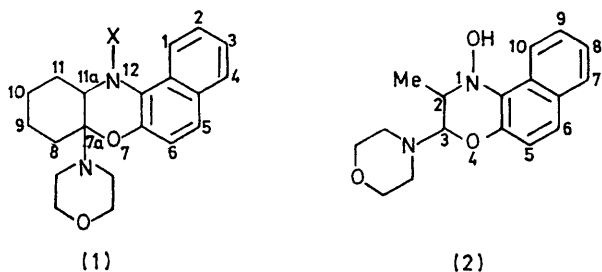


Reaction of Aromatic Nitroso-compounds with Enamines. Part II.¹ Reaction of 1-Nitroso-2-naphthol with Enamines

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The reactions of 1-nitroso-2-naphthol with 1-morpholinocyclohexene and 1-morpholinopropene give the dihydro-oxazine derivatives (1; X = OH) and (2), respectively. Attempts to extend the reaction to a variety of enamines and 1-nitroso-2-phenols have been unsuccessful.

We have shown previously¹ that hydroxylamine derivatives are obtained by the reaction of enamines with aromatic nitroso-compounds. A report² of the cycloaddition reaction between enamines and salicylaldehyde led us to investigate the analogous reaction between 1-nitroso-2-naphthol and morpholine enamines of cyclohexanone and propionaldehyde.



The reaction of 1-nitroso-2-naphthol with 1-morpholinocyclohexene proceeded exothermically in benzene solution and the product (1; X = OH) was precipitated as a crystalline solid. Its structure was confirmed by elemental analysis and spectral evidence. It showed i.r. absorption at 3250 cm^{-1} (OH), and its n.m.r. spectrum contained a one-proton signal at τ 6.00, attributable to the proton at C-11a. The multiplicity of this signal suggests that (1; X = OH) is a single stereoisomer about the C-7a,C-11a ring junction. Hydrogenation of compound (1; X = OH) gave the corresponding amine (1; X = H), but attempts to convert this into the amide (1; X = COEt) with propionyl chloride were unsuccessful.

The addition of 1-morpholinopropene to 1-nitroso-2-naphthol in ethanol gave a solid product (2) which showed hydroxy-absorption at 3390 cm^{-1} ; the mass spectrum did not show a molecular ion, but contained a peak at m/e 282.1362 ($M - 18$).

Attempts to extend the reaction to other 1-nitroso-2-phenols, such as 5-methoxy-2-nitrosophenol and 2-nitroso-1-naphthol, were unsuccessful; presumably the instability of the products prevents their isolation unless they are sufficiently crystalline to precipitate from the reaction mixture. Similarly, reactions of 1-nitroso-2-naphthol with other enamines of cyclohexanone and propionaldehyde yielded no isolable products.

EXPERIMENTAL

8,9,10,11,11a,12-Hexahydro-12-hydroxy-7a-morpholino-7aH-benzo[a]phenoxazine (1; X = OH).—1-Morpholinocyclohexene (12.5 g) was added during 10 min to a stirred suspension of 1-nitroso-2-naphthol [12.5 g; recrystallised from light petroleum (b.p. $60\text{--}80^\circ$) before use if obtained as a fine powder] in benzene (50 ml) at $0\text{--}5^\circ$. The mixture was stirred for 30 min, then allowed to warm to room temperature and set aside for 4 h (occasional cooling may be necessary if the reaction becomes too exothermic). The solid product (10.1 g) was filtered off, washed with a small volume of benzene, then light petroleum, and dried. Recrystallisation from ethyl methyl ketone gave the benzo-phenoxazine (1; X = OH) as prisms, m.p. $137\text{--}139^\circ$ (decomp.) (Found: C, 70.8; H, 7.3; N, 8.6. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_3$ requires C, 70.55; H, 7.1; N, 8.2%); ν_{max} 3250 (OH), and 1597 and 1625 cm^{-1} (ArC=C); τ (CDCl_3) 7.2 (4H, m, $\text{CH}_2\text{-N}\cdot\text{CH}_2$), 6.4 (4H, m, $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2$), 6.0br (1H, dd, 11a-H), 2.8 (1H, d, J 8.5 Hz, 6-H), 2.0—2.7 (5H, m, ArH), and 1.45 (1H, dd, J 2 and 8.5 Hz, 1-H).

2,3-Dihydro-1-hydroxy-2-methyl-3-morpholino-1H-naphth-[2,1-b][1,4]oxazine (2).—1-Morpholinopropene (10 g) was added to a stirred suspension of 1-nitroso-2-naphthol (10 g) in ethanol (40 ml) at 0° . After 30 min the mixture was allowed to warm to room temperature and set aside for 3 h. The naphthoxazine (2) was obtained as a pale yellow solid (12.9 g), m.p. $166\text{--}168^\circ$ (decomp.). Attempts to recrystallise it from a variety of solvents resulted in its decomposition (Found: C, 68.2; H, 6.7; N, 9.4. $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_3$ requires C, 68.0; H, 6.7; N, 9.3%); m/e 282.1362 [$\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$ ($M - 18$) requires 282.1368]; ν_{max} 3390 (OH), and 1596 and 1625 cm^{-1} (ArC=C).

Hydrogenation of Compound (1; X = OH).—A suspension of compound (1; X = OH) (4 g) and 10% palladium-charcoal (400 mg) in ethanol (125 ml) was hydrogenated for 2.5 h (uptake 1.2 mol). Benzene (500 ml) was added and the catalyst was filtered off. Removal of the organic solvents gave 8,9,10,11,11a,12-hexahydro-7a-morpholino-7aH-benzo[a]phenoxazine (1; X = H), which crystallised from benzene in needles (2.5 g), m.p. $211\text{--}213^\circ$ (decomp.) (Found: C, 74.0; H, 7.7; N, 8.4. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ requires C, 74.0; H, 7.45; N, 8.65%); ν_{max} 3350 (NH), and 1597 and 1623 cm^{-1} (ArC=C).

[2/2727 Received, 4th December, 1972]

¹ Part I, J. W. Lewis, P. L. Myers, and J. A. Ormerod, *J.C.S. Perkin I*, 1972, 2521.

² L. A. Paquette and H. Stucki, *J. Org. Chem.*, 1966, **31**, 1232.