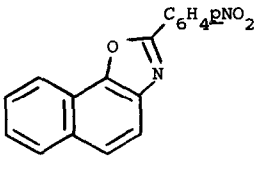
Tetrahedron Letters No.34, pp. 3019-3022, 1970. Pergamon Press. Printed in Great Britain.

REACTION OF 3-AROYLAZIRIDINES WITH 2-NITROSO-1-NAPHTHOL

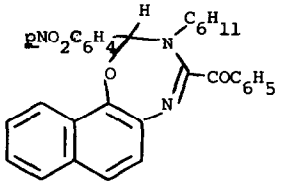
J. W. Lown and J. P. Moser

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada
(Received in USA 19 May 1970; received in UK for publication 23 June 1970)

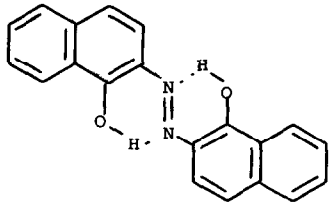
3-Aroylaziridines undergo thermally induced 1,3-dipolar cycloaddition via azomethine ylides to the N=O bond of 1-nitroso-2-naphthol in both orientations to form 2-aryl and 2-aroyl-naphtho[1,2-d]-oxazoles in good yield.[1,2] We report the reaction of 3-aroylaziridines with 2-nitroso-1-naphthol (I) which forms in addition to 2-arylnaphtho[2,1-d]oxazoles, 22'-azodi-1-naphthol and examples of the hitherto undescribed naphtho[2,1-f]-2H-1,3,5-oxadiazepine system.



II



III

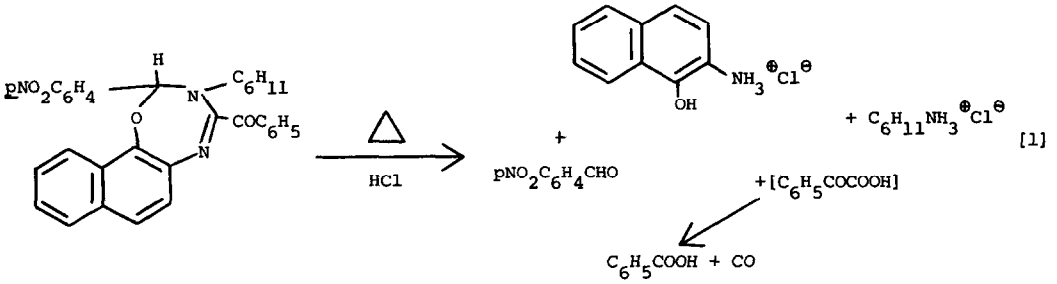


IV

Reaction of (I) with one equivalent of 3-benzoyl-1-cyclohexyl-2-*p*-nitrophenylaziridine[3] in refluxing benzene for 24 h followed by chromatographic separation on alumina afforded three products (a) 2-*p*-nitrophenylnaphtho[2,1-d]-oxazole II, $C_{17}H_{10}N_2O_3$* m.p. 152-3° (8.4% yield),[1] (b) a red crystalline solid $C_{31}H_{27}N_3O_4$*, m.p. 220° (8.5% yield): infrared ν_{max} ($CHCl_3$): 1667 (aryl C=O); 1520 and 1344 cm^{-1} (aryl NO_2); δ Me_4Si($CDCl_3$): 0.82 - 2.14 (m, 10H, cyclohexyl CH_2); 2.57 - 2.98 (m,1H, cyclohexyl CH); 6.36 (s, 1H, 2-oxadiazepine proton); 7.10 - 8.74 (m, 15H, aryl protons); λ_{max} (CH_3CN) 438 mμ (log ε 4.23), 290 mμ (sh) (log ε 4.46) 271 mμ (log ε 4.59), 221 mμ (log ε 4.45) formulated as 4-benzoyl-3-cyclohexyl-2-*p*-nitrophenylnaphtho-[2,1-f]-2H-1,3,5-oxadiazepine (III), (c) 22'-azodi-1-naphthol as a purple crystalline solid $C_{20}H_{14}N_2O_2$* m.p. 160° (IV): infrared spectrum ν_{max}($CHCl_3$): 3500 and 3390 (OH inter and intramolecularly bonded) 1630 cm^{-1} (N=N); λ_{max}($CHCl_3$), 545 mμ [4] (log ε 3.52), 346 mμ (sh) (log ε 3.88),

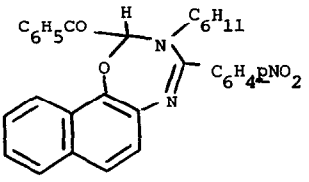
285 mμ (sh) (log ε 4.09).

Hydrolysis of (b) with 2N hydrochloric acid gave p-nitrobenzaldehyde (isolated and identified as the 2,4-dinitrophenylhydrazone m.p. 315.5*)[5], benzoic acid* (isolated by sublimation), and cyclohexylamine hydrochloride (see equation 1)

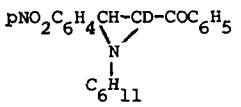


[1]

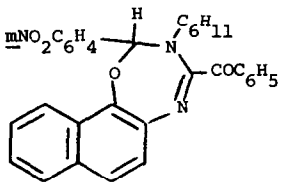
Further evidence in support of structure (III) and against the isomeric structure V for (b) is provided by reaction of (I) with 3-benzoyl-1-cyclohexyl-3-deutero-2-p-nitrophenylaziridine (VI)[6] (containing 88% deuterium by n.m.r. integration) which gave (b) containing no trace of deuterium (see scheme 1).



V



VI

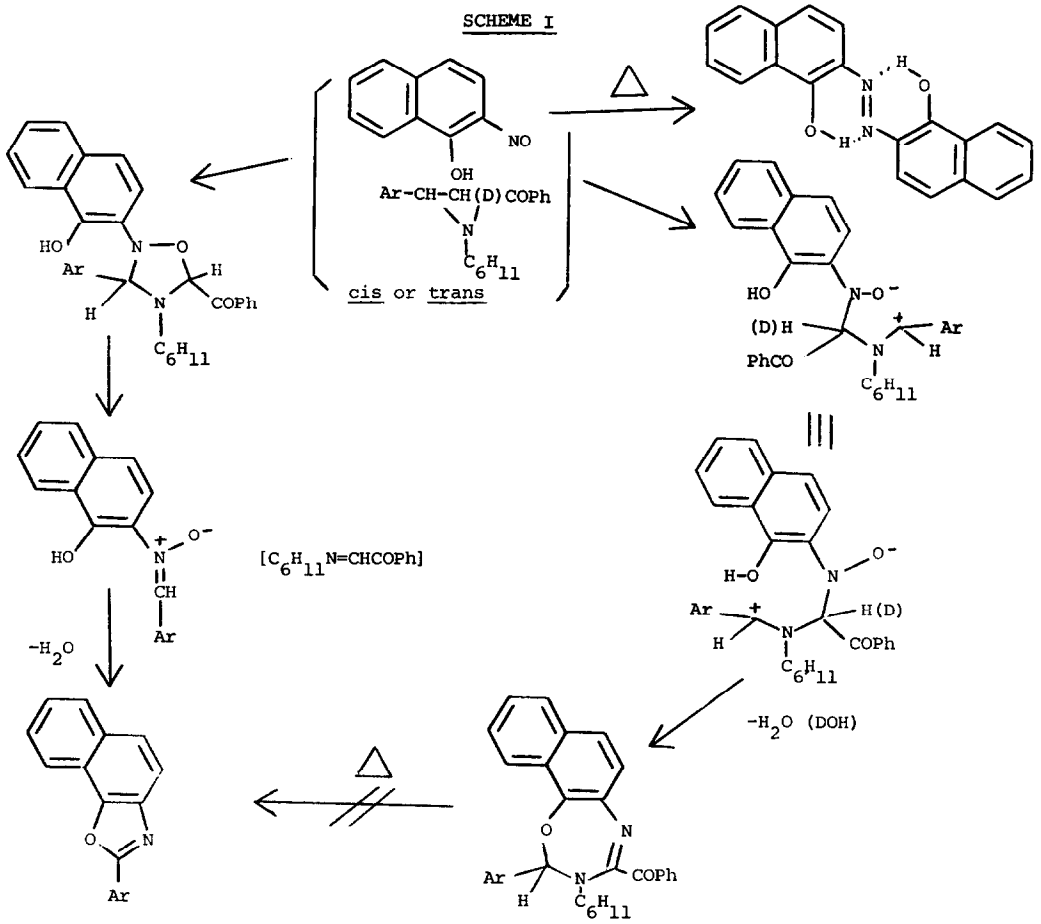


VII

Reaction of either pure cis or trans-3-benzoyl-1-cyclohexyl-2-m-nitrophenylaziridine[7] with (I) gave VII, $C_{31}H_{27}N_3O_4$* m.p. 160°, a further example of a substituted naphtho[2,1-f]-2H-1,3,5-oxadiazepine system. This result is consistent with scheme 1 since azomethine ylides derived from the conrotatory cleavage[8,9] of cis and trans N-alkyl-3-aroylaziridines equilibrate rapidly to the more stable trans form prior to cycloaddition.[6,10] In agreement with the independent formati of II, III and IV, heating of III under conditions of formation of II did not produce II.

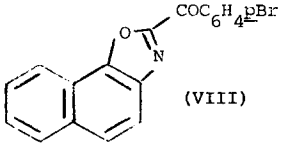
22'-Azodi-1-naphthol (IV) is an artifact derived from (I) (an independent experiment gave (IV) quantitatively by heating (I) in benzene) and presumably arises from deoxygenation of the

SCHEME I



nitroso dimer by the nitroso monomer, a reaction for which precedents exist.[11]

In the reactions of (I) with 3-aroylaziridines, the 2-aroylnaphtho[2,1-d]oxazoles were not formed, in contrast to reactions of 1-nitroso-2-naphthol.[1] Compound (VIII) $C_{18}H_{10}BrNO_2$*, m.p. 191° however was prepared from(I) by reaction with N-p-bromopnenacyl pyridinium bromide [12] with two equivalents of 1NNaOH at -10°.



(VIII)

REFERENCES AND NOTES

* Satisfactory analyses were obtained on all new compounds reported.

1. J.W. Lown and J. P. Moser, Can. J. Chem., in press (1970).
2. J. W. Lown and J. P. Moser, Chem. Commun., 247 (1970).
3. P. L. Southwick and R. J. Shozda, J. Amer. Chem. Soc., 82, 2888 (1960).
4. Absorption λ_{max} for 1,1'-azodi-2-naphthol is 525 mμ.
   F. Lindstrom and R. Isaac, Talanta, 13, 1003 (1966).
5. N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis", second edition, Wiley (New York) 1957, p.586.
6. G. Dallas, J. W. Lown, and J. P. Moser, J. Chem. Soc., in press (1970).
7. J.W. Lown, J. P. Moser, and R.Westwood, Can. J. Chem., 47, 4335 (1969).
8. R. Huisgen, W. Scheer, H. Mader, and E. Brunn, Angew. Chem. Intern. Edition, 8, 604 (1969).
9. R. Huisgen, W. Scheer, and H. Huber, J. Amer. Chem. Soc., 89, 1753 (1967).
10. J. W. Lown and K. Matsumoto, Can. J. Chem., in press (1970).
11. E. Bamberger, Chem. Ber., 33, 1939 (1900).
12. F. Krohnke, Angew. Chem. Intern. Edition 2, 388 (1963).