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Studies on Novel Heterocyclic Ring Systems. Reactions of 2-[p-(N,N'-Dimethylaminophenyl)]-naphtho[2,1-b]2,3-dihydropyran-4-one with 2-Mercaptoaniline and Formation of Naphtho[2,1-b]-pyrano[4,3-c]pyridazin-3-one Derivative

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SYNTHETIC COMMUNICATIONS, 24(14), 2057-2062 (1994)

STUDIES ON NOVEL HETEROCYCLIC RING SYSTEMS.

Reactions of 2-[p-(N,N'-dimethylaminophenyl)]-naphtho [2,1-b] 2,3-dihydropyran-4-one with 2-mercaptoaniline & formation of naphtho[2,1-b] pyrano [4,3-c] pyridazin-3- one derivative.

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Abstract

The reaction of 2-[p-(N,N'-dimethylaminophenyl)]- naphtho [2,1-b] - 2,3 - dihydropyran -4- one 1 with 2- mercaptoaniline 2 has been investigated. The yet unreported 6-(p-N,N'-dimethylaminophenyl)-naphtho [2,1-b]- pyrano- [3,4-b] benzo- (4H) -1,4-thiazine 3 system has been synthesised and characterised on the basis of spectral and analytical data. A novel synthestic route to naphtho (2,1-b)-pyrano (4,3-c) pyridazin-3-one 6 is reported.

With the aim to broaden further the range of useful synthetic applications of compound 1, which provide easy access to polycyclic system of potential biological[1-3] interest and in continuation our

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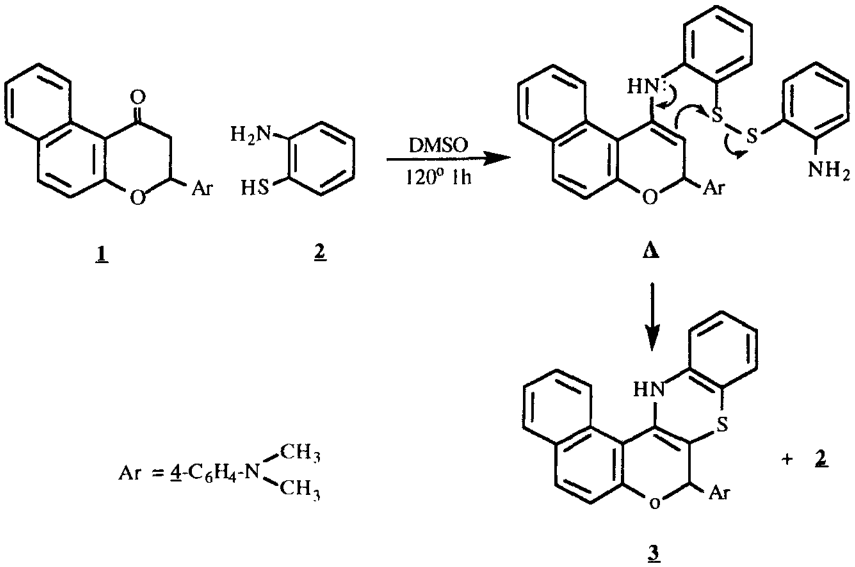
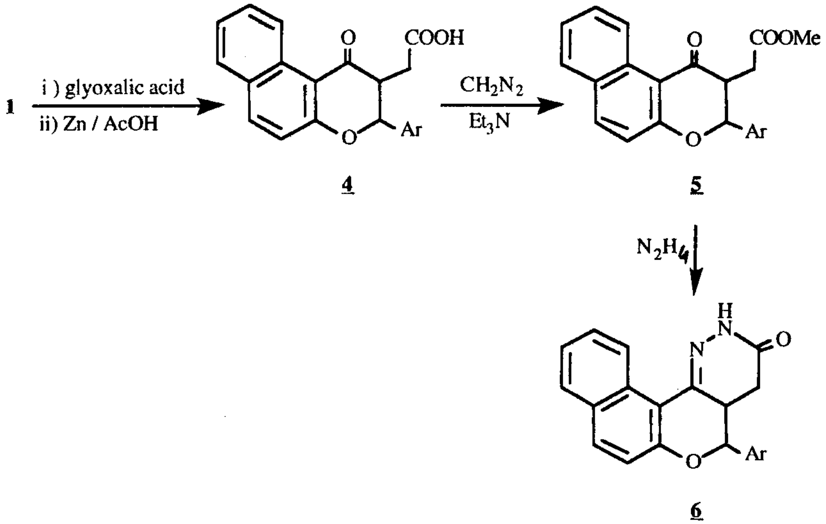


(Scheme 1)

work[4-7] on the chemistry of fused pyranes derivatives, we have studied the reaction of 1 with 2 in presence of DMSO. The starting material 1 was recently prepared in our laboratories by condensation of ethyl 2-carboethoxy-3-[4-(N,N'- dimethylaminophenyl)] acrylate with 2-naphthol in presence of NaOEt[4]. The ring system 3 was obtained via oxidative cyclization [8-10] by merely heating a mixture of 1 and 2 in DMSO at 120°C for one hour. Under the experimental conditions the compound 2 is readily oxidized to bis (o-aminophenyl) disulphide and therefore the reaction is considered to proceeds via the intermediate A which readily cyclized by the scission of the S-S bond [11,12] upon nucleophilic attack of the enamine system to furnish the brick red crystalline title compound 3 (Scheme 1). The structure of 3 is assigned on the basis of the spectral data (see Exp.) and the elemental analysis.



(Scheme 2)

The synthesis of compound 6 was carried out in the following way: A mixture of compound 1 and glyoxalic acid disolved in sodium hydroxide was stirred for 3h, followed by reduction with a mixture of Zn and acetic acid to give 2-aryl naphtho [2,1-b]-2,3-dihydro-4-oxo-pyranyl acetic acid 4. Treatment of 4 with diazomethane afforded the methyl ester 5 which subsequently cyclized with hydrazine hydrate to give 6 (Scheme 2).

Experimental

Melting points were determined with a Buchi 510 capillary melting apparatus and are uncorrected. The IR spectra were recorded on a Perkin - Elmer M-377 spectrophotometer. The ^{1}H-NMR spectra were recorded on a Hitashi. Perkin - Elmer R 600 F.T using TMS spectrometer as internal standard. TLC on silica gel plates (Merck, 60, F_{254}) was used to control the purity of products. Silica gel 60 (Merck; 70 - 230 mesh) was used for column chromatography and the mass spectra were recorded on a Hitachi Perkin - Elmer RMV - 6L mass spectrometer.

6-[p-N,N'-Dimethylaminophenyl]- naphtho [2,1-b] pyrano [3,4-b] benzo(4H)-1,4- thiazine 3 .

Compound 1 (3.17 g, 0.01 mol), 2-mercaptoaniline (2,1.25 g, 0.01 mol) and dimethylsulphoxide (10 ml) were stirred and heated together at 120° for one hour (TLC). The product 3 precipitated on cooling, filtered and recrystallized from methanol (20 ml) as brick red crystals (1.9 g, 46 %) m.p > 315°; IR (KBr) 3323 cm^{-1} (NH), 3055 (CH, aromatic), 1608, 770, 762 cm^{-1} (C=C aromatic); ^{1}H-NMR (DMSO-d_6) δ 8.1 (br. NH), 7.8 - 7.1 (m, 14H, aromatic), 6.8 (m, 1H, benzylic proton) and δ 2.9 (s, 6H,N(CH_3)$_2$) ; MS. m/e 422 ($M^{+\cdot}$). Anal. Calcd. for $C_{27}H_{22}N_2OS$: C, 76.77; H, 5.2; N, 6.6; S, 7.58. Found: C, 76.61; H, 5.3; N, 6.9; S, 7.2.

2-[p-(N,N'-Dimethylamino) phenyl]-naphtho [2,1-b]- 1,3-dihydro-4-oxo-pyranylacetic acid 4.

To an ice-cooled mixture of substituted naphthopyranone 1 (1 mol) and glyoxalic acid (4 mol) in water, a solution of sodium hydroxide (4 mol) in water was added dropwise. The mixture was stirred at R.T for 4 hours (TLC) and then acidified to pH≈2 by adding concentrated HCl. The precipitate was filtered and stirred with acetic acid (300 ml), water (75 ml) and zinc (2 mol) on a steam bath for one hour. The reaction mixture filtered while hot and diluted with water. The solution was extracted with ether. The ethereal solution was dried over Na_2SO_4. Evaporation of ether left a solid crystallized product (1.7 g, 45.2 %), m.p.173-175°C. IR (KBr)1682 cm^{-1} (υ C=O ketone), 1708 cm^{-1} (>C=O acid), 3540 - 3120 cm^{-1} (br. OH). ^{1}H-NMR (DMSO - d_6) δ10.6 (s, 1H, COOH), 8.1 - 7.3 (m, 10H, aromatic), 4.3 (m, 4H), 3.0 (s, 6H, N(CH_3)$_2$); MS.

m/e 375 ($M^{+\cdot}$) Anal. Calcd. for $C_{23}H_{21}NO_4$: C, 73.6; H, 5.6; N, 3.7; Found: C,73.5; H,5.3; N, 4.0.

Methyl ester of 4

The acid 4 (0.375 g, 0.001 mol) was stirred in an excess of ethereal solution of diazomethane (from diazald) for 5 h at R.T (TLC). After evaporation of the solvent the residue was chromatographed on silica gel (cyclohexane / ethylacetate, 90 / 10, R_f = 4.3) give 0.25 g (64.2 %) of 5 m.p. 108° C. IR (KBr) 1726 cm^{-1} ($>$C=O ester). ^{1}H-NMR (DMSO - d_6) δ 3.6 (s,3H, -$COOCH_3$). Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.03; H, 5.9; N, 3.6; Found: C, 73.9; H, 6.0; N, 3.9.

6-[p-(N,N'-dimethylamino)phenyl]- naphtho [2,1-b] pyrano [4,3-c] - 4,5-dihydro-pyridazin-3-one 6.

Amixture of methyl ester 5 (3.89 g, 0.01 mol), hydrazine hydrate (5 ml) and ethanol (20 ml) was refluxed for 4 h (TLC). After cooling, the solid was filtered off and recrystallized from benzene (30 ml) to give 2.1 g (56.6 % of 6, m.p. 192 - 194°C. IR (KBr) 3250 cm^{-1} (NH), 3050 (CH, aromatic). 1652 cm^{-1} ($>$C=O amide), 1600, 767, 760 cm^{-1} (C=C aromatic). ^{1}H-NMR (DMSO-d_6) δ 8.6 (br.s, 1H,NH), 8.0 - 7.3 (m, 10H, Ar-H), 6.3 (s, 1H, C_6-H), 4.4 (br.s, 2H, CH_2CO), 3.2 (m, 1H, C_5-H) and 2.91 (s,6H, $N(CH_3)_2$)M.S m/e 371 ($M^{+\cdot}$) Anal. Calcd for $C_{23}H_{21}N_3O_2$:C, 74.39; H, 5.66; N, 11.3. Found: C, 74.1; H, 5.6; N, 11.0.

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