

## New Heterocyclic Derivatives of 1'- and 3'-Amino-5',6',7',8'-tetrahydro-2'-Acetonaphthones

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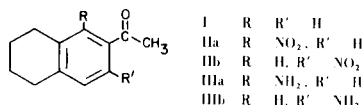
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The preparation of 1'- and 3'-amino-5',6',7',8'-tetrahydro-2'-acetonaphthones (IIIa and IIIb) is described, by reduction of the low temperature nitration products of 5',6',7',8'-tetrahydro-2'-acetonaphthone (I). The structures of the nitro isomers (IIa and IIb), and the reduction products, IIIa and IIIb, were elucidated spectroscopically. By known reactions, a series of new heterocyclic compounds prepared from the *o*-aminoketones, IIIa and IIIb, resulted in two series of new heterocyclic compounds.

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1'-Nitro-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIa) has been described (1,2) as the sole product of the nitration of 5',6',7',8'-tetrahydro-2'-acetonaphthone (I), which by reduction was converted to 1'-amino-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIIa). 3'-Amino-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIIb) was obtained (2) by an indirect method, using 2-acetamido-5,6,7,8-tetrahydronaphthalene as the starting product.



Nitration of I, at low temperature (-5 to -10°), with nitric acid in concentrated sulphuric acid, gave a mixture of the nitro compounds, IIa and IIb, from which IIa was obtained in the pure state by crystallisation. It was not possible to isolate isomer IIb, in the pure state. The pure amine IIIa was obtained by reduction of the nitro compound, IIa; the pure amine, IIIb, could be crystallised from the products of reduction of a mixture of nitro compounds IIa and IIb.

The presence of IIa and IIb in the nitration mixture was studied by pmr. An acetyl group (CH<sub>3</sub>, δ 2.58) and an AB system in the aromatic region with two doublets indicating the presence of a pair of vicinal protons in the positions 3' and 4' (δ 7.65, 7.30 ppm, J<sub>3'-4'</sub> = 9.0 Hz) were detected in the pmr spectrum of IIa. The presence of the nitro compound, IIb, in the nitration

mixture could be detected by a singlet for the methyl protons of the acetyl group at δ 2.48 and in the aromatic region by two singlets representing the two protons in the positions 1' and 4' (δ 7.71 and 7.13).

Parallel conclusions can be drawn from the pmr spectra of the amines, IIIa and IIIb. In both isomers there is a displacement of the 4'-proton in the aromatic nucleus to higher field (δ 6.53 and 6.35, respectively) due to hydrogen bonding of the amino group with the carbonyl group in the position 2'. This increases conjugation of the lone pair of electrons on the nitrogen atom with the π electron cloud of the nucleus leading to a deshielding effect on the protons in the *para* (IIIa) and *ortho* (IIIb) position with respect to the amino group (3). Acetylation of the amine to give the compounds of type IVa or IVb causes delocalisation of the lone pair of electrons on nitrogen and the chemical shift of the 4'-proton returns to lower fields (4).

Starting from IIIa and IIIb and using known methods, two series of new heterocyclic compounds (Schemes I and II) were obtained. Tetrahydronaphthodiazepinones (Va,b) and tetrahydrobenzoquinazolinones (VIIa,b) were obtained by cyclisation of the corresponding α-halocetamide derivatives (IVa,b, VIa,b) with ammonia in organic solvents (5). Tetrahydrobenzoquinazoline-3-oxides (IXa,b) were the products of reaction of oximes (VIIIa,b) with α-chloroacetyl chloride (6). Diketene (7) reacted with IIIa and IIIb to give the tetrahydrobenzoquinolinones (Xa,b), which were reduced with sodium borohydride to the corresponding alcohols (XIa,b). Xa and Xb treated with phosphorus oxychloride gave 2-chlorotetrahydrobenzo-



1/2 hour to concentrated sulphuric acid (500 ml.) at  $-10^{\circ}$ . To the solution kept between  $-10^{\circ}$  -  $-15^{\circ}$  was added dropwise nitric acid (130 ml., d. 1.40) in concentrated sulphuric acid (200 ml.) during 1 hour. The mixture was stirred for a further 2 hours at  $-10^{\circ}$  -  $-15^{\circ}$ . The reaction mixture was poured onto ice and extracted with chloroform. The organic layers were washed with water, sodium bicarbonate solution, dried over sodium sulfate and concentrated to dryness to give an oil which, when treated with ether, yielded a yellow solid which recrystallized from acetone to give 156 g. (42%) of pale yellow needles, m.p.  $148^{\circ}$  [lit. (2),  $142$ - $143^{\circ}$ ];  $\nu$  max (potassium bromide): 1680 (C=O), 1530 and 1370 ( $\text{NO}_2$ )  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.85 (m, 4H,  $\text{CH}_2$ ), 2.58 (s, 3H,  $\text{CH}_3$ ), 2.80 (m, 4H,  $\text{CH}_2$ ), 7.30 (d, 1H,  $\text{H}_4'$ ), 7.65 (d, 1H,  $\text{H}_3'$ ,  $\text{J}_{3'-4'} = 9.0$  Hz) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{13}\text{NO}_3$ : C, 65.7; H, 6.6; N, 6.4. Found: C, 65.65; H, 5.9; N, 6.3.

Mixture of 1'-Nitro and 3'-Nitro-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIa + IIb).

The mother liquors from crystallization of IIa were taken to dryness, and the residue crystallized from ethanol to give 100 g. of a yellow solid (27%), m.p.  $34$ - $37^{\circ}$ . This solid was a mixture of IIa (9%) and IIb (18%) as shown by nmr analysis;  $\delta$  (deuteriochloroform): 2.48 (s, 3H,  $\text{CH}_3$ , IIb), 2.60 (s, 3H,  $\text{CH}_3$ , IIa), 7.13 (s, 1H,  $\text{H}_4'$ , IIb), 7.30 (d, 1H,  $\text{H}_4'$ , IIa), 7.65 (d, 1H,  $\text{H}_3'$ ,  $\text{J}_{3'-4'} = 9.0$  Hz, IIa) 7.71 (s, 1H,  $\text{H}_1'$ , IIb) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{13}\text{NO}_3$ : C, 65.7; H, 6.0; N, 6.4. Found: C, 65.7; H, 5.95; N, 6.35.

1'-Amino-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIIa).

To a vigorously boiling stirred suspension of iron powder (reduced) (26.5 g.) and IIa (34.5 g., 0.157 mole), in aqueous ethanol (50% w/w), (150 ml.), was added slowly (60 minutes) a solution of concentrated hydrochloric acid (2.7 ml.) in aqueous ethanol (50% w/w) (12.2 ml.). The reaction mixture was then boiled for 2 hours, diluted with ethanol (200 ml.) and filtered. The filtrate was concentrated to small volume to yield a crystalline product, which was recrystallized from aqueous-ethanol to give 24 g. (80%) of pale yellow needles, m.p.  $89$ - $91^{\circ}$ ;  $\nu$  max (potassium bromide): 3460 and 3310 (NH), 1635 (C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.90 (m, 4H,  $\text{CH}_2$ ), 2.50 (m, 2H,  $\text{CH}_2$ ), 2.65 (s, 3H,  $\text{CH}_3$ ), 2.85 (m, 2H,  $\text{CH}_2$ ), 6.33 (s, 2H,  $\text{NH}_2$ ), 6.53 (d, 1H,  $\text{H}_4'$ ), 7.62 (d, 1H,  $\text{H}_3'$ ,  $\text{J}_{3'-4'} = 9.0$  Hz) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{NO}$ : C, 76.2; H, 8.0; N, 7.4. Found: C, 76.1; H, 7.8; N, 7.4.

The above compound gave a hydrochloride salt m.p.  $205$ - $207^{\circ}$  from ethanol-ether.

3'-Amino-5',6',7',8'-tetrahydro-2'-acetonaphthone (IIIb).

This compound was prepared from the mixture (IIa + IIb) by the procedure described for IIIa. The crude product was recrystallized from ethanol to give pale yellow needles (12%), m.p.  $123$ - $125^{\circ}$ ;  $\nu$  max (potassium bromide): 3430 and 3310 (NH), 1625 (C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.80 (m, 4H,

$\text{CH}_2$ ), 2.50 (s, 3H,  $\text{CH}_3$ ), 2.70 (m, 4H,  $\text{CH}_2$ ), 6.15 (s, 2H,  $\text{NH}_2$ ), 6.35 (s, 1H,  $\text{H}_4'$ ), 7.43 (s, 1H,  $\text{H}_1'$ ) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{NO}$ : C, 76.2; H, 8.0; N, 7.4. Found: C, 76.3; H, 8.2; N, 7.5.

The above compound gave a hydrochloride salt m.p.  $210$ - $212^{\circ}$  from ethanol-ether.

1'-( $\alpha$ -Chloroacetamido)-5',6',7',8'-tetrahydro-2'-acetonaphthone (IVa).

Chloroacetyl chloride (11.3 g., 0.1 mole) was added dropwise with stirring to a solution of IIa (18.9 g., 0.1 mole) and triethylamine (10.1 g., 0.1 mole) in methyl ethyl ketone (100 ml.). The reaction was stirred at room temperature for three hours, then filtered and the filtrate evaporated to dryness *in vacuo*. Recrystallization from ethanol-ether gave 23.8 g. (90%) of white crystals, m.p.  $123$ - $125^{\circ}$ ;  $\nu$  max (potassium bromide): 3260 (NH), 1674 (amide C=O), (ketone C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.75 (m, 4H,  $\text{CH}_2$ ), 2.55 (s, 3H,  $\text{CH}_3$ ), 2.75 (m, 4H,  $\text{CH}_2$ ), 4.10 (s, 2H,  $\text{Cl-CH}_2$ ), 7.02 (d, 1H,  $\text{H}_4'$ ), 7.50 (d, 1H,  $\text{H}_3'$ ,  $\text{J}_{3'-4'} = 9.0$  Hz), 9.82 (broad band, 1H, NH) ppm.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{ClNO}_2$ : C, 63.2; H, 6.0; N, 5.3; Cl, 13.35. Found: C, 63.2; H, 6.0; N, 5.4; Cl, 13.4.

3'-( $\alpha$ -Chloroacetamido)-5',6',7',8'-tetrahydro-2'-acetonaphthone (IVb).

This compound was prepared from IIIb by the procedure described for IVa. The crude product was recrystallized from ethanol to give a white solid (93%), m.p.  $154$ - $155^{\circ}$ ;  $\nu$  max (potassium bromide): 3160 (NH), 1675 (amide C=O), 1650 (ketone C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform) 1.85 (m, 4H,  $\text{CH}_2$ ), 2.60 (s, 3H,  $\text{CH}_3$ ), 2.80 (m, 4H,  $\text{CH}_2$ ), 4.15 (s, 2H,  $\text{Cl-CH}_2$ ), 7.52 (s, 1H,  $\text{H}_4'$ ), 8.38 (s, 1H,  $\text{H}_1'$ ), 12.35 (broad band, 1H, NH).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{ClNO}_2$ : C, 63.2; H, 6.0; N, 5.3; Cl, 13.35. Found: C, 63.0; H, 5.9; N, 5.3; Cl, 13.4.

1,3-Dihydro-5-methyl-8,9,10,11-tetrahydro-2H-naphtho[1,2-*e*]-[1,4]diazepin-2-one (Va).

Into a solution of IVa (21.0 g., 0.079 mole) in dry dioxane (150 ml.) kept between  $10$ - $15^{\circ}$ , ammonia was bubbled at a moderate rate for 30 minutes. The flask was stoppered and allowed to remain at  $10$ - $15^{\circ}$  for two hours and then at room temperature for 72 hours. The solution was filtered and evaporated to dryness *in vacuo*. The residue was dissolved in chloroform (250 ml.), washed with water and extracted with 5 x 50 ml. of 2N hydrochloric acid. The aqueous extracts were combined, made alkaline with ammonia and extracted with chloroform. The organic layer was dried over sodium sulfate, filtered, evaporated and the crystalline residue recrystallized from methanol to give 13.5 g. (75%) of white crystals, m.p.  $206$ - $208^{\circ}$ ;  $\nu$  max (potassium bromide): 3180 (NH), 1655 (C=O), 1630 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.86 (m, 4H,  $\text{CH}_2$ ), 2.48 (s, 3H,  $\text{CH}_3$ ), 2.83 (m, 4H,  $\text{CH}_2$ ), 4.06 (s, 2H,  $\text{-CH}_2\text{-N=}$ ), 6.98 (d, 1H,  $\text{H}_7$ ), 7.38 (d, 1H,  $\text{H}_6$ ,  $\text{J}_{6-7} = 9.0$  Hz), 9.14 (s, 1H, NH) ppm.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ : C, 73.7; H, 7.1; N, 12.3. Found: C, 73.3; H, 7.2; N, 12.4.

1,3-Dihydro-5-methyl-7,8,9,10-tetrahydro-2H-naphtho[2,3-*e*]-[1,4]diazepin-2-one (Vb).

This compound was prepared from IVb by the procedure described for Va. The crude product was recrystallized from methanol to give white crystals (70%), m.p.  $230$ - $232^{\circ}$ ;  $\nu$  max (potassium bromide): 3185 (NH), 1668 (C=O), 1635 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.80 (m, 4H,  $\text{CH}_2$ ), 2.38 (s, 3H,  $\text{CH}_3$ ), 2.70 (m, 4H,  $\text{CH}_2$ ), 4.02 (s, 2H,  $\text{N-CH}_2$ ), 6.72 (s, 1H,  $\text{H}_{11}$ ), 7.10 (s, 1H,  $\text{H}_6$ ), 9.60 (s, 1H, NH) ppm.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ : C, 73.7; H, 7.1; N, 12.3. Found: C, 73.6; H, 7.1; N, 12.3.

1'-( $\alpha,\alpha,\alpha$ -Trichloroacetamido)-5',6',7',8'-tetrahydro-2'-acetonephthone (VIa).

Trichloroacetyl chloride (18.2 g., 0.1 mole) was added dropwise with stirring to a solution of IIIa (18.9 g., 0.1 mole) and triethylamine (10.1 g., 0.1 mole) in methyl ethyl ketone (100 ml.). The reaction was stirred at room temperature for 3 hours, then filtered and the filtrate evaporated to dryness *in vacuo*. Recrystallization from ethanol-ether gave 31.2 g. (93%) of a white solid, m.p. 87-89°;  $\nu$  max (potassium bromide): 3230 (NH), 1715 (amide C=O) 1660 (ketone C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.80 (m, 4H,  $\text{CH}_2_{6',7'}$ ), 2.60 (s, 3H,  $\text{CH}_3$ ), 2.80 (m, 4H,  $\text{CH}_2_{5',8'}$ ), 7.12 (d, 1H,  $\text{H}_4'$ ), 7.65 (d, 1H,  $\text{H}_3'$ ,  $J_{3'-4'} = 9.0$  Hz), 10.8 (broad band, 1H, NH) ppm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_3\text{NO}_2$ : C, 50.3; H, 4.2; N, 4.2; Cl, 31.8. Found: C, 50.2; H, 4.2; N, 4.1; Cl, 32.1.

3'-( $\alpha,\alpha,\alpha$ -Trichloroacetamido)-5',6',7',8'-tetrahydro-2'-acetonephthone (VIb).

This compound was prepared from IIIb, by the procedure described for VIa. The crude product was recrystallized from ethanol to give a white solid (93%), m.p. 122-124°;  $\nu$  max (potassium bromide): 3100 (NH), 1700 (amide C=O), 1655 (ketone C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform) 1.85 (m, 4H,  $\text{CH}_2_{6',7'}$ ), 2.65 (s, 3H,  $\text{CH}_3$ ), 2.75 (m, 4H,  $\text{CH}_2_{5',8'}$ ), 7.60 (s, 1H,  $\text{H}_4'$ ), 8.35 (s, 1H,  $\text{H}_1'$ ) 13.0 (broad band, 1H, NH) ppm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_3\text{NO}_2$ : C, 50.3; H, 4.2; N, 4.2; Cl, 31.8. Found: C, 50.2; H, 4.1; N, 4.1; Cl, 31.9.

4-Methyl-7,8,9,10-tetrahydrobenzo[h]quinazolin-2(1H)one (VIIa).

Into a solution of VIa (16.7 g., 0.05 mole) in dry dioxane (150 ml.) kept between 10-15°, ammonia was bubbled at a moderate rate for 30 minutes. The flask was stoppered and allowed to remain at 10-15° for 2 hours and then at room temperature for 24 hours. The precipitate was removed by filtration, washed with dioxane and acetone and recrystallized from DMF to give 8.8 g. (83%) of a white solid, m.p. 294-296°;  $\nu$  max (potassium bromide): 3140 (NH), 1660 (C=O), 1650 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (DMSO- $d_6$ ): 1.80 (m, 4H,  $\text{CH}_2_{8,9}$ ), 2.68 (s, 3H,  $\text{CH}_3$ ), 2.80 (m, 4H,  $\text{CH}_2_{7,10}$ ), 7.03 (d, 1H,  $\text{H}_6$ ), 7.75 (d, 1H,  $\text{H}_5$ ),  $J_{5-6} = 9.0$  Hz) ppm.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ : C, 72.9; H, 6.6; N, 13.1. Found: C, 72.9; H, 6.6; N, 13.0.

4-Methyl-6,7,8,9-tetrahydrobenzo[g]quinazolin-2(1H)one (VIIb).

This compound was prepared from VIIb by the procedure described for VIIa. The crude product was recrystallized from DMF to give a white solid (85%), m.p. 308-310°;  $\nu$  max (potassium bromide): 3130 (NH), 1655 (C=O), 1635 (C=N)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ : C, 72.9; H, 6.6; N, 13.1. Found: C, 72.7; H, 6.6; N, 12.8.

1'-Amino-5',6',7',8'-tetrahydro-2'-acetonephthone Oxime (VIIIa).

A mixture of IIIa (9.5 g., 0.05 mole), ethanol (80 ml.), water (5 ml.) hydroxylamine hydrochloride (5.6 g., 0.08 mole) and potassium hydroxide (15 g.) was heated on the steam bath with stirring for 30 minutes. The reaction mixture was cooled to room temperature and poured into 150 ml. of 1.5 N hydrochloric acid. The crude product was filtered and dried to give a yield of 9.4 g. (92%) of a product, m.p. 108-112°. The pure compound crystallized from ethanol 75% (w/w) as white needles, m.p. 113-115°;  $\nu$  max (potassium bromide): 3460 and 3300 (NH), 3160 (NOH), 1595 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.80 (m, 4H,  $\text{CH}_2_{6',7'}$ ), 2.30 (s, 3H,  $\text{CH}_3$ ), 2.55 (m, 4H,  $\text{CH}_2_{5',8'}$ ), 5.40

(broad band, 2H,  $\text{NH}_2$ ), 6.52 (d, 1H,  $\text{H}_4'$ ), 7.10 (d, 1H,  $\text{H}_3'$ ,  $J_{3'-4'} = 9.0$  Hz), 8.70 (broad band, 1H, NOH) ppm.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$ : C, 70.6; H, 7.9; N, 13.7. Found: C, 70.6; H, 8.0; N, 13.8.

3'-Amino-5',6',7',8'-tetrahydro-2'-acetonephthone Oxime (VIIIb).

This compound was prepared from IIIb by the procedure described for VIIIa. The crude product was crystallized from ethanol 75% (w/w) as white needles (90%), m.p. 158-160°;  $\nu$  max (potassium bromide): 3370 and 3270 (NH), 3140 (NOH), 1615 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.80 (m, 4H,  $\text{CH}_2_{6',7'}$ ), 2.30 (s, 3H,  $\text{CH}_3$ ), 2.70 (m, 4H,  $\text{CH}_2_{5',8'}$ ), 5.20 (broad band, 2H,  $\text{NH}_2$ ), 6.45 (s, 1H,  $\text{H}_4'$ ), 7.05 (s, 1H,  $\text{H}_1'$ ) ppm.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$ : C, 70.6; H, 7.9; N, 13.7. Found: C, 70.5; H, 8.0; N, 13.7.

2-Chloromethyl-4-methyl-7,8,9,10-tetrahydrobenzo[h]quinazolin-3-Oxide (IXa).

Chloroacetyl chloride (9.0 g., 0.08 mole) was added dropwise with stirring to a warmed (50-60°) solution of VIIIa (7.9 g., 0.039 mole) in acetic acid (100 ml.). The mixture was allowed to stand overnight at room temperature and then concentrated *in vacuo*. The residue was crystallized from acetone to give 5.3 g. (52.4%) of the pure compound, m.p. 158-159°;  $\nu$  max (potassium bromide): 1618 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.95 (m, 4H,  $\text{CH}_2_{8,9}$ ), 2.90 (s, 3H,  $\text{CH}_3$ ), 3.15 (m, 4H,  $\text{CH}_2_{7,10}$ ), 5.12 (s, 2H,  $\text{CH}_2\text{Cl}$ ), 7.42 (d, 1H,  $\text{H}_6$ ), 7.64 (d, 1H,  $\text{H}_5$ ,  $J_{5-6} = 9.0$  Hz) ppm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{ClN}_2\text{O}$ : C, 64.0; H, 5.8; N, 10.7; Cl, 13.5. Found: C, 63.9; H, 5.8; N, 10.7; Cl, 13.3.

2-Chloromethyl-4-methyl-6,7,8,9-tetrahydrobenzo[g]quinazolin-3-Oxide (IXb).

This compound was prepared from VIIIb by the procedure described for IXa. The crude product was crystallized from acetone to give a white solid (55%), m.p. 145-146°;  $\nu$  max (potassium bromide): 1610 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.90 (m, 4H,  $\text{CH}_2_{7,8}$ ), 2.80 (s, 3H,  $\text{CH}_3$ ), 2.95 (m, 4H,  $\text{CH}_2_{6,9}$ ), 5.00 (s, 2H,  $\text{CH}_2\text{Cl}$ ), 7.45 (s, 1H,  $\text{H}_5$ ), 7.60 (s, 1H,  $\text{H}_{10}$ ) ppm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{ClN}_2\text{O}$ : C, 64.0; H, 5.8; N, 10.7; Cl, 13.5. Found: C, 64.0; H, 5.8; N, 10.6; Cl, 13.5.

3-Acetyl-4-methyl-7,8,9,10-tetrahydrobenzo[h]quinolin-2(1H)one (Xa).

To a solution of IIIa (18.9 g., 0.1 mole) in benzene (50 ml.) was added slowly while stirring (30 minutes) a solution of diketene (13.5 g., 0.15 mole) in benzene (15 ml.), and the solution was heated under reflux for 24 hours. The precipitate was filtered, washed with ether, and recrystallized from ethanol, to give 21.7 g. (85%) of white plates, m.p. 218-219°;  $\nu$  max (potassium bromide): 3150 (NH), 1680 (ketone C=O), 1630 (amide C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.90 (m, 4H,  $\text{CH}_2_{8,9}$ ), 2.43 (s, 3H,  $\text{CH}_3$ ) 2.62 (s, 3H,  $\text{CH}_3\text{-CO}$ ), 2.75 (m, 4H,  $\text{CH}_2_{7,10}$ ), 6.95 (d, 1H,  $\text{H}_6$ ) 7.50 (d, 1H,  $\text{H}_5$ ,  $J_{5-6} = 9.0$  Hz), 11.05 (broad band, 1H, NH) ppm.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{17}\text{NO}_2$ : C, 75.3; H, 6.7; N, 5.5. Found: C, 75.2; H, 6.7; N, 5.5.

3-Acetyl-4-methyl-6,7,8,9-tetrahydrobenzo[g]quinolin-2(1H)one (Xb).

This compound was prepared from IIIb by the procedure described for Xa. The crude product was recrystallized from DMF to give a white solid (90%), m.p. 297-298°;  $\nu$  max (potassium bromide): 3140 (NH), 1680 (ketone C=O), 1635 (amide C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.83 (m, 4H,  $\text{CH}_2_{7,8}$ ), 2.42 (s,

3H, CH<sub>3</sub>), 2.60 (s, 3H, CH<sub>3</sub>-CO), 2.85 (m, 4H, CH<sub>2</sub><sub>6,9</sub>), 7.00 (s, 1H, H<sub>10</sub>), 7.40 (s, 1H, H<sub>5</sub>) ppm.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>: C, 75.3; H, 6.7; N, 5.5. Found: C, 75.1; H, 6.6; N, 5.4.

3-( $\alpha$ -Hydroxyethyl)-4-methyl-7,8,9,10-tetrahydrobenzo[h]quinolin-2(1H)one (XIa).

To a warmed solution of Xa (10.2 g., 0.04 mole) in DMF (75 ml.) sodium borohydride (2.0 g., 0.052 mole) was added portionwise (30 minutes), and then the solution heated to 130° for 5 hours. The reaction mixture was cooled, poured into ice water and the precipitate filtered off, washed with water and recrystallized from chloroform-ethanol to give 9.2 g. (90%) of a white solid, m.p. 236-238°;  $\nu$  max (potassium bromide): 3360 (OH), 3140 (NH), 1620 (C=O) cm<sup>-1</sup>;  $\delta$  (deuteriochloroform): 1.65 (d, 3H, CH<sub>3</sub>-CH-), 1.95 (m, 4H, CH<sub>2</sub><sub>8,9</sub>), 2.50 (s, 3H, CH<sub>3</sub>-C=), 2.95 (m, 4H, CH<sub>2</sub><sub>7,10</sub>), 5.15 (m, 1H, CH), 7.00 (d, 1H, H<sub>6</sub>), 7.60 (d, 1H, H<sub>5</sub>, J<sub>5-6</sub> = 9.0 Hz), 11.05 (broad band, 1H, NH) ppm.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>: C, 74.7; H, 7.4; N, 5.4. Found: C, 74.6; H, 7.4; N, 5.3.

3-( $\alpha$ -Hydroxyethyl)-4-methyl-6,7,8,9-tetrahydrobenzo[g]quinolin-2(1H)one (XIb).

This compound was prepared from Xb by the procedure described for XIa. The crude product was recrystallized from DMF to give a white solid (85%), m.p. 283-285°;  $\nu$  max (potassium bromide): 3360 (OH), 3120 (NH), 1625 (C=O) cm<sup>-1</sup>;  $\delta$  (DMSO-d<sub>6</sub>): 1.45 (d, 3H, CH<sub>3</sub>-CH-), 1.85 (m, 4H, CH<sub>2</sub><sub>7,8</sub>), 2.50 (s, 3H, CH<sub>3</sub>-C=), 2.85 (m, 4H, CH<sub>2</sub><sub>6,9</sub>), 5.25 (m, 1H, CH), 7.13 (s, 1H, H<sub>10</sub>), 7.58 (s, 1H, H<sub>5</sub>) ppm.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>: C, 74.7; H, 7.4; N, 5.4. Found: C, 74.8; H, 7.6; N, 5.5.

2-Chloro-3-acetyl-4-methyl-7,8,9,10-tetrahydrobenzo[h]quinoline (XIIa).

A mixture of Xa (11.7 g., 0.05 mole) and phosphorus oxychloride (50 ml.) was heated in a water bath at 70° for 6 hours. The excess reagent was removed by distillation under reduced pressure. The residue was cooled and dissolved in chloroform. The organic solution was washed with sodium carbonate solution and water, and dried with anhydrous sodium sulfate. The solvent was removed and the residue recrystallized from methanol to give 10.2 g. (75%) of the pure compound, m.p. 74-76°;  $\nu$  max (potassium bromide) 1690 (C=O) cm<sup>-1</sup>;  $\delta$  (deuteriochloroform): 1.84 (m, 4H, CH<sub>2</sub><sub>8,9</sub>), 2.50 (s, 3H, CH<sub>3</sub>-C=), 2.60 (s, 3H, CH<sub>3</sub>-CO), 2.87 (m, 2H, CH<sub>2</sub><sub>7</sub>), 3.20 (m, 2H, CH<sub>2</sub><sub>10</sub>), 7.20 (d, 1H, H<sub>6</sub>), 7.64 (d, 1H, H<sub>6</sub>), 7.64 (d, 1H, H<sub>5</sub>, J<sub>5-6</sub> = 9.0 Hz) ppm.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>ClNO: C, 70.2; H, 5.9; N, 5.1; Cl, 13.0. Found: C, 70.1; H, 5.8; N, 5.1; Cl, 12.9.

2-Chloro-3-acetyl-4-methyl-6,7,8,9-tetrahydrobenzo[g]quinoline (XIIb).

This compound was prepared from Xb by the procedure described for XIIa. The crude product was crystallized from methanol to give a white solid (70%), m.p. 84-85°;  $\nu$  max (potassium bromide); 1705 (C=O) cm<sup>-1</sup>;  $\delta$  (deuteriochloroform): 1.95 (m, 4H, CH<sub>2</sub><sub>7,8</sub>), 2.55 (s, 3H, CH<sub>3</sub>-C=), 2.63 (s, 3H, CH<sub>3</sub>-CO), 3.00 (m, 4H, CH<sub>2</sub><sub>6,9</sub>), 7.70 (s, 2H, H<sub>5,10</sub>) ppm.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>ClNO: C, 70.2; H, 5.9; N, 5.1; Cl, 13.0. Found: C, 70.1; H, 5.8; N, 5.1; Cl, 12.9.

2-Diethylamino-3-acetyl-4-methyl-7,8,9,10-tetrahydrobenzo[h]quinoline Hydrochloride (XIIIa).

A mixture of XIIa (13.6 g., 0.05 mole) and diethylamine (25 ml.) was placed in a closed tube and heated in an oil bath at 150° for 24 hours. The mixture was cooled, and the precipitated diethylamine hydrochloride was removed by filtration, and the filtrate evaporated to dryness *in vacuo*. The residue was dissolved in dilute hydrochloric acid. The acid solution was extracted with chloroform, and the resulting aqueous solution was made alkaline with 20% sodium hydroxide and extracted with chloroform. The organic extracts were washed, dried and evaporated to dryness to give a viscous oil, which was dissolved in acetone, made acidic by adding a saturated solution of alcoholic hydrogen chloride gas. The precipitated hydrochloride was filtered and recrystallized from acetone to give 10.0 g. (75%) of solid, m.p. 155-156°;  $\nu$  max (potassium bromide): 2700-2500 (NH<sub>4</sub><sup>+</sup>), 1690 (C=O) cm<sup>-1</sup>;  $\delta$  (DMSO-d<sub>6</sub>): 1.10 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>), 1.80 (m, 4H, CH<sub>2</sub><sub>8,9</sub>), 2.48 (s, 6H, CH<sub>3</sub>-CO and CH<sub>3</sub>-C=), 2.80 (m, 2H, CH<sub>2</sub><sub>7</sub>), 3.10 (m, 2H, CH<sub>2</sub><sub>10</sub>), 3.35 (q, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 7.10 (d, 1H, H<sub>6</sub>), 7.70 (d, 1H, H<sub>5</sub>, J<sub>5-6</sub> = 9.0 Hz) ppm.

*Anal.* Calcd. for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O·HCl: C, 69.2; H, 7.8; N, 8.1; Cl, 10.2. Found: C, 69.0; H, 7.65; N, 7.9; Cl, 10.1.

2-Diethylamino-3-acetyl-4-methyl-6,7,8,9-tetrahydrobenzo[g]quinoline (XIIIb).

This compound was prepared from XIIIb by the procedure described for XIIIa. It was isolated as free base (72%), m.p. 61-63° from petroleum ether;  $\nu$  max (potassium bromide): 1675 (C=O);  $\delta$  (deuteriochloroform): 1.10 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>), 1.85 (m, 4H, CH<sub>2</sub><sub>7,8</sub>), 2.50 (s, 6H, CH<sub>3</sub>-CO and CH<sub>3</sub>-C=), 2.95 (m, 4H, CH<sub>2</sub><sub>6,9</sub>), 3.40 (q, 4H, -CH<sub>2</sub>-CH<sub>3</sub>), 7.60 (s, 2H, H<sub>5,10</sub>) ppm.

*Anal.* Calcd. for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O: C, 77.4; H, 8.4; N, 9.0. Found: C, 77.2; H, 8.6; N, 8.8.

N-Benzoyl-N'-[1'-(5',6',7',8'-tetrahydro-2'-acetonaphthyl)]thiourea (XIVa).

To a solution of ammonium thiocyanate (4.1 g., 0.055 mole) in dry acetone (25 ml.), benzoyl chloride (7.0 g., 0.05 mole) was added slowly while stirring. The reaction mixture was heated at reflux for 15 minutes, the heating bath was removed and a solution of IIIa (9.4 g., 0.05 mole) in dry acetone (50 ml.) was added to maintain reflux. After the addition was complete, the mixture was stirred for 90 minutes, poured into ice water, and the precipitate was filtered off, washed with water and recrystallized from ethanol to give 15.8 g. (90%) of pale yellow needles, m.p. 143-145°;  $\nu$  max (potassium bromide); 1680 (ketone C=O), 1670 (amide C=O) cm<sup>-1</sup>;  $\delta$  (deuteriochloroform): 1.72 (m, 4H, CH<sub>2</sub><sub>6,7</sub>), 2.50 (s, 3H, CH<sub>3</sub>), 2.75 (m, 4H, CH<sub>2</sub><sub>5,8</sub>), 7.50 (m, 7H, Ar), 9.35 (s, 1H, NHCS), 12.30 (s, 1H, NHCO) ppm.

*Anal.* Calcd. for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: C, 68.2; H, 5.7; N, 7.9; S, 8.9. Found: C, 68.0; H, 5.9; N, 7.7; S, 8.75.

N-Benzoyl-N'-[3'-(5',6',7',8'-tetrahydro-2'-acetonaphthyl)]thiourea (XIVb).

This compound was prepared from IIIb by the procedure described for XIVa. The crude product was recrystallized from chloroform-ethanol to give pale yellow needles (93%), m.p. 158-159°;  $\nu$  max (potassium bromide): 3400 (NH), 1680 (ketone

C=O), 1650 (amide C=O)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.75 (m, 4H,  $\text{CH}_2_{6,7}$ ), 2.55 (s, 3H,  $\text{CH}_3$ ), 2.78 (m, 4H,  $\text{CH}_2_{5,8}$ ), 7.50 (m, 4H, m, p,  $\text{H}_4'$ ), 7.85 (m, 2H, o, o), 8.12 (s, 1H,  $\text{H}_1'$ ), 9.10 (s, 1H, NHCS), 13.52 (s, 1H, NHCO).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ : C, 68.2; H, 5.7; N, 7.9; S, 8.9. Found: C, 68.2; H, 5.8; N, 7.9; S, 9.1.

#### 4-Methyl-7,8,9,10-tetrahydrobenzo[h]quinazoline-2(1H)thione (XVa).

A mixture of XIVa (8.8 g., 0.025 mole) sodium hydroxide (3.0 g.) and water (50 ml.) was heated under reflux for 15 minutes, cooled, diluted with water and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water, dried, and recrystallized from DMF to give 3.8 g. (70%) of a yellow solid, m.p. 192-194°;  $\nu$  max (potassium bromide): 1620 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.90 (m, 4H,  $\text{CH}_2_{8,9}$ ),

2.78 (s, 3H,  $\text{CH}_3\text{-C=}$ ), 2.90 (m, 4H,  $\text{CH}_2_{7,10}$ ), 7.10 (d, 1H,  $\text{H}_6$ ), 7.60 (d, 1H,  $\text{H}_5$ ,  $J_{5,6} = 9.0$  Hz) ppm.

Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}$ : C, 67.8; H, 6.1; N, 12.2; S, 13.9. Found: C, 67.6; H, 6.3; N, 12.0; S, 13.6.

#### 4-Methyl-6,7,8,9-tetrahydrobenzo[g]quinazoline-2(1H)thione (XVb).

This compound was prepared from XIVb by the procedure described for XVa. The crude product was recrystallized from DMF to give a yellow solid (75%), m.p. 258-260° dec.;  $\nu$  max (potassium bromide): 1630 (C=N)  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}$ : C, 67.8; H, 6.1; N, 12.2; S, 13.9. Found: C, 68.0; H, 6.0; N, 11.9; S, 13.7.

#### S-(4-Methyl-7,8,9,10-tetrahydrobenzo[h]quinazolin-2-yl)mercaptoacetic Acid (XVIa).

To a solution of chloroacetic acid (2.1 g., 0.022 mole) and sodium carbonate (1.2 g., 0.011 mole) in water (10 ml.) was added slowly while stirring (30 minutes), a solution of XVa (5.0 g., 0.021 mole) and sodium hydroxide (3.4 g., 0.063 mole) in water (25 ml.), and the reaction mixture was stirred overnight at room temperature, acidified with dilute hydrochloric acid and extracted with chloroform. The organic layers were dried over sodium sulfate, filtered, evaporated and the crystalline residue recrystallized from methanol to give 5.0 g., (83%) of a solid, m.p. 236-237°;  $\nu$  max (potassium bromide): 1710 (C=O), 1610 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (DMSO- $d_6$ ): 1.80 (m, 4H,  $\text{CH}_2_{8,9}$ ), 2.70 (s, 3H,  $\text{CH}_3$ ), 2.90 (m, 4H,  $\text{CH}_2_{7,10}$ ), 4.00 (s, 2H, S- $\text{CH}_2$ ), 7.05 (d, 1H,  $\text{H}_6$ ), 7.65 (d, 1H,  $\text{H}_5$ ) ppm.

Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ : C, 62.5; H, 5.6; N, 9.7; S, 11.1. Found: C, 62.3; H, 5.5; N, 9.7; S, 11.0.

#### S-(4-Methyl-6,7,8,9-tetrahydrobenzo[g]quinazolin-2-yl)mercaptoacetic Acid (XVib).

This compound was prepared from XVb by the procedure described for XVIa. The crude product was recrystallized from methanol to give a solid (86%), m.p. 183-185°;  $\nu$  max (potassium bromide): 1690 (C=O), 1625 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.85 (m, 4H,  $\text{CH}_2_{7,8}$ ), 2.80 (s, 3H,  $\text{CH}_3$ ), 2.95 (m, 4H,  $\text{CH}_2_{6,9}$ ), 3.80 (s, 2H, S- $\text{CH}_2$ ), 7.42 (s, 1H,  $\text{H}_5$ ), 7.60 (s, 1H,  $\text{H}_{10}$ ), 12.20 (s, 1H, COOH) ppm.

Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ : C, 62.5; H, 5.6; N, 9.7; S, 11.1. Found: C, 62.3; H, 5.5; N, 9.5; S, 10.9.

#### 2-( $\alpha$ -Hydroxyethyl)-5,6,7,8-tetrahydro-1-naphthylamine (XVIIa).

To a solution of IIIa (18.9 g., 0.1 mole) in methanol (150 ml.), sodium borohydride (1.9 g., 0.05 mole) was added portionwise (30 minutes), and the solution refluxed for 1 hour, then cooled in an ice bath and treated with dilute acetic acid. Evaporation of

the methanol *in vacuo* afforded an oil which was made basic by addition of 5% sodium hydroxide and extracted with chloroform. The organic layers were dried over sodium sulfate, filtered, evaporated and the crystalline residue recrystallized from ether-ligroin to give 17.5 g. (92%) of a white solid, m.p. 86-88°;  $\nu$  max (potassium bromide): 3240 (OH)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.45 (d, 3H,  $\text{CH}_3$ ), 1.75 (m, 4H,  $\text{CH}_2_{6,7}$ ), 2.30 (m, 2H,  $\text{CH}_2_8$ ), 2.70 (m, 2H,  $\text{CH}_2_5$ ), 3.65 (broad band, 2H,  $\text{NH}_2$ ), 4.75 (q, 1H, -CH- $\text{CH}_3$ ), 6.40 (d, 1H,  $\text{H}_4$ ), 6.80 (d, 1H,  $\text{H}_3$ ) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{17}\text{NO}$ : C, 75.4; H, 9.0; N, 7.3. Found: C, 75.2; H, 9.0; N, 7.2.

#### 3-( $\alpha$ -Hydroxyethyl)-5,6,7,8-tetrahydro-2-naphthylamine (XVIIb).

This compound was prepared from IIIb by the procedure described for XVIIa. The crude product was recrystallized from ether-ligroin to give a white solid (93%), m.p. 78-80°;  $\nu$  max (potassium bromide): 3440 (OH), 3400 and 3300 (NH)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.50 (d, 3H,  $\text{CH}_3$ ), 1.70 (m, 4H,  $\text{CH}_2_{6,7}$ ), 2.65 (m, 4H,  $\text{CH}_2_{5,8}$ ), 3.20 (broad band, 2H,  $\text{NH}_2$ ), 4.80 (q, 1H, -CH- $\text{CH}_3$ ), 6.30 (s, 1H,  $\text{H}_4$ ), 6.70 (s, 1H,  $\text{H}_1$ ) ppm.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{17}\text{NO}$ : C, 75.4; H, 9.0; N, 7.3. Found: C, 75.3; H, 8.9; N, 7.3.

#### 2-Methylamino-4-methyl-7,8,9,10-tetrahydro-4H-naphtho[1,2-d]-[3,1]thiazine (XVIIIa).

A mixture of XVIIa (7.2 g., 0.038 mole) methyl isothiocyanate (2.8 g., 0.038 mole) and chloroform (50 ml.) was heated under reflux for 2 hours. The reaction mixture was concentrated to dryness, and the residue was treated with concentrated hydrochloric acid (30 ml.); then ethanol was added dropwise under refluxing conditions until the solid dissolved. The resulting solution was boiled for three hours, cooled, diluted with water, made strongly alkaline with 20% sodium hydroxide and extracted with chloroform. The organic layers were dried over sodium sulfate, filtered, evaporated and the crystalline residue recrystallized from benzene-*n*-hexane to give 7.2 g. (77%) of a white solid, m.p. 90-92°;  $\nu$  max (potassium bromide): 3310 (NH), 1605 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.5 (d, 3H,  $\text{CH}_3\text{-CH}$ ), 1.85 (m, 4H,  $\text{CH}_2_{9,10}$ ), 2.85 (m, 4H,  $\text{CH}_2_{8,11}$ ), 3.10 (s, 3H,  $\text{CH}_3\text{-NH}$ ), 4.05 (q, 1H, -CH- $\text{CH}_3$ ), 4.55 (broad band, 1H, NH), 6.90 (s, 2H,  $\text{H}_5$ ,  $\text{H}_6$ ) ppm.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{S}$ : C, 68.3; H, 7.4; N, 11.4; S, 13.0. Found: C, 68.5; H, 7.5; N, 11.4; S, 13.1.

#### 2-Methylamino-4-methyl-6,7,8,9-tetrahydro-4H-naphtho[2,3-d]-[3,1]thiazine (XVIIIb).

This compound was prepared from XVIIb by the procedure described for XVIIIa. The crude product was recrystallized from benzene-*n*-hexane to give a white solid (80%), m.p. 121-122°;  $\nu$  max (potassium bromide): 3300 (NH), 1575 (C=N)  $\text{cm}^{-1}$ ;  $\delta$  (deuteriochloroform): 1.50 (d, 3H,  $\text{CH}_3\text{-CH}$ ), 1.80 (m, 4H,  $\text{CH}_2_{8,9}$ ), 2.80 (m, 4H,  $\text{CH}_2_{7,11}$ ), 3.10 (s, 3H,  $\text{CH}_3\text{-NH}$ ), 4.05 (q, 1H, -CH- $\text{CH}_3$ ), 4.40 (broad band, 1H, NH), 6.85 (s, 1H,  $\text{H}_6$ ), 7.00 (s, 1H,  $\text{H}_{11}$ ) ppm.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{S}$ : C, 68.3; H, 7.4; N, 11.4; S, 13.0. Found: C, 68.3; H, 7.2; N, 11.2; S, 13.0.

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#### REFERENCES AND NOTES

(1) W. Borsche and C. A. Bodenstein, *Chem. Ber.*, **59**, 1915 (1926).

(2) K. Schofield, T. Swain and R. S. Theobald, *J. Chem. Soc.*,

2399 (1949).

(3) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(4) R. F. C. Brown, I. D. Rae and S. Sternhell, *Aust. J. Chem.*, **18**, 61 (1965).

(5) L. H. Sternbach, R. I. Fryer, W. Metlesics, E. Reeder, G. Sancy and A. Stempel, *J. Org. Chem.*, **27**, 3788 (1962).

(6) A. Stempel, E. Reeder and L. H. Sternbach, *ibid.*, **30**, 4267 (1965).

(7) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p. 264.

(8) H. Hartmann and R. Mayer, *J. Prakt. Chem.*, **30**, 87 (1965).

(9) I. B. Douglass and F. B. Daisn, *J. Am. Chem. Soc.*, **56**, 719 (1934).