SYNTHESIS OF 3-AMINO-4-BENZOYLSYDNONES

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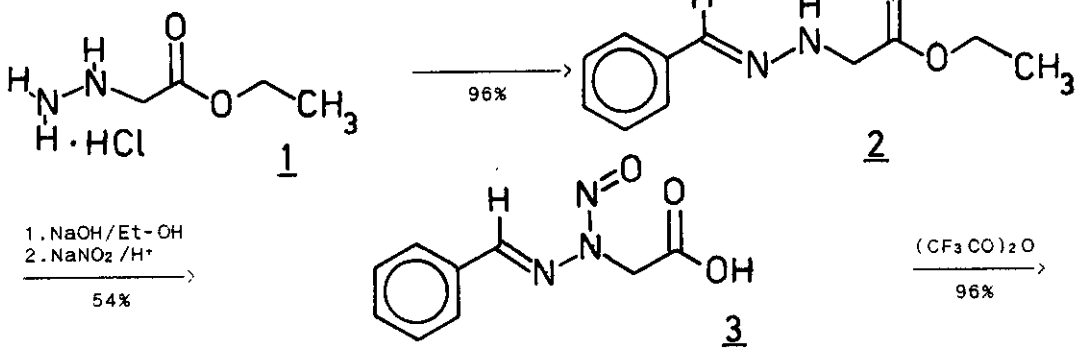
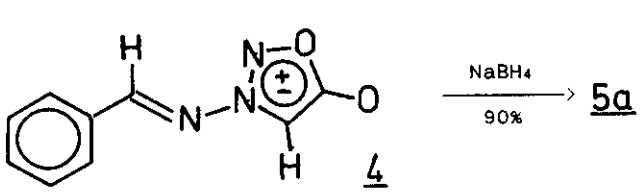
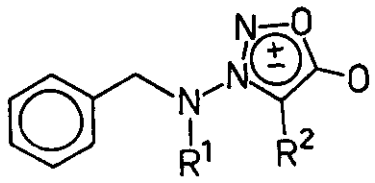
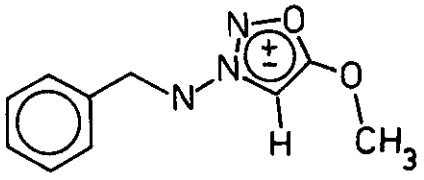
Abstract - In a three step synthesis starting from ethyl hydrazinoacetate HCl (1), 3-benzylidenaminosydnone (4) was available in good yields. Reduction with sodium boranate gave 3-benzylaminosydnone (5a). Lithiation and electrophilic substitution of 5a was studied. Reacting lithiated 5a with N,N-dimethylbenzamide afforded 3-benzylamino-4-benzoylsydnone (5i) which could be deprotected to give 3-amino-4-benzoylsydnone (8b).

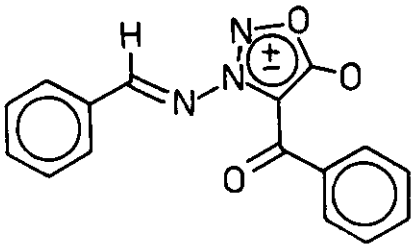
Sydnones are heterocyclic compounds which have been widely investigated in recent years [1]. Nearly all sydnones described so far are substituted by alkyl, aryl or aralkyl substituents in position 3 and also 4. 3-Aminosydnones which have been published till now [2], carry two equivalent substituents at the exocyclic nitrogen. In order to get condensed 3-aminosydnones intermediates were needed which carry a primary or secondary amino group in position 3 of the sydnone ring.
Such primary or secondary 3-aminosydnones cannot be synthesised from primary or secondary hydrazinoacetic acids without protection of the terminal N, because these compounds are not stable under nitrosation conditions [3]. After use of acyl protection groups had failed, the application of the benzylidene group was tried. Thus commercially available ethyl hydrazinoacetate HCl (1) was treated with benzaldehyde according to an usual procedure [4] to afford hydrazone 2. Hydrolysis of the ester group was manufactured by ethanolic sodium hydroxide followed by nitrosation with sodium nitrite in acidic medium to give the nitrosohydrazinoacetic acid 3. Dilute acid for acidification, low temperature and short reaction time at the nitrosation step was necessary to avoid hydrolysis of the hydrazone bond. Cyclisation of 3 to 3-benzylideneaminosydnone (4) was obtained by treatment with trifluoroacetic anhydride in ether. The overall yield in this three step procedure starting from 1 was 50%.



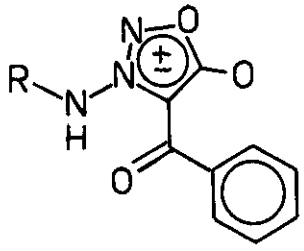








	R^1	R^2
5a	H	H
5b	CH_3	H
5c	CH_3CO	H
5d	Li	H
5e	Li	Li
5f	H	CH_3
5g	CH_3	CH_3
5h	H	HCO
5i	H	C_6H_5CO
5k	CH_3	C_6H_5CO



	R
8a	H
8b	CH_3

^1H, ^{13}C-nmr and ir studies of 4 showed the typical parameters [5] for a 4-unsubstituted sydnone ring. Characteristic fragments [6] in mass spectrometry proved the constitution of 4. Selective deprotection of 4 to the unknown 3-aminosydnone by acidolysis or hydrogenolysis failed; only benzaldehyde and decomposition products were detected.

Reduction of 4 with sodium boranate afforded 5a, the first known 3-aminosydnone with a secondary amino group. Compound 5a is structurally analogous to N-benzylaniline, but it is not possible to extract 5a from alkaline solution; only after acidification of the aqueous layer 5a was extractable by dichloromethane. Compound 5a reacts rather as a phenolic compound than as an aromatic amine. The low basicity of the exocyclic nitrogen was explained by the conjugation of the free electron pair to the mesoionic sydnone ring.

In contrast to 3-alkyl-substituted sydnones secondary 3-aminosydnones like 5a can theoretically exist in two tautomeric forms; one carrying the negative charge at the exocyclic oxygen and another at the exocyclic nitrogen. In order to get more information about the reactivity of secondary 3-aminosydnones 5a was dissolved in aqueous sodium hydroxide and treated with excess iodomethane. Only an N-methylated compound (5b) was obtained. No O-methylation or quaternisation of the exocyclic nitrogen were observed. If the reaction was carried out by diazomethane, a mixture of N-methylated and C-methylated product (5b:6 = 70:30) was found. Identification and quantitative determination of the two methylation products 5b and 6 was practicable by the different resonance frequencies of the methyl groups. A separation of 6 by crystallisation or chromatography unfortunately failed. Reaction of 5a with acetic anhydride gave - as expected - N-acetylation to compound 5c.

After substitution at the exocyclic nitrogen had been studied, introduction of alkyl or acyl groups in position 4 of the 3-aminosydnone ring should be explorated. Alkylation or acylation at 3-alkyl-substituted sydnones was practicable by electrophilic substitution of lithiated sydnones in moderate to good yields [7]. We intended to transfer these results to 3-aminosydnones like 5a. The secondary 3-aminosydnone 5a has two acidic protons; one at the exocyclic nitrogen and another at C-4 of the sydnone ring. When 5a was lithiated with n-butyllithium, the hydrogen at the exocyclic nitrogen was abstracted first in order to yield 5d. Reaction of monoanion 5d with iodomethane gave the N-methylated compound 5b. Lithiating 5a with two equivalents of n-butyllithium gave the red coloured dianion 5e which could be selectively C-methylated with one equivalent iodomethane to 4-methylsyd-

none 5f. When 5e was treated with excess iodomethane the C,N-dimethylated product 5g was obtained. Thus alkylation could be controlled by the ratio of sydnone to metallation and alkylation agent.

Selective C-substitution at 5a should now be studied under the use of acylating agents. Acylation at 3-alkyl-substituted sydnones was afforded by reacting lithiated sydnones with acetic anhydride or benzoyl chloride [8]. In contrast to that dianion 5e gave only decomposition products with those reagents. Tertiary amides like dimethylformamide or dimethylbenzamide were successfully reacted with metallated benzene aromatics [9]. These results could be transfered to dilithiated 3-aminosydnones. Thus dianion 5e afforded selective C-acylation with dimethylformamide (5h,90%) and dimethylbenzamide (5i,76%) in good yields. Spectroscopy of 5h and 5i indicates a strong intramolecular hydrogen bridge bond between the carbonyl group and the hydrogen at the exocyclic nitrogen. Significant was a low field signal in ^{1}H-nmr (~10.5ppm) for the proton at the exocyclic nitrogen and an ir absorption at a low wavenumber (~1604 cm^{-1}) for the carbonyl group. In contrast to 5a the benzoylated compound 5i was not methylated with iodomethane in aqueous sodium hydroxide. Otherwise reacting 5i with sodium hydride/THF/iodomethane gave the N-methylation product 5k in good yield. These methylation conditions indicate a very low basicity of the exocyclic nitrogen in 5i corresponding to its character as vinylogous amide.

The next aim was to vary the substituents at the exocyclic nitrogen. Cleavage of the benzylic group at 5i should afford the primary 3-aminosydnone 8a. But all experiments to remove the benzyl group in 5i or 5k by hydrogenolysis failed. Therefore oxidation of 5i to the benzylidene derivative 7 and hydrolysis to 8a was aspired. Oxidation should be managed by bromination of 5i with N-bromosuccinimide and elimination of hydrobromic acid by potassium carbonate. But reacting 5i with one equivalent of N-bromosuccinimide gave only 50% conversion to 7. Transformation to 7 was only complete using two equivalents of the reagent. Addition of potassium carbonate proved to be not necessary, because no hydrobromic acid was formed in the reaction, but free bromine and succinimide. A secondary exocyclic nitrogen seems to be essential in the educt for this conversion, because 5k remained unreacted under above oxidation conditions. Hydrolysis of 7 to the first known primary 3-aminosydnone 8a was obtained by aqueous hydrochloric acid in THF. After deprotonation of 8a with sodium hydride in THF followed by treatment with iodomethane a mixture of the starting material and the desired monomethylation product

8b was isolated. Separation by preparative thin layer chromatography yielded 8b in pure form but low yield (29%).

This paper demonstrates an access to 3-amino-4-benzoylsydnones especially compound 5l, 5k, 7, 8a and 8b. Further investigations will be made to show the usefulness of these intermediates for the syntheses of anellated 3-aminosydnones.

EXPERIMENTAL

All melting points were determined on a KOFLER melting point apparatus and are uncorrected. ^1H and ^{13}C-nmr were recorded on a VARIAN EM 390 and a BRUKER AC 80, using tetramethylsilane as internal standard. Infrared spectra were recorded on a PERKIN ELMER 298 spectrophotometer. Mass spectra were detected on a MAT CH-7 by Dr. Nikiforov, Institut fur Organische Chemie. Microanalyses were determined by Dr. Zak, Institut fur Physikalische Chemie.

Ethyl N-Benzylidenehydrazinoacetate (2)

An effective stirred suspension of ethyl hydrazinoacetate hydrochloride (1) (46.4g, 0.3M), sodium acetate (122.4g, 0.9M) and benzaldehyde (31.8g, 0.3M) in ethanol was refluxed for 3 h. After evaporation of the solvent the residue was dissolved in 2N aqueous sodium carbonate (200ml) and extracted with dichloromethane (3x200ml). The combined organic layers were dried (Na_2SO_4) and evaporated to give 2 (59.4g, 96%, yellow oil). ^1H-Nmr: ($CDCl_3$), (δ,ppm) 7.65 (s,1H,imine-H), 7.6 - 7.1 (m,5H,aromatic-H), 5.85 (t,1H,N-H), 4.15 (q,2H,methylen-H), 3.95 (d,2H, glycine-H), 1.25 (t,3H,methyl-H).

N-Benzylidene-N-nitrosohydrazinoacetic Acid (3)

Ethyl N-benzyliden-hydrazinoacetate (2) (56.4g, 288mM) was dissolved in ethanol (100ml) and poured into ethanolic NaOH (460ml, 10%). Within a few seconds the mixture turned into an orange gel. After heating to 70°C on a rotatory evaporator, the solvent was eliminated at reduced pressure. This residue was dissolved in water (200ml), cooled to 0°C and acidified to pH 4 by slow addition of 2N HCl (580ml). Then sodium nitrite (22.8g, 330mM) dissolved in water (80ml) was added to the cooled solution and the ph was adjusted to 3 by addition of 2N HCl (180ml). After a reaction time of 5 min the mixture was extracted with dichloromethane (4x200ml) and the solvent was eliminated at reduced pressure (bath temperature below 40°C !). Crystallisation of the residue from chloroform yielded 3 (32.2g, 54%, yellow crystalls). ^1H-Nmr: (d_6-Aceton), (δ,ppm) 8.76 (s,1H,imine-H), 8.1 - 7.5

(m,5H,aromatic-H), 5.0 (s,2H,glycine-H). Ir: (KBr) 1740 cm^{-1} (carboxylic acid).

3-Benzylideneaminosydnone (4)

N-Benzyliden-N-nitrosohydrazinoacetic acid (3) (32.2g, 155mM) was suspended in dry ether (300ml) by an effective stirrer in an argon atmosphere at 0°C. Trifluoroacetic anhydride (26ml, 184mM) was added and the mixture kept at 0°C for 1 h. The precipitated crystals were removed by filtration through a funnel with a fritted disc. Recrystallisation from methanol afforded 4 (28.2g, 92%, yellow needles), mp 120°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 9.1 (s,1H,imine-H), 7-8 (m,5H,aromatic-H), 6.66 (s,1H,sydnonering-H). ^{13}C-Nmr: (d_6-DMSO), (δ,ppm) 167.41 (sydnonecarbonyl); 134.66, 130.28, 129.40 (aromatic-C); 90.61 (sydnonering-C). Ir: (KBr), 1750 cm^{-1}, 1734 cm^{-1} (sydnonecarbonyl). Ms: m/z 189 (M^+), 159 (M^+-NO), 131 (M^+-NO-CO). Anal. calcd for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.21. Found: C, 56.81; H, 3.70; N, 21.98.

3-Benzylaminosydnone (5a)

3-Benzylideneaminosydnone (4) (28.2g, 149mM) was dissolved in methanol (400ml) and cooled to 0°C. In small portions sodium borohydride (10g) was added to the cooled solution. After stirring for 1 h the solvent was evaporated, 2N HCl (170ml) was added and the aqueous layer extracted with dichloromethane (3x150ml). The collected organic layers were dried (Na_2SO_4) and the solvent evaporated to give a yellow oil. Crystallisation from methanol afforded 5a (25.6g, 90%, colourless prism), mp 90°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.56 (t,1H,N-H,J = 6Hz) 7.4 (s,5H,aromatic-H), 6.2 (s,1H,sydnonering-H), 4.5 (d,2H,benzylic-H,J = 6Hz). ^{13}C-Nmr: ($CDCl_3$), (δ,ppm) 168.66 (sydnonecarbonyl); 133.97, 128.72, 128.45 (aromatic-C); 90.79 (sydnonering-C); 53.70 (benzylic-C). Ir: (KBr) 1740 cm^{-1}, 1715 cm^{-1} (sydnonecarbonyl). Ms: m/z 191 (M^+), 161 (M^+-NO), 133 (M^+-NO-CO). Anal. calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.46; H, 4.80; N, 21.97.

3-(N-Benzyl-N-methylamino)sydnone (5b)

Procedure A: 3-Benzylaminosydnone (5a) (382mg, 2mM) was dissolved in dry THF (20ml) in an argon atmosphere. After the solution had been cooled to -50°C, n-butyllithium (1.3ml, 2.1mM) in hexane was slowly added and the temperature was kept below -20°C for 1 h (A yellow colour of the solution indicates single metallation). The solution was cooled to -78°C, iodomethane (710mg, 5mM) in THF (5ml) was added and the reaction mixture was allowed to warm to room temperature. To work up the reaction 2N HCl (50ml) was added at 0°C and THF was evaporated. The remaining aqueous layer was extracted with dichloromethane (3x50ml), the collected organic

layers were dried (Na_2SO_4) and the solvent evaporated at reduced pressure. Crystallisation from isopropanol gave 5b (370mg, 90%).

Procedure B: 3-Benzylaminosydnone (5a) (6.69g, 35mM) was dissolved in 1N NaOH (44ml), iodomethane (6.3ml, 100mM) was added and the mixture was refluxed for 1 h. Excess iodomethane was removed at reduced pressure and the aqueous layer extracted with dichloromethane (3x50ml). The combined organic layers were dried (Na_2SO_4) and the solvent was removed at reduced pressure. Pure compound 5b was obtained by crystallisation from isopropanol (Yield 6.3g, 88%, colourless needles), mp 68°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.3 (s,5H,aromatic-H), 6.33 (s,1H,sydnonering-H), 4.4 (s,2H,benzylic-H), 3.1 (s,3H,methyl-H). ^{13}C-Nmr: (d_6-DMSO), (δ,ppm) 167.53 (sydnonecarbonyl); 132.61, 129.00, 128.41, 128.24 (aromatic-C); 91.78 (sydnonering-C); 61.11 (benzylic-C); 42.97 (methyl-C). Ir: (KBr), 1725 cm^{-1} (sydnonecarbonyl). Ms: m/z 205 (M^+), 175 (M^+-NO), 147 (M^+-NO-CO). Anal. calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.38; H, 5.45; N, 20.69.

N-Acetyl-N-benzyl-3-aminosydnone (5c)

3-Benzylaminosydnone (5a) (0.5g, 2.6mM) was stirred in acetic anhydride (10ml) in the presence of a catalytical amount of 4-dimethylaminopyridine for 20 h at 20°C. Excess acetic anhydride was removed by evaporation at reduced pressure. The residue was dissolved in dichloromethane (50ml), washed with 0.5N HCl (3x30ml) and saturated $NaHCO_3$ solution (3x30ml). The organic layer was dried (Na_2SO_4) and evaporated to dryness. Crystallisation from methanol afforded 5c (560mg, 77%), mp 90-91°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.3 (s,5H,aromatic-H), 6.3 (s,1H,sydnonering-H), 5.0 (s,2H,benzylic-H), 2.1 (s,3H, acetyl-H). Ir: (KBr), 1775 cm^{-1} (sydnonecarbonyl), 1700 cm^{-1} (amidecarbonyl). Ms: m/z 203 (M^+-NO), 175 (M^+-NO-CO). Anal. calcd for $C_{11}H_{11}N_3O_3$: C, 56.65; H, 4.75; N, 18.02. Found: C, 56.69; H, 4.,82; N, 17.,91.

3-Benzylamino-4-methylsydnone (5f)

3-Benzylaminosydnone (5a) (382mg, 2mM) was dissolved in dry THF (20ml) in an argon atmosphere. After the solution had been cooled to -50°C, n-butyllithium (2.6ml, 4.2mM) in hexane was slowly added and the temperature was kept below -20°C for 1 h (A dark red colour of the solution indicates double metallation). The solution was cooled to -78°C, iodomethane (300mg, 2.1mM) in THF (2.1ml) was added and the reaction mixture was allowed to warm to room temperature. To work up the reaction 2N HCl (50ml) was added at 0°C and THF was evaporated. The remaining aqueous layer was extracted with dichloromethane (3x50ml), the collected organic layers were dried (Na_2SO_4) and the solvent evaporated at reduced pressure to give 5f (350mg,

85%, yellow oil). ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.3 (s,5H,aromatic-H), 4.4 (s,2H,benzylic-H), 1.9 (s,3H,C-methyl-H).

3-(N-Benzyl-N-methylamino)-4-methylsydnone (5g)

3-Benzylaminosydnone (5a) (382mg, 2mM) was dissolved in dry THF (20ml) in an argon atmosphere. After the solution had been cooled to -50°C, n-butyllithium (2.6ml, 4.2mM) in hexane was slowly added and the temperature was kept below -20°C for 1 h (A dark red colour of the solution indicates double metallation). The solution was cooled to -78°C, iodomethane (710mg, 5mM) in THF (5ml) was added and the reaction mixture was allowed to warm to room temperature. To work up the reaction 2N HCl (50ml) was added at 0°C and THF was evaporated. The remaining aqueous layer was extracted with dichloromethane (3x50ml), the collected organic layers were dried (Na_2SO_4) and the solvent evaporated at reduced pressure to give 5g (330mg, 75%, yellow oil). ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.3 (s,5H,aromatic-H), 4.3 (s,2H,benzylic-H), 3.1 (s,3H,N-methyl-H), 1.9 (s,3H,C-methyl-H).

3-Benzylamino-4-formylsydnone (5h)

3-Benzylaminosydnone (5a) (1.91g, 10mM) was dissolved in dry THF (30ml) in an argon atmosphere. After the solution had been cooled to -50°C, n-butyllithium (13.8ml, 22mM) in hexane was slowly added and the temperature was kept below -20°C for 1 h (A dark red colour of the solution indicates double metallation). The solution was cooled to -78°C, dimethylformamide (1.09g, 15mM) in THF (15ml) was added and the reaction mixture was allowed to warm to room temperature overnight. To work up the reaction 2N HCl (25ml) was added at 0°C and THF was evaporated. The remaining aqueous layer was extracted with dichloromethane (3x50ml), the collected organic layers were dried (Na_2SO_4) and the solvent evaporated at reduced pressure. Crystallisation from methanol gave 5h (1.98g, 90%). mp 96-97°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 10.1 (m,1H,N-H), 9.4 (s,1H,aldehyde-H), 7.4 (s,5H,aromatic-H), 4.8 (m,2H, benzylic-H). ^{13}C-Nmr: (d_6-DMSO), (δ,ppm) 175.98 (aldehydecarbonyl); 163.95 (sydnonecarbonyl); 134.59, 128.52, 128.16, 127.92 (aromatic-C); 100.34 (sydnonering-C); 50.22 (benzylic-C). Ir: (KBr), 1790 cm^{-1} (sydnonecarbonyl), 1645 cm^{-1} (aldehydecarbonyl). Ms: m/z 219 (M^+), 189 (M^+-NO), 161 (M^+-NO-CO). Anal. calcd for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.14; N, 19.17. Found C, 54.88; H, 4.21; N, 19.37.

3-Benzylamino-4-benzoylsydnone (5i)

3-Benzylaminosydnone (5a) (19.1g, 0.1M) was dissolved in dry THF (500ml) in an argon atmosphere. After the solution had been cooled to -50°C, n-butyllithium (144ml, 230mM) in hexane was slowly added and the temperature was kept below -20°C

for 1 h (A dark red colour of the solution indicates double metallation). The solution was cooled to -78°C, dimethylbenzamide (17.9g, 120mM) in THF (120ml) was added and the reaction mixture was allowed to warm to room temperature overnight. To work up the reaction 2N HCl (250ml) was added at 0°C and THF was evaporated. The remaining aqueous layer was extracted with dichloromethane (3x150ml), the collected organic layers were dried (Na_2SO_4) and the solvent evaporated at reduced pressure. Crystallisation from methanol/ether gave 5l (22.4g, 76%, colourless crystal sand). mp 99-100°C. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 10.5 (t,1H,N-H,J = 6Hz), 7-8 (m,10H,aromatic-H), 4.72 (d,2H,benzylic-H,J = 6Hz). ^{13}C-Nmr: ($CDCl_3$), (δ,ppm) 183.9 (ketonecarbonyl); 162.98 (sydnonecarbonyl); 134.95, 133.33, 133.09, 128.89, 128.59, 128.25, 128.01 (aromatic-C); 99.63 (sydnonering-C); 51.06 (benzylic-C). Ir: (KBr), 1760 cm^{-1} (sydnonecarbonyl), 1604 cm^{-1} (ketonecarbonyl). Ms: m/z 265 (M^+-NO), 237 (M^+-NO-CO). Anal. calcd for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23. Found C, 65.01; H, 4.42; N, 14.37.

3-(N-Benzyl-N-methyl)-amino-4benzoylsydnone (5k)

3-Benzylamino-4-benzoylsydnone (5l) (885mg, 3mM) was dissolved in dry THF (20ml) in an argon atmosphere. This solution was dropped to a suspension of sodium hydride (100mg, 80% dispersion in mineral oil, 3.3mM) in dry THF (20ml) at 0°C. After 2 h at 20°C iodomethane (0.5ml, 8mM) was added and the reaction mixture was stirred for 30 min at 20°C. Water (2ml) was added and the solvent removed at reduced pressure. The residue was dissolved in dichloromethane (50ml), washed with 2N HCl (2x50ml) and saturated $NaHCO_3$ solution, dried (Na_2SO_4) and the solvent was evaporated at reduced pressure to yield 5k (710mg, 77%, yellow oil). ^{1}H-Nmr: ($CDCl_3$), (δ,ppm)= 7-8 (m,10H,aromatic-H), 4.50 (s,2H,benzylic-H), 3.20 (s,3H,methyl-H).

3-Benzylamino-O-methylsydnone (6)

An ethereal diazomethane solution was prepared from nitrosomethylurea (2g, 19.3mM) and KOH (7ml, 40%) at 0°C. 3-Benzylaminosydnone (5b) (500mg, 2.6mM) dissolved in methanol/water (18+2ml) was added and this mixture stirred at 20°C for 20 h. After evaporation of the solvent at reduced pressure the residue was dissolved in dichloromethane, dried (Na_2SO_4) and the solvent evaporated at reduced pressure to give a mixture of 30% 6 + 70% 5b (510mg, yellow oil), which could not be separated. ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 7.3 (s,5H,aromatic-H), 6.5 (s,1H,sydnonering-H), 4.35 (s,2H,benzylic-H), 3.95 (s,3H,O-methyl-H).

3-Benzylidenamino-4-benzoylsydnone (7)

A solution of 3-benzylamino-4-benzoylsydnone (5l) (7.38g, 25mM) and N-bromosuc-

cinimide in dry chloroform (150ml) was refluxed for 1 h. The cooled red brown solution was washed with 2N sodium carbonate, dried and the solvent evaporated at reduced pressure. The residue was recrystallised from chloroform to give 7 (6.2g, 85%, yellow needles). ^{1}H-Nmr: ($CDCl_3$), (δ,ppm)= 9.0 (s,1H,imine-H), 8.1-7.5 (m,10H,aromatic-H). Ir: (KBr), 1755 cm^{-1}(sydnonecarbonyl), 1643 cm^{-1} (ketonecarbonyl). Ms: m/z 293 (M^+), 263 (M^+-NO), 235 (M^+-NO-CO).

3-Amino-4-benzoylsydnone (8a)

3-Benzylidenamino-4-benzoylsydnone (7) (6.2g, 21mM) was dissolved in THF (60ml), mixed with 2N HCl (60ml) and heated to 40°C for 1 h. THF was removed at reduced pressure and the aqueous residue extracted with dichloromethane (3x75ml). The collected organic layers were dried (Na_2SO_4), the solvent was evaporated at reduced pressure and the residue was recrystallised from toluene to yield 8a (3.73, 87%). mp 146-147°C. ^{1}H-Nmr: (d_6-acetone), (δ,ppm) 9.45 (m,2H,amine-H), 8-7 (m,5H,aromatic-H). Ir: (KBr), 1765 cm^{-1}(sydnonecarbonyl). Ms: 205 (M^+), 175 (M^+-NO), 147 (M^+-NO-CO). Anal. calcld for $C_9H_7N_3O_3$: C, 52.68; H, 3.44; N, 20.48. Found C, 52.35; H, 3.53; N, 20.42.

3-Methylamino-4-benzoyl-sydnone (8b)

3-Amino-4-benzoylsydnone (8a) (820mg, 4mM) was dissolved in dry THF (20ml) in an argon atmosphere. This solution was dropped into a suspension of sodium hydride (120mg, 80% dispersion in mineral oil, 4mM) in dry THF (20ml) at 0°C. After 2 h at 20°C iodomethane (0.5ml, 8mM) was added and the reaction mixture was stirred for 30 min at 20°C. Water (2ml) was added and the solvent evaporated at reduced pressure. The residue was dissolved in dichloromethane (50ml), washed with 2N HCl (2x50ml) and saturated $NaHCO_3$ solution, dried (Na_2SO_4) and the solvent was evapotated at reduced pressure to yield a yellow oil (mixture of 8a + 8b). Separation was carried out by chromatography (silica gel preparative TLC plates, thickness of layer 2mm, eluent chloroform+THF=97+3, Rf=0.52 400mg 8b, Rf=0.23 185mg 8a). Crystallisation from methanol yielded pure 8b (240mg, 27%). ^{1}H-Nmr: ($CDCl_3$), (δ,ppm) 10.8 (m,1H,N-H), 8.1-7.4 (m,5H,aromatic-H), 3.35 (d,3H,methyl-H). Ms: 189 (M^+-NO), 161 (M^+-NO-CO). Anal. calcld for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.15; N, 19.17. Found C, 54.55; H, 4.19; N, 19.31.

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