

Tautomerism of Enamines derived from 2-Tetralone. Difference in Nucleophilic Behaviour between Morpholine and Pyrrolidine Enamines

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Phenyl isocyanate attacks both the morpholine and the pyrrolidine enamine derived from 2-tetralone at C-1, whereas β -nitrostyrene attacks the former 80% at C-1 and 20% at C-3 and the latter exclusively at C-3. These results confirm the existence of an equilibrium between the 3,4- and 1,4-dihydro-forms of the enamines.

TETRALONIC systems have been often regarded as intermediates in the synthesis of several compounds of biological interest. In continuation of our work on conjugated enamines,¹ we have now studied the behaviour of enamines derived from 2-tetralone towards some electrophilic reagents. Pandit and his co-workers² have shown that enamines from 1- and 2-tetralone react with chlorocarbenes in refluxing dioxan. In particular

¹ F. P. Colonna, G. Pitacco, and E. Valentin, *Tetrahedron*, 1971, **27**, 5481.

they report that 2-tetralone enamines generally undergo electrophilic attack at C-1; in some cases attack at C-3 takes place but the corresponding products are obtained in low yield and only under forcing conditions.³ We have found however that morpholine and pyrrolidine enamines from 2-tetralone show high reactivity towards

² U. K. Pandit, S. A. G. de Graaf, C. T. Braams, and J. S. T. Raaphorst, *Rec. Trav. chim.*, 1972, **91**, 799; S. A. G. de Graaf and U. K. Pandit, *Tetrahedron*, 1973, **29**, 2141.

³ U. K. Pandit, K. de Jonge, G. J. Koomen, and H. O. Huisman, *Tetrahedron Letters*, 1967, 3529.

certain electrophiles at both C-1 and C-3 even under mild conditions (48 h at 5° in deaerated anhydrous ether).

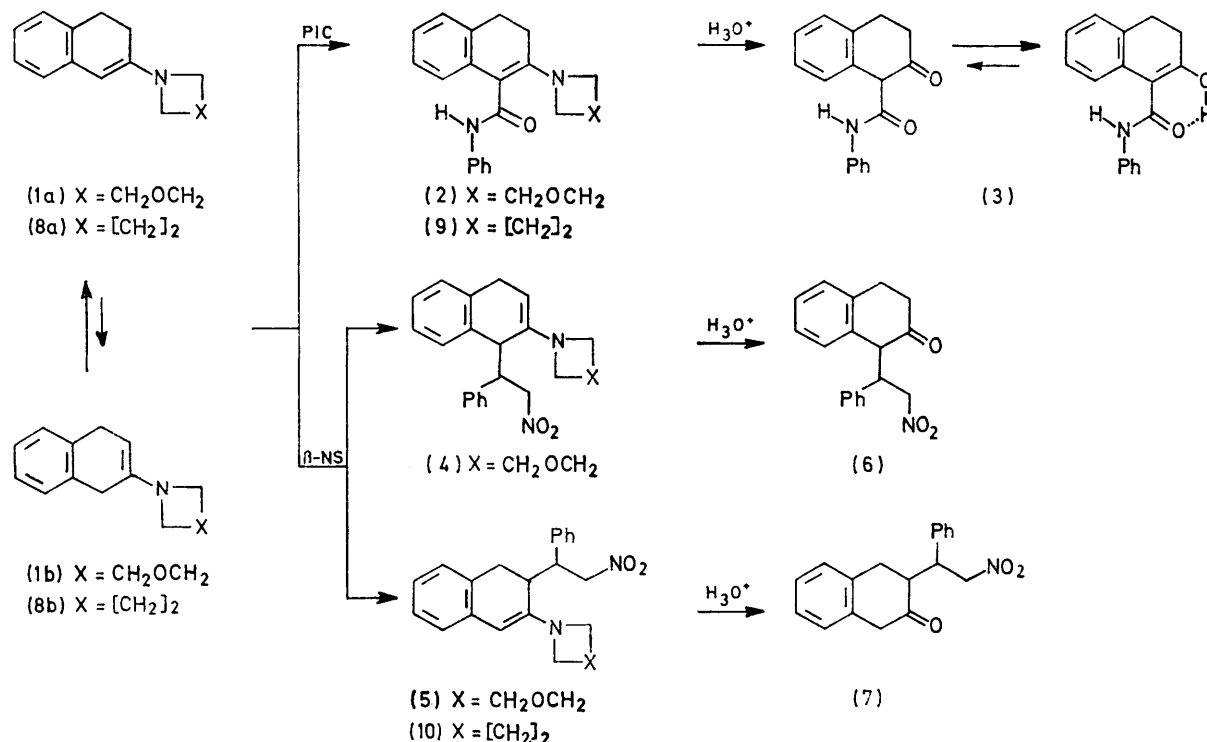
2-Morpholinodihydronaphthalene (1) reacted with phenyl isocyanate (PIC) to give the C-1 adduct (2), which shows no vinylic proton n.m.r. signal. Acidic hydrolysis of (2) gave the ketone (3), which exists partly in the enol form as shown by n.m.r.

β -Nitrostyrene (β -NS), however, reacted with the enamine (1) to give the C-1 and C-3 adducts [(4) and (5)] in the ratio 80 : 20. Acidic hydrolysis of the adducts gave the ketones (6) and (7), respectively. Each

enaminic i.r. band at 1618 cm^{-1} and on acidic hydrolysis gave the ketone (7).

DISCUSSION

The behaviour of PIC with both enamines (1) and (8) was as expected, as PIC usually gives enaminic adducts in which overlap between the nitrogen lone pair of the amine with the phenylcarbamoyl group is maximal.¹ Moreover, in this case the conjugation can extend to the fused benzene ring; hence the exclusive formation of the C-1 adducts (2) and (9). β -NS reacts with the enamines (1) and (8) with the usual stereochemistry⁴



molecule contains two asymmetric carbon atoms, but in each case only one isomer was isolated, to which the *erythro*-configuration was assigned on the basis of n.m.r. analysis of the nitromethylene proton signals (*cf.* model compounds reported in ref. 4).

The reaction of PIC with 2-pyrrolidinodihydronaphthalene (8) proceeded like that of the morpholine enamine to give the C-1 adduct (9), which yielded the ketone (3) on acidic hydrolysis. The adduct (9) shows enamine i.r. absorption at 1638 cm^{-1} whereas the parent enamine (8) shows absorption at 1612 cm^{-1} . In structure (9), however, the phenylcarbamoyl group at C-1 interferes both with the pyrrolidino-group and with the *peri*-hydrogen atom of the fused benzene ring, thus preventing maximum overlap of the nitrogen lone pair of the amine with the π -orbitals.

Surprisingly the enamine (8) underwent nitroalkylation by β -NS exclusively at C-3 to give the adduct (10) in quantitative yield. This adduct shows the conjugated

but with different results. In the case of the morpholine enamine, the higher yield of the C-1 adduct (4) than of the C-3 adduct (5) is explicable if the interconversion (1a) \rightleftharpoons (1b) is slow compared with the attack of β -NS on (1a). This hypothesis is supported by the fact that when the reaction is carried out at 48°, the adducts (4) and (5) are obtained in the ratio 1 : 1. In the case of the pyrrolidine enamine, which reacts only at C-3, the interconversion (8a) \rightleftharpoons (8b) must be very fast, thus leading exclusively to (10). Attempts to carry out the reaction at 48° failed; only gummy products were obtained.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls with a Perkin-Elmer 257 spectrophotometer and n.m.r. spectra for solutions in CDCl₃ with a JEOL 3NM-C-60 HL spectrometer.

3,4-Dihydro-2-morpholino-N-phenylnaphthalene-1-carboxamide (2).—Phenyl isocyanate (1.1 g) was added to a solution of the enamine (1) (2.0 g) in dry ether at 5°. The isolated adduct (2) (2.9 g, 90%) had m.p. 136–138° (from

⁴ F. P. Colonna, E. Valentin, G. Pitacco, and A. Risaliti, *Tetrahedron*, 1973, **29**, 3011.

benzene-light petroleum (Found: C, 75.65; H, 6.4; N, 8.15. $C_{21}H_{22}N_2O_2$ requires C, 75.4; H, 6.65; N, 8.9%); ν_{\max} 3320, 3280, 3260 (NH), 1640 (N:C:C), and 1565 cm^{-1} (CO:NH); δ 3.15 (4H, m, $CH_2\cdot N\cdot CH_2$), 3.60 (4H, m, $CH_2\cdot O\cdot CH_2$), 7.40 (9H, m, Ph and C_6H_4), and 10.05 (1H, s, NH).

1,2,3,4-Tetrahydro-2-oxo-N-phenylnaphthalene-1-carboxamide (3).—The adduct (2) was hydrolysed with acetic acid in water under nitrogen to afford the ketone (3), m.p. 103–105° (from benzene-light petroleum) (Found: C, 76.0; H, 5.45; N, 5.1. $C_{17}H_{15}NO_2$ requires C, 76.95; H, 5.7; N, 5.3%); ν_{\max} 3290, 3260, 3215, 3150 (NH), 1715 (CO), 1648, and 1550 cm^{-1} (CO:NH); δ 4.55 (0.25H, s, CO:CH:CO), 7.40 (10H, m, NH, Ph, and C_6H_4), and 14.32 (0.75H, s, OH).

1,4-Dihydro-2-morpholino-1-(2-nitro-1-phenylethyl)naphthalene (4) and 3,4-Dihydro-2-morpholino-3-(2-nitro-1-phenylethyl)naphthalene (5).— β -Nitrostyrene (1.39 g) was treated with the enamine (1) (2.0 g) in ether at 5°. Removal of the solvent left an oil which was fractionally crystallized from benzene-light petroleum to give the C-1 adduct (4), m.p. 115–116° (Found: C, 72.0; H, 6.65; N, 7.7. $C_{22}H_{24}N_2O_3$ requires C, 72.5; H, 6.65; N, 7.7%); ν_{\max} 1648 (N:C:C), 1604 (Ph), and 1552 cm^{-1} (NO_2); δ 4.08 (m, CHPh), 4.80 (2H, m, $CH_2\cdot NO_2$), and 4.96 (1H, dd, CH:C); and the C-3 adduct (5), m.p. 162.5° (Found: C, 72.95; H, 6.55; N, 7.65%); ν_{\max} 1618 (N:C:C), 1600 (Ph), and 1555 cm^{-1} (NO_2); δ 4.82 (2H, m, $CH_2\cdot NO_2$), 5.82 (1H, s, CH:C), and 7.20 (9H, m, Ph and C_6H_4). The ratio (4):(5) was determined by n.m.r. analysis of the crude reaction mixture as 4:1.

3,4-Dihydro-1-(2-nitro-1-phenylethyl)naphthalen-2(1H)-one (6).—The enamine (4) was dissolved in acetone, water, and acetic acid and heated for 1 h under nitrogen to give the ketone (6), m.p. 104°; ν_{\max} 1710 (CO), 1600 (Ph), and 1548 cm^{-1} (NO_2); δ 3.67 (1H, d, H-1), 4.35 (1H, m, CHPh),

4.90 (2H, m, $CH_2\cdot NO_2$, J 12 Hz), 6.80 (4H, m, C_6H_4), and 7.30 (5H, m, Ph); 2,4-dinitrophenylhydrazone, m.p. 194–195° (from ethanol) (Found: C, 60.6; H, 4.25; N, 14.6. $C_{23}H_{21}N_5O_6$ requires C, 59.6; H, 4.55; N, 15.1%).

3,4-Dihydro-3-(2-nitro-1-phenylethyl)naphthalen-2(1H)-one (7).—The enamine (5) was heated in acetone, water, and hydrochloric acid for 3 h under nitrogen to give the ketone (7), m.p. 127–129° (from benzene-light petroleum) (Found: C, 73.15; H, 6.05; N, 4.7. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%); ν_{\max} 1720 (CO), 1600 (Ph), and 1550 cm^{-1} (NO_2); δ 3.80 (m, CHPh), 4.88 (2H, m, $CH_2\cdot NO_2$, J 12 Hz), and 7.20 (9H, m, Ph and C_6H_4).

3,4-Dihydro-2-pyrrolidino-N-phenylnaphthalene-1-carboxamide (9).—Phenyl isocyanate (0.78 g) was added to a solution of the enamine (8) (1.3 g) in dry ether to give the C-1 adduct (9) (1.95 g, 93%), m.p. 123–124° (from benzene-light petroleum) (Found: C, 78.9; H, 6.9; N, 8.6. $C_{21}H_{22}N_2O$ requires C, 79.2; H, 6.95; N, 8.9%); ν_{\max} 3290 (NH), 1638 (N:C:C), 1595 and 1575 (Ph), and 1550 cm^{-1} (CO:NH); δ 3.43 (4H, m, $CH_2\cdot N\cdot CH_2$), 7.27 (9H, m, Ph and C_6H_4), and 9.92 (1H, s, NH). Acidic hydrolysis of (9) afforded the ketone (3) in quantitative yield.

3,4-Dihydro-3-(2-nitro-1-phenylethyl)-2-pyrrolidinonaphthalene (10).— β -Nitrostyrene (1.59 g) reacted with the enamine (8) (2.0 g) to give the C-3 adduct (10) (3.60 g, 98%), m.p. 134–135° (from benzene-light petroleum) (Found: C, 75.65; H, 8.6; N, 7.95. $C_{22}H_{24}N_2O_2$ requires C, 75.85; H, 6.95; N, 8.05%); ν_{\max} ($CHCl_3$) 1618 (N:C:C), 1608 (Ph), and 1550 cm^{-1} (NO_2); δ 3.22 (4H, m, $CH_2\cdot N\cdot CH_2$), 3.50 (m, CHPh), 4.70 (2H, d, $CH_2\cdot NO_2$), 5.22 (1H, s, CH:C), and 7.10 (9H, m, Ph and C_6H_4). Acidic hydrolysis of (10) gave the ketone (7).

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