Synthesis and Reactions of 9,10-Diazatetracyclo-[6.3.0.0.^{4,11}0.^{5,9}]undecanes

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This paper is dedicated to the memory of Dr. Nicholas Alexandrou

The tandem 1,3-dipolar cycloaddition between sydnones and 1,5-cyclooctadiene provides 9,10-diazatetracyclo[6.3.0.0.^{4,11}0.^{5,9}]undecanes (the Weintraub reaction) in modest to good yields.

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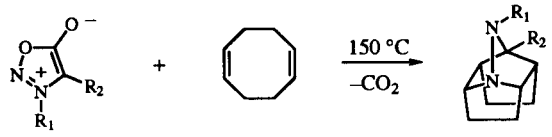
In 1970, Weintraub reported the then remarkable reaction between mesoionic sydnones **1** and 1,5-cyclooctadiene (**2**) to give the novel 9,10-diazatetracyclo[6.3.0.0.^{4,11}0.^{5,9}]-undecanes **3**, the products of a tandem 1,3-dipolar cycloaddition reaction [1].



1 **2** **3**

In continuation of our studies of the chemical and physical properties of azapolycyclic hydrocarbons [2], we now describe further extensions of the Weintraub reaction, encompassing the synthesis and chemistry of several new examples of this ring system **3**, including the parent compound **3** (R_1 = R_2 = H). The requisite sydnones **1** were all prepared according to literature procedures [3-8] or variations thereof (see Experimental) and are tabulated in Table 1. Only **1h** is new, and its synthesis is shown below.

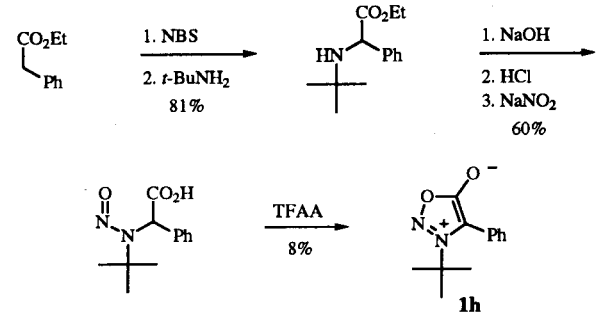
Reaction of the sydnones **1a-1g** with 1,5-cyclooctadiene (**2**) at reflux afforded the corresponding diazatetracyles **3a-3f** in variable yields (Table 1). Compounds **3d-3f** are new. Attempts to prepare **3g-3h** were unsuccessful. The structures of **3a-3f** were supported by spectral and elemental analytical data. The interesting restricted nitrogen inversion properties of these compounds will be reported separately.

Table 1

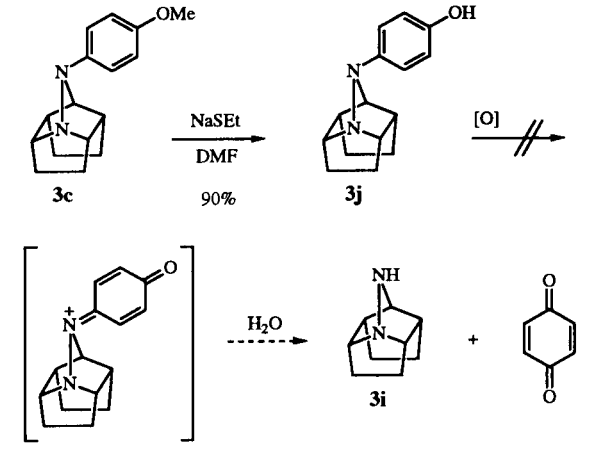
Preparation of Sydnones **1** and Diazatetracycles **3**

Compound	R_1	R_2	%1 [a]	%3
a	Bn	H	21	43
b	Ph	H	41	81
c	4-MeOPh	H	21	70
d	3,4-diMeOPh	H	12	74
e	Me	H	51	22
f	*t*-Bu	H	20	62
g	allyl	H	44	0
h	*t*-Bu	Ph	4	0
i	H	H	—	97
j	4-HOPh	H	—	90
k	CHO	H	—	18
l	NO	H	—	78

[a] Overall yield from commercial materials.

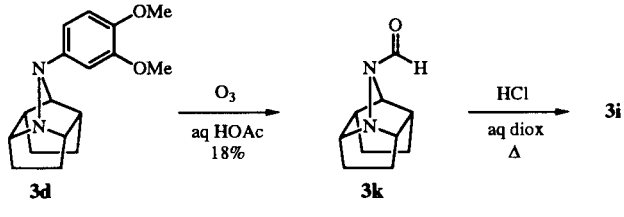


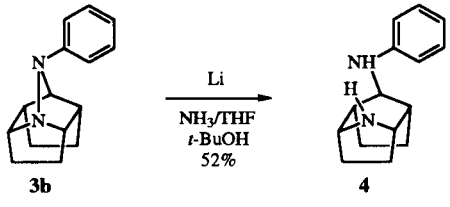
Our first approach to the generation of the parent compound **3i** (R_1 = R_2 = H) involved catalytic hydrogenation of **3a** under several conditions (10% Pd/C [9], Pearlman's catalyst [10]; ammonium formate, 10% Pd/C [11]). However, these debenzylation attempts failed and starting material was recovered. Likewise, attempted cleavage of the *N*-benzyl group in **3a** and the *N*-methyl group in **3e** with 1-chloroethyl chloroformate [12] and 2,2,2-trichloroethyl chloroformate [13] failed, perhaps due to lower basicity of the targeted nitrogen (increased %s character due to ring strain). An attempted benzylic bromination of **3a** and solvolysis protocol [14] gave a complex mixture. Similarly, attempted oxidative cleavage of the 4-methoxyphenyl



group in **3c** with ceric ammonium nitrate [15], hydrogen peroxide-peroxidase [16], and sodium persulfate/silver nitrate [17] was unrewarding. Although **3c** could be smoothly converted into phenol **3j** using the procedure of Feutrill and Mirrington [18,19], attempts to cleave oxidatively the latter compound (DDQ [20], ferric chloride [21], ceric ammonium nitrate [22]) gave complex mixtures. Phenol **3j** could be converted back into **3c** by treatment with sodium hydride/methyl iodide.

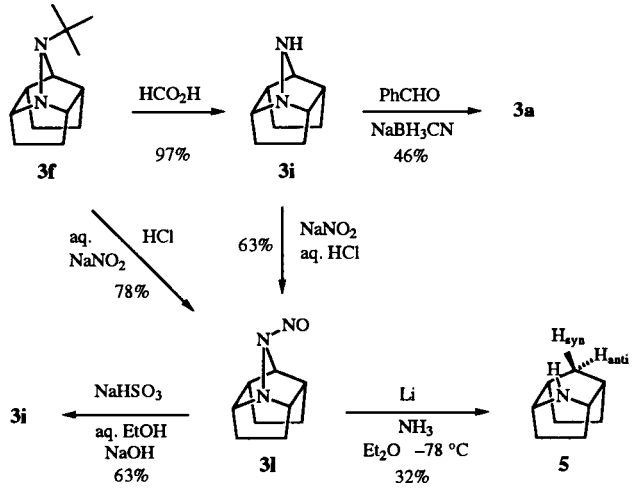
Attempted cleavage of the 3,4-dimethoxyphenyl group in **3d** with ozone [23] and subsequent hydrolysis gave a low yield of the unexpected *N*-formyl derivative **3k**, which could be hydrolyzed to the parent compound **3i**, identical to material prepared later (*vide infra*). Interestingly, Birch reduction conditions [24] on **3b** did not reduce the phenyl ring, but, rather effected cleavage of the hydrazine bond to afford a compound to which we assign structure **4**. Both **3c** and **3j** were resistant to these reaction conditions.





Finally, we examined the *N*-*t*-butyl derivative **3f** as a vehicle for the synthesis of the parent compound **3i**. Indeed, exposure of **3f** to refluxing 90% formic acid led to **3i** in nearly quantitative yield. The structure of this compound is fully supported by spectral and analytical data, and by its conversion to the *N*-benzyl derivative **3a** (benzaldehyde/sodium cyanoborohydride). Moreover, **3i** formed a very stable *N*-nitroso derivative **3l** (63% yield). A one-pot procedure involving the dealkylation of **3f** in concentrated hydrochloric acid, followed by the addition of sodium nitrite afforded **3l** in 78% yield.

Nitrosamine **3l** shows the expected [25] restricted rotation about the *N*-NO bond, and, at room temperature, exists as a 60:40 mixture of *E* and *Z* forms. Heating **3l** in arene solvents leads to slow denitrosation affording **3i** (49% in refluxing mesitylene). Likewise, treatment of **3l** with sodium hydrosulfite, a reagent that is known to reduce *N*-nitroso compounds to diazenes [26] gave **3i** in 63% yield. However, treatment of **3l** with lithium/ammonia yielded the novel cleavage product **5** in modest yield. It is interesting to



note that H_{anti} is strongly shielded (0.61 ppm) in the proton nmr spectrum, presumably as a result of steric compression of H_{syn} by the nitrogen lone pair. Such chemical shift effects have been observed in several oxygen-substituted polycyclic and other systems [27]. A possible mechanism for the formation of **5** involves reduction of **3l** to the diazene and then to the *N*-amino derivative **3** ($R_1 = NH_2$, $R_2 = H$), which suffers fragmentation to a diimide. Loss of nitrogen yields the final product. *N*-Aminohydrazines are notoriously prone to this type of fragmentation [28].

In conclusion, the tandem 1,3-dipolar cycloaddition reaction between sydnones and 1,5-cyclooctadiene is a facile route to the title ring system. We are continuing to explore the chemistry of these polycyclic amines as well as extensions to other systems.

EXPERIMENTAL

General Methods.

Melting points were determined using open capillary tubes with a Büchi 510 melting point apparatus and are reported uncorrected for stem expansion. Infrared (ir) spectra were recorded with a Bio-Rad Digilab FTS-40 Fourier transform ir and are referenced to the 1601 cm^{-1} absorption band of polystyrene. Nuclear magnetic resonance spectra were recorded on a Varian XL-300 multinuclear Fourier transform instrument and are reported in parts per million from tetramethylsilane (TMS) using an internal standard of TMS (δ_H 0.00, δ_C 0.00) or the carbon signal of deuterated chloroform (δ_C 77.0) unless stated otherwise. Mass spectra (ms) were recorded by electron impact ionization on a Hewlett Packard 8451A instrument. Gas chromatography (gc) was performed on a Hewlett Packard 5890 instrument. Combustion analyses were performed by Atlantic Microlabs (Norcross, Alabama). Flash chromatography was performed with EM Reagents Silica Gel 60 (230-400 mesh) unless indicated otherwise. Analytical thin layer chromatography (tlc) was carried out on pre-coated Silica Gel 60 F254 plates from EM Reagents. Visualization was accomplished with 254 nm uv

light or by iodine vapor development. All reactions (except those conducted in an aqueous medium) were performed under a predried (cupric sulfate and potassium hydroxide) nitrogen or argon atmosphere in oven- or flame-dried glassware. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride and dimethylformamide (DMF) were freshly distilled from calcium hydride under nitrogen.

3-Benzylsydnone (**1a**).

A solution of benzylamine (50 ml, 0.46 mole) and ethyl chloroacetate (24 ml, 0.23 mole) in dry benzene (230 ml) was heated at reflux for 5 hours. The white benzylamine hydrochloride precipitate was removed by filtration and the filtrate was concentrated *in vacuo* to afford crude *N*-benzylglycine ethyl ester as a yellow oil (60 g). The crude ester (60 g) was added dropwise with stirring over 20 minutes to a boiling solution of sodium hydroxide (14.7 g, 0.37 mole) in water (75 ml). After continued reflux for 40 minutes the mixture was allowed to cool to rt and acidified to *p*H 2 with concentrated hydrochloric acid. The solution was cooled in an ice bath, and a cold solution of sodium nitrite (12.6 g, 0.18 mole) in water (23 ml) was added dropwise over 30 minutes. The mixture was stirred with cooling for an additional 2 hours and then reacidified to *p*H 2 with concentrated hydrochloric acid. A light yellow solid precipitated and, after overnight refrigeration, was collected by filtration. Vacuum oven drying afforded the crude *N*-nitroso-*N*-benzylglycine (31 g, 71% from ethyl chloroacetate). To an ice cold stirred solution of the crude *N*-nitroso-*N*-benzylglycine (31 g) in ethyl acetate (500 ml) was added *via* syringe trifluoroacetic anhydride (30 ml, 0.21 mole). The mixture was stirred with cooling for an additional 1 hour. A white solid was removed by filtration and the filtrate was washed with saturated aqueous sodium bicarbonate (4 x 100 ml) until the washing was basic. The organic layer was washed with brine (1 x 100 ml), dried (magnesium sulfate) and concentrated *in vacuo* to afford a light yellow viscous oil (21 g). Flash chromatography on silica (ethyl acetate/hexanes (2:1)) gave **1a** (8.5 g, 21% overall) as a white solid, mp 66-68° (lit [7] mp 68-69°); ir (potassium bromide): 3443, 3125, 3010, 1730, 1491, 1453, 1351, 1184, 1066, 937 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.54-7.26 (m, 5 H), 6.18 (s, 1 H), 5.35 (s, 2 H); ^{13}C nmr (deuteriochloroform): δ 169.1, 130.4, 130.1, 129.5, 128.6, 94.6, 57.2; ms: m/e 176 (M$^+$), 147, 92, 91 (100), 89, 65.

3-Phenylsydnone (**1b**).

This was prepared by the procedure of Earl and Mackney [6]. A solution of chloroacetic acid (19.07 g, 201.8 mmoles) in water (40 ml) was neutralized by the addition of 10% aqueous sodium hydroxide (*ca.* 75 ml). To the solution of sodium chloroacetate was added aniline (21 ml, 0.23 mole) and the mixture was heated under reflux for 30 minutes. After cooling to rt, sodium hydroxide pellets (10 g) were added with swirling. The reaction solution was extracted with dichloromethane (2 x 50 ml) and then acidified to *p*H 4 by dropwise addition of concentrated aqueous hydrochloric acid. A light yellow solid precipitated from the solution and was collected by filtration. Vacuum oven drying afforded crude *N*-phenylglycine (22.51 g, 75%). To an ice cold stirred suspension of crude *N*-phenylglycine (21.79 g) in water (240 ml) was added a cold solution of sodium nitrite (11.05 g, 160.1 mmoles) in water (75 ml) dropwise over 25 minutes. The resulting dark green solution was filtered free of solid material, shaken with decolorizing charcoal and filtered again. Concentrated aqueous hydrochloric acid (22 ml) was added with swirling and the mixture was refrigerated overnight. A light brown solid which crystallized from the solution was collected by filtration. Vacuum oven drying afforded the crude *N*-nitroso-*N*-phenylglycine (16.30 g, 63%). A solution of crude *N*-nitroso-*N*-phenylglycine (16.02 g) in acetic anhydride (100 ml) was heated at 100° for 1.5 hours. The solvent was removed under reduced pressure and the resulting solid was recrystallized from benzene to afford **1b** (12.51 g, 41% overall) as a light tan solid, mp 133-134° (lit [6] 134-134.5°): ir (potassium bromide): 3182, 1759, 1470, 1438, 1175, 1088, 948, 852 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.78-7.59 (m, 5 H), 6.79 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 168.9, 134.7, 132.4, 130.2, 121.2, 93.7; ms: m/e 162 (M$^+$), 132, 104, 77, 51.

3-(3,4-Dimethoxyphenyl)sydnone (**1d**).

This was prepared according to the method of Turnbull [5]. A solution of chloroacetic acid (6.17 g, 65.3 mmoles) in water (12 ml) was basified by the addition of 10% aqueous sodium hydroxide solution (24 ml, 66 mmoles). 4-Aminoveratrole (10.0 g, 65.3 mmoles) was added and the resulting suspension was heated at reflux for 2 hours, during the first 60 minutes of which an additional 23 ml of 10% sodium hydroxide (3 x 7 ml, 58 mmoles) was slowly added dropwise. The mixture was allowed to cool to rt and filtered free of a small amount of black solid. The filtrate was extracted with dichloromethane (2 x 30 ml), acidified to *p*H 4 with concentrated hydrochloric acid, and refrigerated overnight. Crude *N*-(3,4-dimethoxyphenyl)glycine, which precipitated from the solution as a light purple-brown solid (8.25 g, 60%), was collected by filtration and vacuum-oven dried. To an ice cold stirred suspension of the crude *N*-(3,4-dimethoxyphenyl)glycine (8.25 g) in 12% aqueous hydrochloric acid (65 ml), was added a solution of sodium nitrite (3.15 g, 45.7 mmoles) in water (12 ml) dropwise over 20 minutes. The mixture was stirred with cooling for an additional 2 hours, after which time dichloromethane (60 ml) was added and stirring was continued for 1 hour. The organic layer was separated and combined with an additional dichloromethane extraction (1 x 60 ml). The organic solution was washed with brine (1 x 30 ml), dried (magnesium sulfate), and concentrated *in vacuo* to afford, as a foamy, bronze solid, crude *N*-nitroso-*N*-(3,4-dimethoxyphenyl)glycine (4.70 g, 30% from 4-aminoveratrole). To an ice cold stirred solution of the crude *N*-nitroso-*N*-(3,4-dimethoxyphenyl)glycine (4.70 g) in dichloromethane (47 ml) was added trifluoroacetic anhydride (4.8 ml, 34 mmoles) *via* syringe over 5 minutes. After 1.5 hours of additional stirring the mixture was neutralized with the cautious addition of a saturated aqueous sodium bicarbonate solution (50 ml). The organic layer was dried (magnesium sulfate), and concentrated *in vacuo* to afford a brown solid. Flash-chromatography on silica gel (ethyl acetate/hexanes (9:1)) gave **1d** (1.70 g, 12% overall) as fluffy, light orange needles, mp 153-155° (lit [5] mp 159-161°): ir (potassium bromide): 3121, 2959, 1748, 1597, 1523, 1428, 1276, 1250, 1017 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.28-7.00 (m, 3 H), 6.71 (s, 1 H), 3.98 (s, 3 H), 3.97 (s, 3 H); ^{13}C nmr (deuteriochloroform): δ 168.9, 152.1, 150.0, 127.7, 113.7, 111.0, 104.3, 93.5, 56.3(2); ms: m/e 207 (M$^+$ -CH_3), 192, 164 (100), 137, 122, 79, 77.

3-Methylsydnone (**1e**).

This was prepared by the method of Hammick and Voaden [3]. To an ice cold stirred solution of *N*-methylglycine (18.12 g,

203.4 mmoles) in water (85 ml) was added a cold solution of sodium nitrite (15.68 g, 227.2 mmoles) in water (30 ml) dropwise over 30 minutes. The reaction mixture was stirred with cooling for an additional 2 hours before acidifying to *p*H 4 with concentrated aqueous hydrochloric acid. The clear yellow solution was concentrated *in vacuo* and the resulting light yellow solid was vacuum oven dried at rt to afford a mixture of unreacted starting material and crude *N*-nitroso-*N*-methylglycine (31.12 g). A solution of the crude *N*-nitroso-*N*-methylglycine (31.12 g) in acetic anhydride (80 ml) was heated at 100° for 5 hours. The dark red-brown suspension was filtered free of white solid and the filtrate was combined with dichloromethane extracts (2 x 10 ml) of the filtercake and water (300 ml). The mixture was swirled vigorously for 10 minutes (to hydrolyze acetic anhydride), basified with the cautious addition of solid sodium carbonate, and extracted with dichloromethane (3 x 50 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a brown oil (7.21 g). Flash chromatography on silica (ethyl acetate) afforded **1e** (6.38 g, 51% overall) as pale yellow oil which solidified upon standing, mp 31.5-33.5° (lit [3] mp 36°); ir (neat): 3149, 2962, 1732, 1465, 1420, 1389, 1201, 1065, 949 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.52 (s, 1 H), 4.12 (s, 3 H); ^{13}C nmr (deuteriochloroform): δ 169.1, 95.8, 39.1.

3-Allylsydnone (**1g**).

To a stirred ice-salt bath cooled solution of allylamine (90 ml, 1.2 moles) in dry diethyl ether (300 ml) was added dropwise over 20 minutes a solution of ethyl bromoacetate (100 g, 0.60 mole) in diethyl ether (100 ml). The addition rate was controlled such that the internal temperature was kept <2°. The reaction mixture was stirred with continued cooling for 3 hours and then allowed to warm to rt overnight. The white allylamine hydrobromide precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The resultant pale yellow oil was distilled under reduced pressure to afford *N*-allylglycine ethyl ester (69 g, 80%) as a colorless oil, bp 90°, *ca.* 25 Torr (lit [4] bp 67°, 20 Torr); ^1H nmr (deuteriochloroform): δ 5.94-5.80 (m, 1 H), 5.23-5.08 (m, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 3.36 (s, 2 H), 3.27 (d, J = 5.9 Hz, 2 H), 1.77 (s, 1 H), 1.28 (t, J = 7.1 Hz, 3 H); ^{13}C nmr (deuteriochloroform): δ 172.2, 135.9, 116.2, 60.4, 51.6, 49.7, 14.0; ms: m/e 143 (M^+), 70 (100), 68, 56. A solution of *N*-allylglycine ethyl ester (60 g, 0.42 mole) in 10% aqueous sodium hydroxide (230 ml, 0.63 mole) was heated at reflux for 5 hour. After acidifying the mixture to *p*H 2 with concentrated aqueous hydrochloric acid and cooling in an ice bath, a cold solution of sodium nitrite (32 g, 0.46 mole) in water (140 ml) was added dropwise with stirring over 15 minutes. The mixture was allowed to warm to rt with continued stirring overnight. The solution was acidified to *p*H 4 with concentrated aqueous hydrochloric acid, saturated with sodium chloride and extracted with ethyl acetate (6 x 175 ml). The combined organic extract was dried (sodium sulfate) and concentrated *in vacuo* to afford crude *N*-nitroso-*N*-allylglycine (45 g, 74%) as a viscous, yellow oil. To an ice cold stirred solution of the crude *N*-nitroso-*N*-allylglycine (45 g) in ethyl acetate (450 ml) was added trifluoroacetic anhydride (45 ml, 0.32 mole) over 20 minutes *via* syringe. The mixture was stirred at 0° for 1 hour and concentrated *in vacuo* to an orange syrup. The crude material was taken up in dichloromethane and washed with a saturated aqueous sodium bicarbonate solution (1 x 300 ml). The organic layer was dried (magnesium sulfate) and concentrated *in vacuo* to afford **1g** (29 g, 44% overall) as a yellow oil. Due to the explosive nature of this sydnone, it is recommended that it not be distilled; ir (neat): 3139, 2991, 1776, 1482, 1438, 1411, 1246, 1188, 939, 721 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.40 (s, 1 H), 6.11-5.96 (m, 1 H), 5.62-5.53 (m, 2 H), 4.91 (d, J = 6.5 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 169.1, 127.5, 123.6, 94.3, 55.4; ms: m/e 126 (M^+, 100), 96, 68.

3-(*t*-Butyl)sydnone (**1f**).

To a stirred ice-salt bath cooled solution of *t*-butylamine (125 ml, 1.19 moles) in dry diethyl ether (300 ml) was added dropwise over 20 minutes a solution of ethyl bromoacetate (100 g, 0.60 mole) in diethyl ether (100 ml). The addition rate was controlled such that the internal temperature was kept <0°. The reaction mixture was stirred with continued cooling for 4 hours and then allowed to warm to rt overnight. The white *t*-butylamine hydrobromide precipitate was removed by filtration and the filtrate was concentrated *in vacuo*. The resultant pale yellow oil was distilled under reduced pressure to afford *N*-(*t*-butyl)glycine ethyl ester (59 g, 61%) as a colorless oil, bp 47°, 2.25 Torr (lit [4] bp 65°, 3 Torr); ^1H nmr (deuteriochloroform): δ 4.19 (q, J = 7.2, 2 H), 3.39 (s, 2 H), 1.44 (broad s, 1 H), 1.28 (t, J = 7.2, 3 H), 1.11 (s, 9 H); ^{13}C nmr (deuteriochloroform): δ 172.8, 60.6, 50.0, 44.7, 28.6, 14.0; ms: m/e 159 (M^+), 144, 116, 86, 70 (100), 57. A solution of *N*-(*t*-butyl)glycine ethyl ester (58 g, 0.36 mole) in 10% aqueous sodium hydroxide (200 ml, 0.55 mole) was heated at reflux for 45 minutes. The mixture was acidified to *p*H 2 with concentrated aqueous hydrochloric acid (ice-bath) and then a cold solution of sodium nitrite (28 g, 0.41 mole) in water (120 ml) was added dropwise with stirring over 15 minutes. The mixture was allowed to warm to rt overnight with stirring. The solution was acidified to *p*H 4 with concentrated aqueous hydrochloric acid, saturated with sodium chloride, and extracted with ethyl acetate (6 x 150 ml). The combined organic extract was dried (sodium sulfate) and concentrated *in vacuo* to afford crude *N*-nitroso-*N*-(*t*-butyl)glycine (24 g, 40%) as a pale yellow solid. To an ice cold stirred solution of the crude *N*-nitroso-*N*-(*t*-butyl)glycine (24 g) in ethyl acetate (200 ml) was added trifluoroacetic anhydride (24 ml, 0.17 mole) over 20 minutes *via* syringe. The mixture was stirred at 0° for 1 hour during which time a white solid precipitated. The mixture was concentrated *in vacuo*, taken up in dichloromethane (200 ml), and washed with saturated aqueous sodium bicarbonate solution (3 x 100 ml). The organic layer was dried (magnesium sulfate) and concentrated *in vacuo* to afford a pale yellow solid. The crude material was swirled in boiling diethyl ether (200 ml) and collected by filtration to give **1f** (17 g, 20% overall) as fine white needles, mp 173-175° (lit [4] mp 168-170°); ir (potassium bromide): 3133, 2993, 1731, 1371, 1243, 1182, 951, 862, 809, 734 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.38 (s, 1 H), 1.70 (s, 9 H); ^{13}C nmr (deuteriochloroform): δ 169.6, 92.0, 65.4, 28.7; ms: m/e 142 (M^+), 87, 69, 57 (100).

Ethyl α-Bromophenylacetate.

This was prepared according to the procedure of Bergmann and Ikan [29]. A solution of ethyl phenylacetate (89 ml, 0.56 mole), *N*-bromosuccinimide (100 g, 0.56 mole), and benzoyl peroxide (0.15 g, 0.62 mmole) in carbon tetrachloride (400 ml) was heated under reflux for 6 hours. The reaction solution was cooled to room temperature and filtered free of succinimide. The filtrate was combined with carbon tetrachloride extracts (2 x 15

ml) of the filtercake and concentrated *in vacuo*. The resultant clear orange oil was distilled under reduced pressure to afford the bromo ester (129 g, 95%) as a pale orange oil, bp 110°, 0.45 Torr (lit [29] bp 117°, 0.8 Torr); ^{1}H nmr (deuteriochloroform): δ 7.57-7.32 (m, 5 H), 5.34 (s, 1 H), 4.36-4.09 (m, 2 H), 1.27 (t, 3 H); ^{13}C nmr (deuteriochloroform): δ 168.2, 135.8, 129.2, 128.7, 126.6, 62.4, 45.8, 13.7.

3-(*t*-Butyl)-4-phenylsydnone (**1h**).

A solution of *t*-butylamine (3.5 ml, 33 mmoles) and ethyl α-bromophenylacetate (4.0 g, 16 mmoles) in dry THF (10 ml) was heated under reflux for 13 hours. The white *t*-butylamine hydrobromide precipitate was removed by filtration and the filtrate was combined with diethyl ether extracts (3 x 2 ml) of the filtercake and concentrated *in vacuo*. The resultant colorless oil was purified by bulb-to-bulb distillation (140°, 1.0 Torr) to afford *N*-(*t*-butyl)-2-phenylglycine ethyl ester (3.1 g, 81%) as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 7.43-7.19 (m, 5 H), 4.45 (s, 1 H), 4.22-4.05 (m, 2 H), 2.12 (broad s, 1 H), 1.20 (t, 3 H), 1.11 (s, 9 H); ^{13}C nmr (deuteriochloroform): δ 175.0, 140.5, 128.4, 127.4, 127.1, 61.0, 59.7, 51.2, 29.4, 14.0. A solution of *N*-(t-butyl)-2-phenylglycine ethyl ester (3.1 g, 13 mmoles) in 10% aqueous sodium hydroxide (6.9 ml, 19 mmoles) was heated at reflux for 70 minutes, after which time the reaction mixture was homogeneous. The mixture was diluted with water (5 ml), acidified to *p*H 2 with concentrated aqueous hydrochloric acid, and cooled in an ice bath. A cold solution of sodium nitrite (0.97 g, 14 mmoles) in water (4 ml) was added dropwise with stirring over 30 minutes. The solution was stirred for an additional 3 hours during which time a cream-colored precipitate formed. The solid was collected by filtration and vacuum oven dried to afford crude *N*-nitroso-*N*-(*t*-butyl)-2-phenylglycine ethyl ester (2.1 g, 60%). To an ice cold stirred suspension of the crude *N*-nitroso-*N*-(*t*-butyl)-2-phenylglycine ethyl ester (2.0 g, 7.4 mmoles) in dichloromethane (20 ml) was added trifluoroacetic anhydride (2.0 ml, 14 mmoles) over 20 minutes *via* syringe. The mixture was stirred at 0° for 2 hours. After this time, the solution was diluted with dichloromethane (10 ml) and washed with saturated aqueous sodium bicarbonate solution (3 x 10 ml) and brine (1 x 10 ml). The organic layer was dried (magnesium sulfate) and concentrated *in vacuo* to afford a clear orange oil. Tituration of the crude material with diethyl ether (5 ml) afforded **1h** (0.11 g, 7%) as a white solid which was collected by filtration and air dried. Flash chromatography of the filtrate on silica (ethyl acetate/hexanes (1:1)) gave additional product (0.02 g, 1%). The analytical sample was crystallized from diethyl ether, mp 122-123°; ir (potassium bromide): 3067, 3000, 1749, 1514, 1306, 1195, 988, 780, 706 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.50-7.27 (m, 5 H), 1.60 (s, 9 H); ^{13}C nmr (deuteriochloroform): δ 159.8, 139.6, 132.2, 130.1, 129.0, 126.3, 68.5, 29.2.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.28; H, 6.56; N, 12.87.

10-Benzyl-9,10-diazatetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3a**).

This was prepared according to the method of Weintraub [1]. A solution of **1a** (1.50 g, 8.53 mmoles) in excess 1,5-cyclooctadiene (17 ml) was heated at 150°C for 42 hours. The reaction mixture was cooled to rt, diluted with diethyl ether (17 ml), and extracted with 5% aqueous hydrochloric acid (3 x 12 ml). The combined aqueous extract was washed with diethyl ether (2 x 12 ml), basified slowly with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 15 ml). The combined organic extract was dried (sodium sulfate) and concentrated *in vacuo* to afford a golden oil (1.10 g). Bulb-to-bulb distillation (200°, 0.15 Torr) furnished **3a** (0.873 g, 43%) as a colorless oil; ir (neat): 3026, 2948, 1495, 1453, 1226, 962, 844, 733, 713 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.42-7.21 (m, 5 H), 3.75 (broad s, 2 H), 3.61 (t, J = 4.2 Hz, 2 H), 3.56-3.49 (m, 2 H), 2.39-2.31 (m, 2 H), 1.88-1.54 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 138.6, 128.6, 128.1, 126.8, 71.3, 64.0, 55.9, 42.5, 22.8, 21.6; ms: m/e 240 (M$^+$), 171, 149, 91 (100), 79, 65.

9,10-Diaza-10-phenyltetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3b**).

This was prepared according to the method of Weintraub [1]. A solution of **1b** (5.00 g, 30.8 mmoles) in 1,5-cyclooctadiene (50 ml) was heated at 150° for 52 hours. The reaction mixture was cooled to rt, diluted with diethyl ether (50 ml), and extracted with 5% aqueous hydrochloric acid (3 x 35 ml). The combined aqueous extract was washed with diethyl ether (3 x 35 ml), basified slowly with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 45 ml). The combined organic extract was dried (sodium sulfate) and concentrated *in vacuo* to afford a brown oil (5.88 g) which solidified upon standing. Flash chromatography on silica (ethyl acetate/hexanes (3:7)) furnished **3b** (5.63 g, 81%) as a light tan solid, mp 77-79° (lit [1b] mp 81-82°): ir (potassium bromide): 3182, 1759, 1470, 1438, 1175, 1088, 948, 853 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.31-6.77 (m, 5 H), 4.43 (t, J = 4.2 Hz, 1 H), 3.50-3.40 (m, 2 H), 2.38-2.26 (m, 2 H), 1.94-1.55 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 148.3, 128.8, 120.3, 116.2, 70.3, 64.4, 43.5, 23.0, 21.8; ms: m/e 226 (M$^+$, 100), 157, 145, 133, 93, 91, 77.

9,10-Diaza-10-(4-methoxyphenyl)tetracyclo[6.3.0.0.^{4,11}0^{5,9}]-undecane (**3c**).

This was prepared according to the method of Weintraub [1]. A solution of **1c** (5.64 g, 30.8 mmoles) in 1,5-cyclooctadiene (50 ml) was heated at 150° for 40 hours. The reaction mixture was cooled to rt, diluted with diethyl ether (50 ml), and extracted with 5% aqueous hydrochloric acid (3 x 35 ml). The combined aqueous extract was washed with diethyl ether (3 x 35 ml), basified slowly with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 45 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a tan solid (6.35 g). Recrystallization from ethanol/hexanes afforded **3c** (5.28 g, 70%) as glistening beige plates, mp 103.5-105° (lit [1b] mp 99-103°); ir (potassium bromide): 3060, 2951, 2827, 1505, 1245, 1037, 834, 690 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 6.94 (m, 4 H), 4.38 (t, J = 4.1 Hz, 1 H), 3.75 (s, 3 H), 3.48-3.42 (m, 2 H), 2.37-2.29 (m, 2 H), 1.92-1.63 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 153.8, 142.1, 117.4, 114.1, 70.8, 64.4, 55.4, 43.4, 23.0, 21.8; ms: m/e 256 (M$^+$, 100), 187, 163, 135, 121, 107, 93, 77.

9,10-Diaza-10-(4-hydroxyphenyl)tetracyclo[6.3.0.0.^{4,11}0.^{5,9}]-undecane (**3j**).

To a stirred suspension of sodium hydride (60% w/w dispersion in mineral oil, pentane washed; 1.45 g, 36.2 mmoles) in dry DMF (25 ml) was added ethanethiol (2.7 ml, 36 mmoles) dropwise *via* syringe. A solution of **3c** (0.929 g, 3.62 mmoles) in DMF (10 ml) was added. The reaction mixture was refluxed for 3 hours, cooled to rt and neutralized by the addition of 10% aqueous hydrochloric acid. The resulting suspension was diluted with water (10 ml) and

extracted with dichloromethane (4 x 15 ml). The combined extract was washed with brine (1 x 20 ml) and concentrated *in vacuo* to afford a tan solid. The crude product was sublimed (200°, 0.1 Torr) to give **3j** (0.761 g, 90%) as an off-white solid, mp 235-237° dec. The analytical sample was crystallized from ethanol, mp 252.5-254° dec; ir (potassium bromide): 3096, 2947, 2884, 1509, 1456, 1261, 1223, 836 cm^{-1}; ^1H nmr (DMF-d_7): δ 8.95 (s, 1 H), 6.86 (m, 4 H), 4.48 (t, J = 3.8 Hz, 1 H), 3.34-3.27 (m, 2 H), 2.25-2.18 (m, 2 H), 1.75-1.60 (m, 8 H); ^{13}C nmr (DMF-d_7): δ 152.1, 142.0, 117.7, 116.0, 71.0, 64.7, 44.1, 23.3, 22.2; ms: m/e 242 (M^+, 100), 173, 149, 121, 93, 79, 65.

Anal. Calcd. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.24; H, 7.52; N, 11.50.

9,10-Diaza-10-(4-methoxyphenyl)tetracyclo[6.3.0.0.^{4,11}0.^{5,9}]-undecane (**3c**) from 9,10-Diaza-10-(4-hydroxyphenyl)tetracyclo-[6.3.0.0.^{4,11}0.^{5,9}]undecane (**3j**).

To an ice cold, stirred suspension of sodium hydride (60% w/w dispersion in mineral oil, pentane washed; 0.044 g, 1.13 mmoles) in dry DMF (3 ml) was added, *via* syringe, a solution of **3j** (0.174 g, 0.718 mmoles) in DMF (6 ml, delivered in 4 and 2 ml portions). The solution was allowed to warm to rt over 1 hour and then cooled to -40°. Iodomethane (76 ml, 1.2 mmoles) was added *via* syringe and the reaction temperature was kept at -30° for 30 minutes. After allowing to warm to rt, the mixture was concentrated *in vacuo* and taken up in 5% aqueous hydrochloric acid (15 ml). The aqueous solution was washed with diethyl ether (3 x 5 ml), basified with concentrated aqueous ammonium hydroxide and extracted with dichloromethane (4 x 5 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford an off-white solid. Flash chromatography on silica (ethyl acetate) gave **3c** (0.042 g, 23%) as a white solid, mp 103.5-104.5° (lit [1b] mp 99-103°). Spectral data and R_f value were identical to those of **3c** prepared from the corresponding sydnone **1c**.

9,10-Diaza-10-(3,4-dimethoxyphenyl)tetracyclo[6.3.0.0.^{4,11}0.^{5,9}]-undecane (**3d**).

This was prepared according to the method of Weintraub [1]. A solution of **1d** (0.224 g, 1.01 mmoles) in 1,5-cyclooctadiene (3 ml) was heated at 150° for 26 hours. The reaction solution was cooled to rt, diluted with diethyl ether (7 ml), and extracted with 5% aqueous hydrochloric acid (3 x 5 ml). The combined aqueous extract was washed with diethyl ether (3 x 5 ml), basified slowly with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 6 ml). The combined organic extract was dried (sodium sulfate) and concentrated *in vacuo* to afford a golden oil (0.248 g). Flash chromatography on silica (ethyl acetate/hexanes (7:3, 9:1)) gave **3d** (0.215 g, 74%) as an extremely viscous, light gold oil; ir (neat): 3054, 2951, 2827, 1609, 1591, 1506, 1452, 1233, 1026, 848 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.87-6.55 (m, 3 H), 4.39 (t, J = 4.2 Hz, 1 H), 3.88 (s, 3 H), 3.82 (s, 3 H), 3.49-3.42 (m, 2 H), 2.37-2.30 (m, 2 H), 1.92-1.62 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 149.2, 143.0, 142.6, 111.6, 107.0, 101.6, 70.6, 64.3, 56.0, 55.8, 43.3, 22.8, 21.6; ms: m/e 286 (M^+, 100), 271, 219, 152, 137, 93, 79. The picrate was made by treating an ethereal solution of **3d** with a saturated ethanolic solution of picric acid. Recrystallization of the resulting precipitate from ethanol afforded the picrate as a yellow solid, mp 176-178°.

Anal. Calcd. for $C_{23}H_{25}N_5O_9$: C, 53.59; H, 4.89; N, 13.59. Found: C, 53.61; H, 4.91; N, 13.53.

9,10-Diaza-10-formyltetracyclo[6.3.0.0.^{4,11}0.^{5,9}]undecane (**3k**).

Through a solution of **3d** (0.362 g, 1.26 mmoles) in acetic acid (10 ml) and water (5 drops) ozone was passed for 22 minutes. The solution was poured into water (10 ml), basified with the slow addition of concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 10 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a light brown oil. Flash chromatography on silica (ethyl acetate, ethyl acetate/methanol (19:1)) gave, as the only appreciable component of the crude mixture, **3k** (0.041 g, 18%) as an off-white solid, mp 95-98°: ir (potassium bromide): 2956, 2884, 1658, 1426, 1359, 1189, 1154, 961, 851, 764 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.37 (s, 1 H), 4.80 (t, J = 4.2 Hz, 1 H), 3.41-3.34 (m, 2 H), 2.43-2.34 (m, 2 H), 1.94-1.61 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 158.7, 66.0, 60.9, 43.8, 22.8, 21.8; ms: m/e 178 (M^+), 150, 136, 111 (100), 93, 81, 67, 54.

9,10-Diaza-10-methyltetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3e**).

This was prepared according to the method of Weintraub [1]. A solution of **1e** (6.69 g, 66.8 mmoles) in 1,5-cyclooctadiene (50 ml) was heated at 150° for 90 hours. The reaction mixture was cooled to rt, diluted with diethyl ether (50 ml), and extracted with 5% aqueous hydrochloric acid (3 x 35 ml). The combined aqueous extract was washed with diethyl ether (3 x 35 ml), basified slowly with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (3 x 40 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a dark brown oil (4.71 g). Flash chromatography on silica (dichloromethane/methanol (4:1)) followed by bulb-to-bulb distillation (100-110°, 0.25 Torr) furnished **3e** (2.39 g, 22%) as a colorless oil; ir (neat): 2949, 1678, 1482, 1461, 1263, 1146, 1117, 1043, 840 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.66 (t, J = 4.2 Hz, 1 H), 3.54-3.36 (m, 2 H), 2.51 (s, 3 H), 2.40-2.32 (m, 2 H), 1.87-1.54 (m, 8 H); ^{13}C nmr (DMSO-d_6, 80°): δ 73.6, 73.4, 62.7, 42.1, 37.6, 22.0, 20.9; ms: m/e 164 (M^+), 109, 98, 95 (100), 93, 83, 67. The picrate was made by treating an ethereal solution of **3e** with a saturated ethanolic solution of picric acid. Recrystallization of the resulting precipitate from ethanol afforded the picrate as a yellow solid, mp 257.5-258°.

Anal. Calcd. for $C_{16}H_{19}N_5O_7$: C, 48.85; H, 4.87; N, 17.80. Found: C, 48.97; H, 4.86; N, 17.85.

10-(*t*-Butyl)-9,10-diazatetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3f**).

This was prepared according to the method of Weintraub [1]. A solution of **1f** (7.00 g, 49.2 mmoles) in 1,5-cyclooctadiene (170 ml) was heated at 150° for 20 days. The reaction solution was cooled to rt and starting material, which crystallized as white needles, was collected by filtration, washed with hexane (3 x 5 ml) and vacuum-oven dried (recovered yield, 1.69 g, 24%). The reaction mixture was combined with the hexane extracts, diluted with diethyl ether (150 ml), and extracted with 5% aqueous hydrochloric acid (3 x 100 ml). The combined aqueous extract was washed with diethyl ether (3 x 100 ml), basified with concentrated aqueous ammonium hydroxide, and extracted with diethyl ether (3 x 100 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a tacky, light-orange solid (4.80 g, 62% based on **1f** consumed). A portion of the crude material was purified by bulb-to-bulb distillation (110°, 0.1 Torr) followed by flash

chromatography on silica gel (ethyl acetate/THF (3:1)) to give **3f** as a white solid, 55.5-57°; ir (potassium bromide): 2969, 2867, 1483, 1387, 1360, 1263, 1231, 855, 840, 652 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.88 (t, J = 3.9 Hz, 1 H), 3.34-3.27 (m, 2 H), 2.28-2.20 (m, 2 H), 1.86-1.50 (m, 8 H), 1.19 (s, 9 H); ^{13}C nmr (deuteriochloroform): δ 167.3, 66.4, 53.7, 44.9, 29.1, 22.9, 21.6; ms: m/e 206 (M$^+$), 191 (100), 149, 93, 81, 67, 57.

Anal. Calcd. for $C_{13}H_{22}N_2$: C, 75.67; H, 10.75; N, 13.58. Found: C, 75.48; H, 10.73; N, 13.53.

9,10-Diazatetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3i**).

A solution of **3f** (0.227 g, 0.110 mmole) in 90% formic acid (3 ml) was heated at reflux for 3 hours. The mixture was allowed to cool to rt, diluted with water (10 ml), and made basic (*p*H 9-10) with the slow addition of concentrated aqueous ammonium hydroxide. The cloudy solution was extracted with dichloromethane (4 x 6 ml) and the combined extract was dried and concentrated *in vacuo* to afford **3i** (0.160 g, 97%) as a tacky, off-white residue; ir (neat): 3209, 2950, 2874, 1677, 1486, 1145, 965, 942, 844 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.97 (t, J = 4.1 Hz, 1 H), 3.25-3.16 (m, 2 H), 3.04 (broad s, 1 H), 2.20-2.12 (m, 2 H), 1.93-1.54 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 68.8, 67.2, 44.4, 23.5, 22.6; ms: m/e 150 (M$^+$), 93, 84 (100), 81, 69, 67, 54. A hydrochloride was made by bubbling hydrogen chloride gas through a solution of **3i** in benzene. The resulting precipitate was recrystallized from ethanol to afford a white solid, mp 254-256° dec.

Anal. Calcd. for $C_9H_{15}ClN_2$: C, 57.90; H, 8.10; N, 15.01. Found: C, 57.80; H, 8.13; N, 14.96.

10-Benzyl-9,10-diazatetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3a**) from 9,10-Diazatetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane (**3i**).

To a stirred solution of freshly prepared **3i** (0.111 g, 0.739 mmole) in 1:1 methanol/benzaldehyde (4 ml) was added sodium cyanoborohydride (0.227 g, 3.61 mmoles). After 2 hours the reaction solution was partitioned between equal amounts (5 ml) of 5% aqueous hydrochloric acid and ethyl acetate. The aqueous layer was separated and combined with a second 5% hydrochloric acid extract (5 ml). The aqueous solution was basified with concentrated aqueous ammonium hydroxide and extracted with dichloromethane (3 x 5 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a colorless oil. Flash chromatography on silica gel(ethyl acetate/methanol (19:1)) gave **3a** (0.081 g, 46% from the *t*-butyl derivative, **3i**) as a colorless oil. The spectral properties, including mass spectra and tlc, were identical with an authentic sample prepared from the corresponding sydnone **1a** as described above.

9,10-Diaza-10-nitrosotetracyclo[6.3.0.0.^{4,11}0.^{5,9}]undecane (**3l**).

A solution of **3f** in 12% hydrochloric acid (15 ml) was heated in a water bath (90-95°) with stirring for 15 minutes. The mixture was cooled to 0° in an ice bath and a solution of sodium nitrite (0.665 g, 9.64 mmoles) in water (2 ml) was added dropwise over 40 minutes. A yellow solid precipitated from the reaction solution which was stirred with cooling for an additional 4 hours. The suspension was diluted with water (10 ml), basified with concentrated aqueous ammonium hydroxide, and extracted with dichloromethane (4 x 8 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford crude product as a yellow solid (1.65 g). Flash chromatography on silica gel (1:1 ethyl acetate/hexanes) afforded **3l** (1.25 g, 78% from **3f**) as a 6:4 mixture of rotamers, mp 168-171°. The analytical sample was obtained from ethanol as bright yellow plates, mp 170-172°; ir (potassium bromide): 3028, 2967, 1484, 1416, 1316, 1291, 1180, 849 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 5.24 (s, 1 H), 5.15 (s, 1 H'), 3.70-3.63 (m, 2 H'), 3.54-3.46 (m, 2 H), 2.63-2.55 (m, 2 H), 2.45-2.37 (m, 2 H'), 2.06-1.72 (m, 8 H + 8 H'); ^{13}C nmr (deuteriochloroform): δ 67.6, 66.6, 65.8, 60.5, 44.2, 42.5, 22.8, 22.6, 21.8, 21.4; ms: (CI) m/e 179 (M$^+$), 151, 137, 121, 69, 57 (100), 55.

Anal. Calcd. for $C_9H_{13}N_3O$: C, 60.32; H, 7.31; N, 23.45. Found: C, 60.43; H, 7.35; N, 23.35.

9-Aza-10-(phenylamino)tricyclo[4.2.1.1^{2,5}]decane (**4**).

To a stirred and cooled (-78°) solution of **3b** (0.500 g, 2.21 mmoles) in ammonia (20 ml) and dry THF (10 ml) was added, in order, lithium (0.080 g, 11.5 mmoles) and *t*-butanol (2 ml). The deep blue reaction mixture was stirred for 1.5 hours before quenching with several drops of water, and then allowing the ammonia to evaporate. The resulting suspension was taken up in 5% aqueous hydrochloric acid (30 ml) and washed with diethyl ether (3 x 10 ml). The aqueous layer was basified with concentrated aqueous ammonium hydroxide, and then extracted with dichloromethane (3 x 12 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a viscous, brown oil (0.351 g). Chromatography on activity 3 basic alumina (dichloromethane/methanol (99:1, 98:2)) afforded **4** (0.266 g, 52%) as a pale yellow oil; ir (neat): 3312, 2949, 1601, 1501, 1370, 1304, 1158, 1015, 856 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.18-6.60 (m, 5 H), 3.65-3.57 (m, 2 H), 3.11 (t, J = 2.8 Hz, 1 H), 2.45-2.37 (m, 2 H), 1.94-1.22 (m, 8 H); ^{13}C nmr (deuteriochloroform): δ 148.6, 129.0, 116.5, 113.5, 56.4, 55.8, 39.2, 22.4, 24.1; ms: m/e 228 (M$^+$), 160, 138, 132 (100), 93, 77. The hydrochloride was made by bubbling hydrogen chloride gas through a solution of **4** in benzene. Recrystallization from 2-propanol afforded the analytical sample as an off-white solid, mp 252-253° dec.

Anal. Calcd. for $C_{15}H_{21}N_2Cl$: C, 68.04; H, 7.99; N, 10.58. Found: C, 68.07; H, 8.06; N, 10.58.

9-Azatricyclo[4.2.1.1^{2,5}]decane (**5**).

To a stirred and cooled (-78°) solution of **3l** (0.500 g, 2.79 mmoles) in ammonia (25 ml) and dry diethyl ether (13 ml) was added lithium (0.080 g, 11.5 mmoles) under a blanket of nitrogen. The deep blue reaction mixture was stirred for 1.5 hours before allowing the ammonia to evaporate. The resulting suspension was taken up in 5% aqueous hydrochloric acid (20 ml) and washed with diethyl ether (3 x 7 ml). The aqueous layer was basified with concentrated aqueous ammonium hydroxide and then extracted with dichloromethane (3 x 8 ml). The combined organic extract was dried (magnesium sulfate) and concentrated *in vacuo* to afford a tacky, off-white residue (0.257 g). Chromatography on activity 3 basic alumina (dichloromethane/methanol (19:1)) afforded **5** (0.126 g, 32%) as a light brown residue; ir (neat): 3253, 3006, 2870, 1633, 1458, 1146, 1041, 881 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.61-3.54 (m, 2 H), 3.27 (broad s, 1 H), 2.41-2.33 (m, 2 H), 1.95-1.23 (m, 10 H), 0.61 (dt, J = 11.3, 2.4 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 55.1, 36.8, 27.4, 25.3, 24.7; ms: m/e 137 (M$^+$), 108, 96, 80, 70, 68. A hydrochloride was made by bubbling hydrogen chloride gas through a solution of **5** in benzene. Recrystallization from hexanes/ethanol afforded the analytical sample as an off-white solid, mp >300° dec.

Anal. Calcd. for $C_9H_{16}NCl$: C, 62.24; H, 9.29; N, 8.06. Found: C, 62.02; H, 9.22; N, 8.02.

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