73.78; H, 9.42; N, 7.70.

The acetyl derivative **11b** was identified by comparison of its IR spectrum and R_f values on TLC with the sample prepared from **9** and acetyl chloride. Treatment of **9** with acetic anhydride in CH_2Cl_2 in the presence of a catalytic amount of sulfuric acid also gave **11b** (37%).

4,5-Dimethyl-4-azahomoadamant-4-enium Iodide (18a). A mixture of **9** (81 mg, 0.50 mmol) and methyl iodide (1.14 g, 8.0 mmol) in chloroform (3 mL) was heated under reflux for 1 day. Removal of the solvent and excess methyl iodide gave a brownish solid which was washed with acetone to afford **18a** as a colorless solid (130 mg, 85.5%): mp 277–280 °C dec; IR (KBr) 2920, 2850, 1660, 1450, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (broad s, 1 H), 3.90 (s, 3 H), 3.19 (broad s, 1 H), 2.87 (s, 3 H), and 2.55–1.81 (m, 12 H).

Anal. Calcd for $C_{12}H_{20}NI$: C, 47.23; H, 6.61; N, 4.59. Found: C, 47.22; H, 6.32; N, 4.62.

The methiodide **18a** was also obtained in 65.5% overall yield from **8** (450 mg, 2.70 mmol) without isolation of **9** by the same procedure.

4-Methyl-5-methylene-4-azahomoadamantane (19) and 4,5-Dimethyl-4-azahomoadamant-4-enium Perchlorate (18b). A solution of **18a** (305 mg, 1.00 mmol) in methanol (10 mL) was poured onto ice-cooled 10% aqueous NaOH (60 mL), and the mixture was extracted with ether (15 mL × 4). The combined extracts were dried (Na_2SO_4–K_2CO_3), and removal of the solvent gave an oil which was purified by Kugelrohr distillation (120 °C, 0.2 mm) to afford the enamine **19** as a colorless oil (142 mg, 80.0%). **19** turned to a yellowish oil rapidly in the air: $n^{19}D$ 1.5487; IR (film) 3120, 2920, 2840, 1600, 1440, 1400, 1300, 1030, and 750 cm^{-1}; ^1H and ^{13}C NMR, see text and Table I.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.50; H, 10.57; N, 7.93.

To a solution of **19** (78 mg, 0.44 mmol) in methanol (2 mL) and ether (10 mL) was added 70% aqueous perchloric acid (0.1 mL) to afford a colorless precipitate which was filtered off and washed with ether to give **18b** (122 mg, 100%): mp >300 °C; IR (KBr) 2920, 2870, 1667, 1450, and 1090 cm^{-1}; ^1H NMR [$CDCl_3$–D_2O–$(CD_3)_2SO$] δ 4.18 (broad s, 1 H), 3.70 (s, 3 H), 3.22 (s, 3 H), 3.4–3.0 (broad m, 1 H), and 2.75–1.50 (m, 12 H).

Anal. Calcd for $C_{12}H_{20}NO_4Cl$: C, 51.89; H, 7.26; N, 5.04. Found: C, 52.12; H, 7.01; N, 4.93.

Registry No.—**8,** 702-98-7; **9,** 65218-97-5; **11a,** 67180-43-2; **11b,** 67180-44-3; **11c,** 67180-45-4; **12** HCl, 65219-01-4; **13,** 67180-48-7; **16,** 67180-46-5; **17,** 67180-49-8; **18a,** 67180-50-1; **18b,** 67180-52-3; **19,** 67180-47-6; dichloroacetyl chloride, 79-36-7; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7.

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(18) See ref 15 in Part 41: T. Sasaki, S. Eguchi, and T. Hioki, *J. Org. Chem.,* companion paper in this issue.
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Methano-Bridged 10π-Electron Aromatic Annulenes. 4-Methoxy-1,6-methanoisoquinoline

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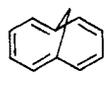
The synthesis of 4-methoxy-1,6-methanoisoquinoline (**2b**), a 10π-electron heterocyclic methano-bridged system, is described. The ring skeleton is generated via a Beckmann rearrangement of tricyclo[4.3.1.$0^{1,6}$]-2,4-decadien-8-one oxime (**3**). Aromatization of the resulting lactam is accomplished by introduction of a methylthio group, its oxidation to a sulfone, amide *O*-methylation, and elimination of methanesulfinic acid. Compound **2b** shows ^1H NMR chemical shifts indicative of a 10π-electron delocalized system.

There have been several examples of aromatic 10π- and 14π-electron methano-bridged systems since the synthesis of 1,6-methano[10]annulene[1] (**1**) but very few have been heterocyclic in nature.[2] Our present concern is with methano-bridged counterparts of indole, quinoline, isoquinoline, carbazole, and similar species from the viewpoint of aromaticity studies and modification of physiological activity in drugs containing such skeletons.



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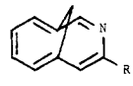
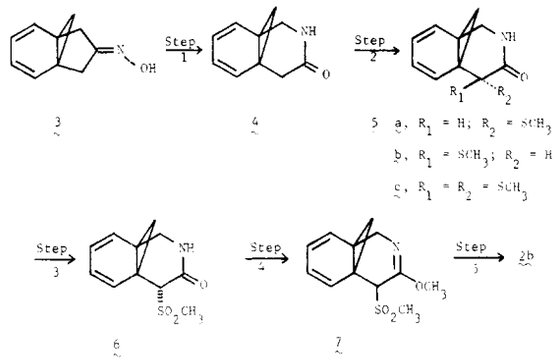


2 (a, R = H; b, R = OCH_3)

The skeletal unit of interest in this work is 1,6-methanoisoquinoline (**2a**), and the synthesis of one of its derivatives, 4-methoxy-1,6-methanoisoquinoline (**2b**) is described.

0022-3263/78/1943-3813$01.00/0

Scheme I



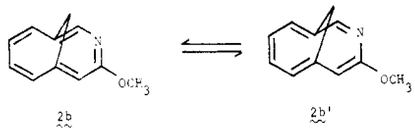
Entry into the 1,6-methanoisoquinoline skeleton (Scheme I) was accomplished via the known oxime of tricyclo[4.3.1.0^{1,6}]-2,4-decadien-8-one[7] (**3**). The sequence involved ring expansion (step 1), substitution (step 2), sulfur oxidation (step 3), *O*-alkylation (step 4), and elimination (step 5).

Two aspects of the structure of **2b** are indicated by its ^{1}H NMR spectrum. The methylene protons at δ −0.05 (d, J = 9.5 Hz) and 0.45 (dd, J = 9.5 Hz, J' = 1.8 Hz) indicate an open-ring structure because of the magnitude of the geminal coupling constant ($J_{\text{cyclopropane}} \approx 5$ Hz). Also, chemical shifts reflect the presence of a diamagnetic ring current, for they span a region between aromatic and vinyl protons (δ 5.94–7.44 for the protons on sp^2 carbons). Finally, the constancy of the ^{1}H NMR spectrum with temperature suggests that there is no bond equilibration between potential structures **2b** and **2b'**, in accord with what might be expected from reported conjugational relationships involving reactions of methyl imidate functionalities.[8]

Discussion

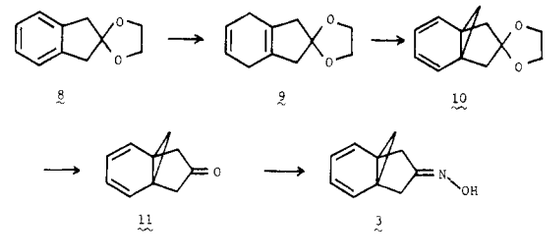
The typical synthetic route to a number of methano-bridged systems utilized a procedure of Birch reduction of the parent aromatic system, cyclopropanation of the tetrasubstituted double bond, and rearomatization directly (oxidative dehydrogenation) or indirectly (substitution–elimination). Such was the case in the conversion of naphthalene to **1**.[1] This type of procedure was not applicable to the preparation of a methano-bridged isoquinoline because Birch reduction of isoquinoline leads to 1,2,3,4-tetrahydroisoquinoline only.[9] Although further reduction might provide a tetrasubstituted double bond, considerable problems were expected from the saturated heterocyclic ring.

These problems led to the consideration of oxime **3** as a target for entry into the 1,6-methanoisoquinoline skeleton, for a Beckmann rearrangement of **3** or one of its derivatives would lead to the correct placement of nitrogen in the ring skeleton. Further transformations would lead to either **2a** or **2b**.



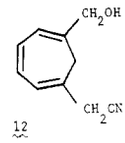
The synthesis of oxime **3** (Scheme II) was carried out with rather extensive modifications of the procedure employed by Vogel.[7] The ethylene ketal of 2-indanone[10] (**8**) was reduced by lithium and isopropyl alcohol in liquid ammonia to 4,7-dihydro-2-indanone ethylene ketal (**9**) in 84% yield. Instead of cyclopropanation via a dichlorocarbene, better yields were obtained with the Simmons–Smith reagent. The nucleophilic tetrasubstituted double bond was expected to show more selectivity toward the reagent, and the ketal oxygens would provide an added directive effect.[11] In this manner, when **9** was treated with a Zn–Cu couple[12] and methylene iodide at

Scheme II

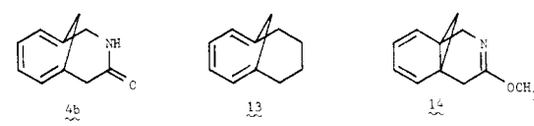


45 °C for 24 h, approximately 50% of cyclopropanation resulted. Longer reaction times usually led to resinification. Such problems were circumvented by the use of a Zn–Ag couple,[13] so that cyclopropanation was complete after 3 h at 45 °C with a yield of 70% of **10**. In this way, no exo or bis product was detectable by ^{1}H NMR. The remainder of the conversion was essentially that described by Vogel,[7] without isolation and characterization of the dibromide addition intermediate or purification of the diene ketal.

Initial attempts to employ acidic conditions for the Beckmann rearrangement of **3** to **4** resulted in very low lactam yields and/or extensive decomposition of the starting material. Solvolytic rearrangement to **4** proceeded in 60% yield when the benzenesulfonate ester of oxime **3** was refluxed with aqueous tetrahydrofuran. The abnormal Beckmann rearrangement product, nitrile alcohol **12** (22% yield), as well as diene ketone **11** (12% yield) were obtained as side products of the reaction.

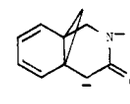


It is interesting to note that the proton geminal coupling constant of the methylene bridge (J = 4.5 Hz) indicated that lactam **4** exists as the norcaradiene rather than the cycloheptatriene (**4b**), even though earlier work[14] had shown that the latter was the preferred form for a hydrocarbon ring system (**13**) of the same size.



Lactam **4** can be considered to be a dihydromethano-bridged aromatic species. This is more clearly shown for its imino ether, **14**, which was made in 94% yield by alkylating **4** with trimethyloxonium fluorborate in the presence of potassium carbonate. Even though **4** and **14** were oxidatively close to the fully aromatic product, no apparent aromatization occurred with reagents such as chloranil, dichlorocyanoquinone, palladium on charcoal, platinum black, trityl fluoroborate, selenium, manganese dioxide, or *N*-lithioethylenediamine. It was clear that a less direct dehydrogenation was needed.

Generation of intermediates suitable for elimination reactions through a monoanion of **4** was also unproductive, but the dianion of **4** showed promise of practicality. Thus, when **4** was treated with an excess of lithiodiisopropylamide or *n*-butyllithium, dianion **15** was formed.



Quenching of **15** with bromine led to extensive decomposition of starting material. The use of disulfides, as described by Trost[15] for quenching enolates of esters and ketones, pro-

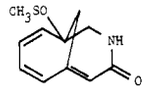
duced stable species that proved to be practical for later elimination. Significant time and concentration dependencies were noted for this reaction, and it was observed that dimethyl disulfide but not diphenyl disulfide was an effective sulfenylating agent.

Operationally, the generation of **15** was best accomplished by adding butyllithium to a stirred solution containing **4**, diisopropylamine, and hexamethylphosphoramide (HMPA) in tetrahydrofuran at 0 °C. The solution of the dianion thus formed was usable for at least 30 min if kept at that temperature. If the ratio of base to lactam was greater than 2.0, the bis-sulfenylated lactam **5c** predominated. As the ratio was decreased to about 1.7, larger amounts of monosulfenylated products **5a** and **5b** were produced. Below 1.7, unreacted starting material became dominant. Dimethyl disulfide was added 5 min after the addition of the base. This sulfenylation reaction was allowed to proceed for 30 min because longer reaction times led to greater quantities of starting lactam and **5c**, apparently via a disproportionation reaction.

The mixture of stereoisomeric, monosulfenylated lactams **5a** and **5b** were difficulty separable, but it was found that isomerization to **5a** only occurred by treatment with potassium carbonate in methanol. No attempt was made to characterize the stereochemical structure of **5a** because later reactions were expected to destroy the isomeric integrity at this position. However, it might reasonably be assumed that the methylthio group is anti to the cyclopropane ring because of steric preference.

Aromatization processes considered for **5a** and/or **5b** involved a sulfonium salt, sulfoxide, or sulfone (**6**). For the first, alkylations of **5a,b** or **5a** only were attempted under a number of conditions with excess trimethyloxonium fluoroborate. The only product isolated was an imino ether.

The sulfoxide had some interesting prospects as an intermediate, particularly as an origin for a 2,3-sigmatropic shift to a sulfenate[16] (**16**). The sulfoxide could be prepared in nearly quantitative yield by oxidation of **5a** with *m*-chloroperbenzoic acid at −78 °C. Attempted rearrangement–hydrolysis reactions produced only starting material or decomposition products.



16

The sulfone **6** could be made nearly quantitatively from **5a**, and methylation to **7** (50:50 mixture of isomers) occurred in 96% yield. Since basic conditions were to be used for the next reaction, separation of the stereoisomers of **7** was not attempted. In that last step, **2b** was isolated in 21% yield from the reaction of **7** with potassium *tert*-butoxide at 80 °C.

The chemical shifts of vinyl and aromatic protons in methano-bridged compounds are essentially the same as those seen for conventional species. In **2b** they fall into the range that indicates aromaticity. The bridge protons, however, show evidence of a weaker ring current than in the carbocyclic species, 1,6-methano[10]annulene.

Experimental Section

Tetrahydrofuran (THF) was purified by distillation from potassium benzophenone ketyl, and other solvents were distilled prior to use. The ^{1}H NMR spectra were recorded on one or more of the following instruments: Varian A-60D, Varian EM-390, Brüker WH-90 Multinuclear, or Varian HR-220 (for compound **2b**). Infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer, ultraviolet spectra from a Carey 14 spectrophotometer, low-resolution mass spectra from a Finnegan 1015 S/L spectrometer, and high-resolution mass spectra from an ARI-MS9 spectrometer (the last at the University of California, Los Angeles). Microanalyses were performed by C. F. Geiger, Ontario, Calif. Melting points are uncorrected.

4,7-Dihydro-2-indanone Ethylene Ketal (9). A solution of 19.7 g (0.112 mol) of 2-indanone ethylene ketal (**8**) in 50 mL of anhydrous ether was added to 200 mL of liquid ammonia at −78 °C. Over a 4-h period lithium wire in 4-cm portions and 2-propanol in 2-mL portions were added, so that a total of 50 cm (2.0 g, 0.29 g-atoms) of the former and 24 mL (18.8 g, 0.31 mol) of the latter were introduced. After 2 h the temperature was allowed to rise to that of refluxing ammonia and kept there for 5 h. After ammonia was allowed to evaporate, water was added and the aqueous layer was extracted three times with ether. The combined organic layers were washed twice with water and once with saturated NaCl, dried with magnesium sulfate, and concentrated by evaporation to yield 15.6 g of a nearly white solid. Crystallization from low-boiling petroleum ether gave **9** (15.0 g, 84% yield) as a white solid, mp 44–45 °C (lit.,[10] 43–44 °C).

Tricyclo[4.3.1.0^{1,6}]-2,4-decadien-8-one Ethylene Ketal (10). The methylene bridge was introduced into **9** using methylene iodide and the zinc–silver couple as described by Denis et al.[13] A mixture of the couple (prepared from 23.8 g of zinc and 130 mg of silver acetate), 25.8 g (0.145 mol) of ketal **9** in 60 mL of ether, and 300 mg (2.80 mg-atoms) of silver dust (as opposed to silver wool) was prepared, and 50.5 g (0.189 mol) of methylene iodide was added at such a rate to maintain gentle reflux. Refluxing was maintained for 3 h after complete addition, then the mixture was cooled, and an equal volume of ether was added. Pyridine was added in two portions, followed by filtration after each addition to remove the inorganic precipitate. Concentration of the filtrate by evaporation yielded 25.5 g of a brown oil. Distillation (62–65 °C at 0.05 mmHg) gave 19.4 g (70%) of **10** as a clear oil: ^{1}H NMR (CCl_4, Me_4Si) δ 0.45 (d, 1, J = 4 Hz, cyclopropyl H anti to ketal), 0.70 (d, 1, J = 4 Hz, cyclopropyl H syn to ketal), 1.94 (s, 4, methylene H of 5-membered ring), 2.22 (m, 4, allylic H), 3.76 (m, 4, ketal H), 5.46 (m, 2, olefinic H).

Tricyclo[4.3.1.0^{1,6}]-2,4-decadien-8-one (11). Ketal **10** (17.5 g, 0.092 mol) in 75 mL of dichloromethane was cooled to −78 °C under nitrogen. Bromine (14.7 g, 0.092 mol) was added dropwise to the stirred solution. After 30 min, excess sodium bisulfite and 10 mL of absolute methanol were added and the mixture was warmed to 0 °C. After filtration and removal of the solvent at 0 °C, the resulting solid was transferred to a hot solution of sodium ethoxide (0.46 mol) in 250 mL of ethanol. The mixture was refluxed for 2 h with stirring, cooled, diluted with water, and extracted five times with pentane. The combined organic phases were washed twice with water, dried over magnesium sulfate, and concentrated to yield the crude diene ketal. A solution of the ketal in 200 mL of THF was refluxed for 2 h with 50 mL of 0.5 M HCl. After cooling, the mixture was neutralized with sodium bicarbonate and extracted three times with ether. The organic phases were washed successively with saturated sodium bicarbonate and saturated sodium chloride and then dried over magnesium sulfate. After removal of the solvent, the product was crystallized from ether to give 7.8 g (59%) of **11** as a white solid: mp 98–100 °C (lit.[7] 99–100 °C).

Tricyclo[4.3.1.0^{1,6}]-2,4-decadien-8-one Oxime (3). The oxime was prepared in 97% yield. Recrystallization did not significantly alter the product: mp 76–78 °C (lit.,[7] 77–78 °C).

Beckmann Rearrangement of Oxime 3. Oxime **3** (7.33 g, 45.5 mmol) in 200 mL of THF was cooled to 0 °C under a nitrogen atmosphere. Then, 23 mL of 2 M sodium hydroxide was added, followed by the dropwise addition of benzenesulfonyl chloride (8.05 g, 45.5 mmol). After the mixture was stirred at 0 °C for 30 min, 200 mL of water was added and the resulting solution was refluxed for 3.5 h. The cooled reaction mixture was poured into dichloromethane and the organic layer was combined with three dichloromethane washings of the aqueous phase. The combined organic phases were washed with saturated sodium chloride, dried over magnesium sulfate, and concentrated, to yield 6.75 g of a tan solid. The product was chromatographed on silica gel with elution by dichloromethane to yield 779 mg (12%) of the diene ketone **11**. Subsequent elution with 2% ethyl acetate/dichloromethane gave 1.57 g (21%) of a yellow oil whose ^{1}H NMR and infrared spectra were consistent with those expected of the abnormal Beckmann product, **12**. Nitrile alcohol **12** was purified and characterized as the phenylurethane: mp 115 °C. Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.38; H, 5.89; N, 10.37.

Final elution of the silica gel column with 10% ethyl acetate/dichloromethane gave 4.40 g (60%) of lactam **4** as a white solid: mp 127 °C; ^{1}H NMR ($CDCl_3$, $CHCl_3$) δ −0.13 (dd, 1, J = 4.5 Hz, J' = 1.5 Hz), 1.71 (d, 1, J = 4.5 Hz), 2.50 (dd, 1, J = 16.5 Hz, J' = 1.5 Hz), 2.90 (d, 1, J = 16.5 Hz), 3.46 (d, 1, J = 13.0 Hz), 3.70 (dd, 1, J = 13.0 Hz, J' = 5.0 Hz; the latter shown by decoupling to be coupled to the NH), 5.91 (s, 4), 6.40–6.71 (s, 1).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.77; H, 6.78; N, 8.60.

Sulfenylation of Lactam 4. To a solution of lactam **4** (906 mg, 5.63 mmol) dissolved in 35 mL of anhydrous THF were added 1.08 g (10.7 mmol) of diisopropylamine and 1.92 g (10.7 mmol) of HMPA. The stirred solution was cooled to −15 °C under argon; then 9.52 mmol of butyllithium in hexane was added as quickly as possible without allowing the temperature to rise above 0 °C. Five minutes after the addition was complete, 616 mg (6.55 mmol) of dimethyl disulfide was added. The cooling bath was removed and after 30 min water was added. The reaction mixture was extracted three times with ether. The combined organic extracts were washed once with 3 M HCl, once with saturated sodium bicarbonate, and once with saturated sodium chloride. The solution was dried over magnesium sulfate, filtered, and concentrated to yield 952 mg of a yellow oil. Chromatography on silica gel and elution with 50% ether/dichloromethane yielded the bis(methylthiolactam) **5c** (184 mg, 13%) as a white solid. Continued elution gave the mono(methylthiolactams) **5a** and **5b** (402 mg, 34%) and finally lactam **4**, the last as an impure solid (20–30%).

Crystallization of **5c** gave a pure product: mp 187–188 °C; ^{1}H NMR ($CDCl_3$, $CHCl_3$) δ 0.07 (d, 1, J = 5.0 Hz, cyclopropyl H syn to diene), 1.97 (d, 1, J = 5.0 Hz, cyclopropyl H anti to diene), 2.09 (s, 3, SCH_3), 2.23 (s, 3, SCH_3), 3.66 (d, 2, J = 6.0 Hz, methylene α to NH, shown by decoupling), 5.75–6.28 (m, 4, olefinic protons), 6.64–6.89 (m, 1, NH); IR (KBr) 3.02, 3.40, 5.98, 6.05, 6.80, 7.05, 7.65, 8.43, 9.20, 9.65, 9.80, 10.40, 11.10, 11.50, 12.00, 12.60, 13.50, 13.90, and 14.50 μm UV ($CHCl_3$) λ_{max} 280 nm, log ϵ 3.41.

Anal. Calcd for $C_{12}H_{15}NOS_2$: C, 56.88; H, 5.97; N, 5.53; S, 25.31. Found: C, 56.94; H, 5.84; N, 5.56; S, 24.98.

Mixture of **5a** and **5b**. Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.32; S, 15.47. Found: C, 63.71; H, 5.93; S, 15.29.

Alternate Procedure for Sulfenylation of Lactam 4. Lithiodiisopropylamide was made by adding 11.5 mL (18.0 mmol) of 1.56 M butyllithium in hexane to a stirred solution of diisopropylamine (2.04 g, 20.2 mmol) in 10 mL of THF at 0 °C under argon. After 20 min, the resulting solution was added as quickly as possible to a stirred solution of lactam **4** (1.81 g, 11.2 mmol) of HMPA (3.62 g, 20.2 mmol) in 40 mL of THF at −10 °C. After 5 min, 1.08 g (11.5 mmol) of dimethyl disulfide was added at once and the cooling bath removed. Water was added after 30 min and the aqueous layer was extracted three times with ether. The combined organic extracts were washed once with 3 M HCl, once with saturated sodium bicarbonate, and once with saturated sodium chloride, dried over magnesium sulfate, filtered, and concentrated to yield 1.32 g of a yellow oil. Chromatography on silica gel and elution with 10% ethyl acetate/dichloromethane gave 589 mg (26%) of a mixture of methylthiolactams **5a** and **5b**. The bis product was not isolated.

***anti*-4-Aza-3-oxo-2-methylthiotricyclo[4.4.1.0^{1,6}]-7,9-undecadiene (5a).** To a solution of mixed methylthiolactams **5a** and **5b** (980 mg, 4.73 mmol) in 50 mL of absolute methanol was added 700 mg (5.06 mmol) of anhydrous potassium carbonate. The mixture was stirred under nitrogen for 48 h. Water was added and the aqueous layer was extracted three times with ether. The organic extracts were washed once with saturated sodium chloride, dried over magnesium sulfate, and concentrated to yield 823 mg (84%) of a white solid: mp 153–153.5 °C; ^{1}H NMR ($CDCl_3$, $CHCl_3$) δ −0.07 (d, 1, J = 4.5 Hz, cyclopropyl H syn to diene), 1.84 (d, 1, J = 4.5 Hz, cyclopropyl H anti to diene), 2.15 (s, 3, SCH_3), 3.63 (d, 2, J = 6.0 Hz, methylene H α to NH as shown by decoupling), 3.80 (s, 1, methine H α to carbonyl), 5.62–6.25 (m, 5, olefinic H and NH); IR (KBr) 3.25, 3.38, 3.55, 6.00, 6.78, 7.10, 7.25, 7.45, 7.62, 7.88, 8.02, 8.38, 8.50, 8.60, 8.90, 9.10, 9.60, 9.80, 10.18, 10.28, 10.52, 11.02, 11.80, 12.24, 12.75, 13.71 and 14.50 μm.

Oxidation of Methylthiolactam 5a. Methylthiolactam **5a** (667 mg, 3.22 mmol) in 60 mL of dichloromethane was cooled to −78 °C under nitrogen. Then 1.31 g (6.5 mmol) of 85% *m*-chloroperbenzoic acid was added and the mixture was stirred at that temperature for 2 h. The solution was warmed to 0 °C and stirred for an additional 2 h. After neutralization with 5% potassium carbonate, the mixture was extracted three times with dichloromethane, which was dried over magnesium sulfate and concentrated to yield 769 mg (99%) of the sulfone lactam **6** as a white solid. A sample for analysis was crystallized from absolute ethanol: mp 192–194 °C; ^{1}H NMR ($CDCl_3$, $CHCl_3$) δ 0.02 (d, 1, J = 5.0 Hz, cyclopropyl H syn to diene), 1.73 (d, 1, J = 5.0 Hz, cyclopropyl H anti to diene), 2.96 (s, 3, SO_2CH_3), 3.67 (dd, 1, J = 11.0 Hz, J' = 6.0 Hz, methylene H, the latter shown by decoupling to be due to NH), 3.84 (d, 1, J = 11.0 Hz, methylene H), 5.77–6.48 (m, 5, olefinic H and NH); IR (KBr) 3.20, 3.45, 3.55, 6.00, 6.12, 6.80, 7.24, 7.65, 8.40, 8.85, 9.12, 9.60, 9.75, 10.30, 11.04, 11.45, 12.20, 12.44 and 13.70 μm; UV (methanol) λ_{max} 272 nm, log ϵ 3.26.

High-resolution MS. Calcd for $C_{11}H_{13}NO_3S$: m/e 239.0615. Found: 239.0627.

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.21; H, 5.48; N, 5.85; S, 13.40. Found: C, 55.23; H, 5.68; N, 5.80; S, 13.22.

Sulfone Imino Ether 7. Anhydrous potassium carbonate (100 mg) was added to a stirred solution of the sulfone lactam **6** in 10 mL of dichloromethane under nitrogen at room temperature. Trimethyloxonium fluoroborate (197 mg, 1.33 mmol) was added and the mixture was stirred for 6 h. After the addition of water the mixture was extracted three times with dichloromethane, the organic layers were dried over magnesium sulfate, and the solvent was removed to yield 108 mg (96%) of the sulfone imino ether **7** as a 50:50 mixture of isomers (approximated from peak sizes in the ^{1}H NMR spectrum). The orange oil resisted further purification by chromatography or distillation: ^{1}H NMR for the mixed isomers ($CDCl_3$, $CHCl_3$) δ −0.02 and 0.24 (d, 1, J = 4.5 Hz, J = 5.0 Hz, cyclopropyl H syn to diene), 1.58 and 2.37 (d, 1, J = 4.5 Hz, J = 5.0 Hz, cyclopropyl H anti to diene), 2.80 and 3.30 (s, 3, SO_2CH_3), 3.73 (s, 3, OCH_3), 3.88–4.60 (m, 3, methylene and methine), 5.90–6.23 (m, 3, vinyl), 6.30–6.60 (m, 1, vinyl); IR (thin film) 3.30, 3.40, 3.50, 6.00, 7.00, 7.55, 7.68, 7.98, 8.08, 8.84, 9.88, 10.35, 11.00, 13.35, and 13.75 μm; UV (methanol) λ_{max} 272 nm, log ϵ 3.12.

High-resolution MS. Calcd for $C_{12}H_{15}NO_3S$: m/e 253.0771. Found: 253.0777.

4-Methoxy-1,6-methanoisoquinoline (2b). Potassium *tert*-butoxide (215 mg, 1.92 mmol) was added to a stirred solution of sulfone imino ether **7** (162 mg, 0.64 mmol) in 10 mL of *tert*-butyl alcohol and heated to 80 °C under nitrogen for 2 h. After cooling to room temperature, water was added and the solution was extracted three times with dichloromethane. The combined organic extracts were washed twice with water and once with saturated sodium chloride, dried over magnesium sulfate, and concentrated to yield 85 mg of a dark oil. Preparative thin-layer chromatography on 2-mm silica gel plates developed with 10% ethyl acetate/hexanes yielded 23 mg (21%) of **2b** as a yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.05 (d, 1, J = 9.5 Hz, bridgehead H over heterocyclic ring), 0.45 (dd, 1, J = 9.5 Hz, J' = 1.8 Hz, bridgehead H over carbocyclic ring), 3.94 (s, 3, OCH_3), 5.94 (d, 1, J = 1.8 Hz, H α to OCH_3, shown by decoupling to be due to NH), 6.53 (dd, 1, J = 10.1 Hz, J' = 8.4 Hz, carbocyclic-ring H), 6.71 (dd, 1, J = 10.1 Hz, J' = 8.4 Hz, carbocyclic-ring H), 7.26 (d, 1, J = 10.1 Hz, carbocyclic-ring H), 7.37 (d, 1, J = 10.1 Hz, carbocyclic-ring H), 7.44 (s, 1, H α to nitrogen); IR (thin film) 3.50, 3.60, 6.50, 6.98, 7.18, 7.38, 7.66, 7.74, 8.02, 8.32, 8.50, 8.68, 9.18, 9.75, 11.25, 11.50, 12.35, 13.65, 14.35, and 14.85 μm; UV (methanol) λ_{max} 258 (log ϵ 4.33), 320 (log ϵ 3.63) and 385 mμ (log ϵ 3.29).

High-resolution MS. Calcd for $C_{11}H_{11}NO$: m/e 173.0840. Found: 173.0838.

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Registry No.—**2b,** 66910-93-8; **3,** 7068-08-8; **4,** 67338-10-7; **5a,** 67272-08-6; **5b,** 67335-64-2; **5c,** 67272-09-7; **6,** 67272-10-0; **7** isomer 1, 67272-11-1; **7** isomer 2, 67335-65-3; **8,** 183-24-4; **9,** 67272-12-2; **10,** 13288-27-2; **11,** 7068-07-7; **12** phenylurethane, 67272-13-3.

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