compounds.

by the following independent synthesis. Treatment of a mixture of 1-nitrosonaphth-2-ol and 1 equiv. of *N*-phenacylpyridinium bromide[9] in 86% ethanol with 1 equiv. of 1N-aqueous NaOH at −20° afforded a quantitative yield of (IVa) m.p. 124°. Reactions between pyridinium or sulphonium ylides and aryl nitroso-compounds to form nitrones have been reported.[10]

Similar 2-aryl- and 2-aroyl-naphtho[1,2-*d*]oxazoles obtained by reaction of 1-nitrosonaphth-2-ol with the appropriate aziridine are summarised in the Table.

The isolation of naphtho-oxazoles (III) and (IV) in approximately equal yields represents the first example of 1,3-dipolar addition of a hetero-multiple bond to aziridines in both possible orientations. This shows that the steric influence on orientation is very small, and a similar conclusion has been reached recently by Kresze and his coworkers in a study of the Diels–Alder additions of nitrosobenzene to substituted dienes.[11]

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