87156-45-4; **12**, 87156-51-2; (*E*)-**13**, 87156-54-5; (*E,E*)-**14**, 87156-46-5; **15**, 87156-55-6; **16**, 87156-56-7; **17**, 87156-52-3; **18**, 87156-53-4; 1,2-divinylcyclohexene, 53081-66-6; 2-(hydroxymethylene)cyclohexanone, 823-45-0; 2-bromopropane, 75-26-3; vinyllithium, 917-57-7; vinyl bromide, 593-60-2; 1-ethyl-2-propyl-1-cyclohexanol, 87156-49-8; ethyl bromide, 74-96-4; 2-propylcyclohexanone, 94-65-5; propynyl bromide, 106-96-7; triethyl phosphonoacetate, 867-13-0; (*p*-methoxyphenyl)acetylene, 768-60-5; methyllithium, 917-54-4; 2-(*p*-methoxyphenyl)ethynyllithium, 52999-18-5; 2-(2-butynylidene)-1-(1-propynyl)cyclohexanol, 87156-57-8.

Benzvalene and Dewar Benzene Type Sulfinamides

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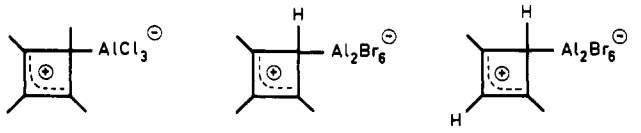
The reaction of cyclobutadiene aluminum halide σ complexes with *N*-arylsulfinylamines leads, depending on the substitution pattern of the phenyl ring, to either bicyclic (Dewar benzene type) or tricyclic sulfinamides, the latter being formed via an intramolecular Friedel–Crafts reaction of an intermediate cyclobutenyl cation. A similar reaction of aluminum halide σ complex **1** with *N*-*tert*-butylsulfinylamine affords both a bicyclic and a tricyclic (benzvalene type) sulfinamide.

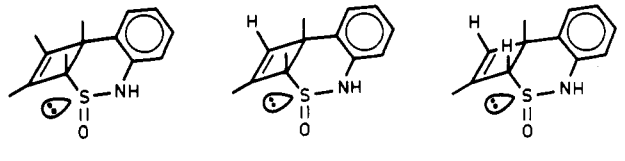
Aluminum halide σ complexes of cyclobutadienes[1] have been known for a decade. These complexes, e.g., **1–3**, are



1 **2** **3**

easily prepared from aluminum halides and alkynes and have proven their synthetic utility in various reactions. Dewar benzenes,[2] bicyclohexenes,[3] Dewar pyridones,[4] pyridines,[5] and a number of other derivatives[6] are obtained upon the reaction of these complexes with appropriate reagents.

Very recently it has been shown that the reaction of **1** with *N*-phenylsulfinylamine[6] at −60 °C leads to sulfinamide **4**. Now we report two novel compound types obtained



4 **5** **6**

in the reaction of the aluminum halide σ complexes of cyclobutadienes with sulfinylamines and, moreover, to point out some of the mechanistic details of the reported reaction by variation of the substituents. Complexes **2** and **3** are very useful in this respect because of their "hydrogen labels". When the reactions of **2** and **3** are performed with *N*-phenylsulfinylamine at −60 °C, only one sulfinamide is isolated (52% and 55% yields, respectively) in each instance. The structural assignments of compounds **5** and **6** are based on a comparison of the ^1H and ^{13}C NMR data with those of sulfinamide **4** and related structures.[7] The regiospecific formation of only one sulfinamide in each case makes a reaction mechanism involving the addition of *N*-phenylsulfinylamine to intermediately formed free tetramethylcyclobutadiene unlikely. We suggest the following mechanism for this reaction (Scheme I): initial attack of the sulfinylamine nitrogen atom at the 1(3)-position of the allylic moiety of **2** affords **7**, which by a successive ring closure at sulfur leads to sulfinamide **8**; ring-opening of **8** by fission of the C–N bond yields **9**,

(1) (a) Koster, J. B.; Timmermans, G. T.; Van Bekkum, H. *Synthesis* **1971**, 139. (b) Hogeveen, H.; Kok, D. M. "The Chemistry of Functional Groups"; Patai, S., Ed., Wiley: New York, 1983; Supplement C. (c) Hogeveen, H.; Kok, D. M. *Tetrahedron Lett.* **1980**, *21*, 659.

(2) Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265.

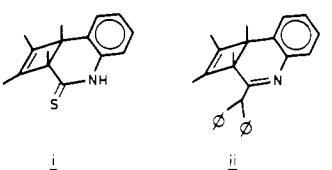
(3) Van Rantwijk, F. J.; Van der Stoel, R. E.; Van Bekkum, H. *Tetrahedron* **1978**, *34*, 569.

(4) Hogeveen, H.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 997.

(5) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 989.

(6) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 1909.

(7) (a) The structure of sulfinamide **4** has been elucidated by X-ray analysis.[6] ^{13}C NMR data of cyclobutene sp^3 carbon atoms in **4–6** (in ppm): **4**, 48.1 (s), 70.6 (s); **5**, 46.8 (s), 72.2 (s); **6**, 43.2 (s), 70.8 (d, J = 150 Hz). Compare with those of a structurally similar thioamide i[6] [48.6 (s) and 57.6 ppm (s)] and compound ii [47.0 (s) and 52.0 ppm (s)]. Comparison of these data clearly shows the absorption near 70 ppm in **4–6** to belong to the bridgehead carbon next to sulfur. Proof for the structure of **6** is found from the ^{13}C–^1H coupled spectrum, the absorption at 70.8 ppm being a doublet.

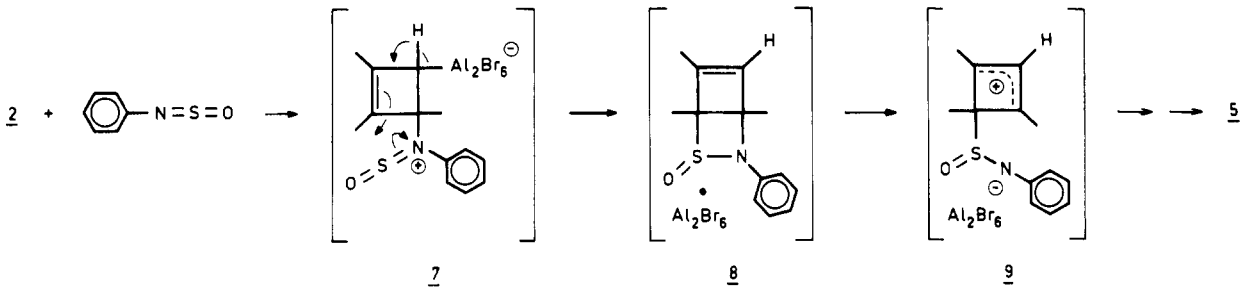


i ii

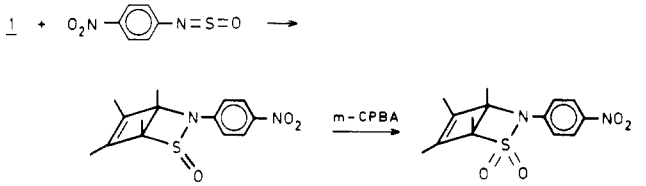
(b) The stereochemistry of the sulfinyl oxygen in **5** and **6** is believed to be the same as in **4** (X-ray structure[6]) because of the similarities in the ^1H NMR spectra. The following ^1H NMR data have been reported[6] ($CDCl_3$) for **4** (mp 185–187 °C): δ 1.25 (s, 3 H), 1.43 (s, 3 H), 1.59 (q, J = 1.1 Hz, 3 H), 1.81 (q, J = 1.1 Hz, 3 H), 6.26 (s, 1 H), 6.40–7.25 (m, 4 H). Compare the NMR data of the isomer of **4** with the sulfinyl oxygen in the exo position (mp 225 °C): δ 1.25 (q, J = 1.1 Hz, 3 H), 1.58 (br, 6 H), 1.60 (q, J = 1.1 Hz, 3 H), 6.58 (br s, 1 H), 6.38–7.38 (m, 4 H). Going from **4** to its exo isomer, one observes a remarkable upfield shift of one of the double bond CH_3 groups, accompanied by downfield shift of both bridgehead CH_3 absorptions to about 1.6 ppm. Looking at the corresponding data of **5** and **6** (Experimental Section), one finds a great resemblance with the endo isomer **4**.

0022-3263/83/1948-4275$01.50/0

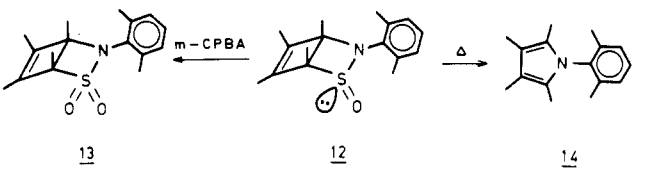
Scheme I



Scheme II



Scheme III



which via an intramolecular Friedel–Crafts reaction and subsequent hydrogen shift affords **5**.

Substituent variation in the sulfinylamine has led to the confirmation of the proposed mechanism and to the synthesis of novel types of bi- and tricyclic sulfinamides. With *N*-(*p*-methylphenyl)-, *N*-(*p*-methoxyphenyl)-, and *N*-(*p*-chlorophenyl)sulfinylamines tricyclic sulfinamides[8] analogous to **4** have been isolated in the reaction with complex **1**. On the reaction of *N*-(*p*-nitrophenyl)sulfinylamine with complex **1** the bicyclic sulfinamide **10** (Scheme II) was observed in the crude reaction product (after the workup). Attempts to purify compound **10** failed, however, due to its thermal instability; oxidation of **10** with *m*-chloroperbenzoic acid gives the stable sulfonamide **11**. We assume that the presence of the electron-withdrawing nitro group on the phenyl ring prevents the Friedel–Crafts reaction so that the bicyclic (Dewar type) compound is the final product. On using *N*-2,6-dimethylphenyl)sulfinylamine, in which, of course an intramolecular Friedel–Crafts reaction is prevented, it was possible to isolate the corresponding sulfinamide **12** in pure form. This was performed in two ways: (i) by a direct reaction between **1** and *N*-(2,6-dimethylphenyl)sulfinylamine in CH_2Cl_2 on warming the reaction mixture from −90 to −40 °C during 1 h, followed by quenching with Me_2SO and a normal workup (yield 30–40% from ^1H NMR); (ii) by a reaction between (2 equiv) *N*-(2,6-dimethylphenyl)sulfinylamine and free tetramethylcyclobutadiene, which was generated by addition of a CH_2Cl_2 solution of Me_2SO to a solution of **1** (and the sulfinylamine) at −90 °C, followed by the workup (isolated yield 37%).[9] Sulfinamide **12** is (as is **10**) thermally unstable at room temperature (both in solution and as solid material) and readily looses "SO", yielding quantitatively the corresponding pyrrole **14**; oxidation of **12** with *m*-chloroperbenzoic acid leads to the stable sulfonamide **13** (Scheme III). In compound **13** a restricted rotation of the 2,6-dimethylphenyl group is observed by ^1H and ^{13}C NMR spectroscopy,[10] which is not the case in sulfinamide **12**. On basis of this observation and a molecular model study of both stereoisomers (with regard to the SO configuration) of **12**, an endo configuration of the sulfinyl oxygen in **12** seems likely.

A unique ring closure has been observed in the reaction of *N*-*tert*-butylsulfinylamine with complex **1**. The course of this reaction was followed by ^{13}C NMR spectroscopic measurements at various temperatures which showed that above −70 °C a reaction took place, leading to a mixture of two products. Careful examination of the ^{13}C NMR data led to the conclusion that both a bicyclohexene-type sulfinamide, **15**($AlCl_3$), and a product containing a bicyclobutane fragment, **17**($AlCl_3$), were formed.[11] Indeed upon workup of the reaction mixture two products were isolated, to which, on basis of analytical and spectroscopic data, the structures **15** and **17** are assigned. The formation of these two products may be explained by assuming intermediate **16** (Scheme IV): nucleophilic attack of nitrogen at the 1(3)-position of the allylic system results in the formation of **15**($AlCl_3$), whereas ring closure at the 2-position (a consequence of the homocyclopropenium ion character[12]) results in the formation of **17**($AlCl_3$), a new type of bicyclobutane bridged by two heteroatoms.[13]

Oxidation of **15** as well as of **17** with *m*-chloroperbenzoic acid leads to sulfonamide **18**, a compound considerably

(8) When *N*-(*p*-chlorophenyl)sulfinylamine is used in the reaction with **1**, a mixture of isomers (with regard to the sulfinyl oxygen) is obtained. From this mixture the exo isomer could be obtained by crystallization; assignment of the exo structure to this compound is based on arguments given in ref 7b. Further proof for the presence of both isomers is found in the oxidation of the mixture to one sulfonamide.

(9) For the synthesis of **12** the latter method is preferred over the former one, because of the greater ease in purification (crystallization from ether/pentane at −50 °C removes octamethyl-*syn*-tricyclo-[4.2.0.$0^{2,5}$]octadiene and small amounts of pyrrole) of the sulfinamide. The excess of 2 equiv of sulfinylamine is used in order to suppress the dimerization of the free cyclobutadiene to octamethyl-*syn*-tricyclo-[4.2.0.$0^{2,5}$]octadiene.

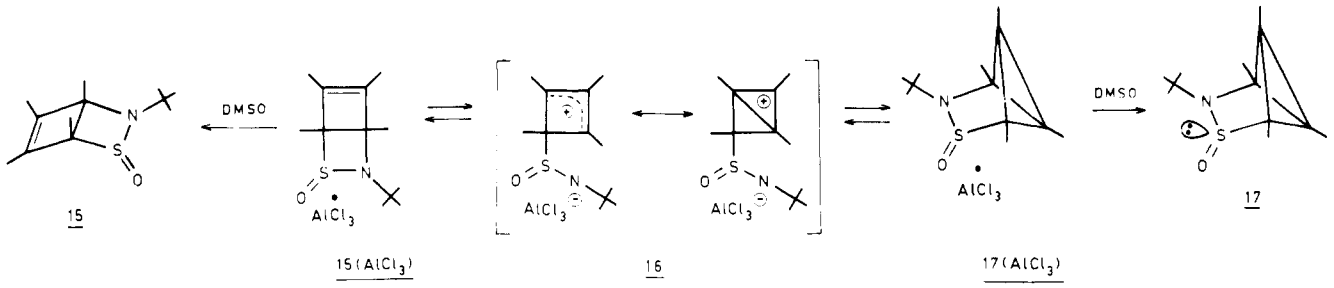
(10) At 27 °C two absorptions are found in the ^1H NMR spectrum of **13** for the aryl CH_3 groups (100 MHz, C_6D_6 solution) at 2.43 and 2.46 ppm; at 54 °C the signals have coalesced. The ^{13}C NMR spectrum of sulfonamide **13** shows the same dissymmetry of the aryl group. Molecular models of sulfinamide **12** and its exo isomer show, assuming a pyramidal nitrogen and the aryl group in the exo position, more steric hinderance of the sulfinyl oxygen with the aryl CH_3 groups in the exo position than in the endo position. Because of the absence of a restricted rotation (at room temperature) in the sulfinamide prepared from **1** and *N*-(2,6-dimethylphenyl)sulfinylamine, structure **12** is most likely.

(11) In the ^{13}C NMR spectrum of the reaction mixture eight CH_3 absorptions (apart from the *tert*-butyl signals) are observed, whereas only two absorptions due to sp^2 C atoms are present. The high field absorptions at 2.2 and 3.1 ppm are characteristic for the tetramethylbicyclobutane moiety: Hogeveen, H.; Zwart, L. *Isr. J. Chem.* **1981**, *21*, 221.

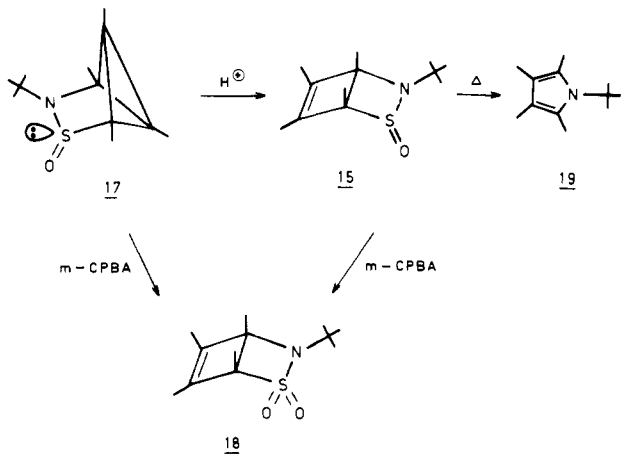
(12) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, J. *J. Am. Chem. Soc.* **1975**, *97*, 5489. Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193.

(13) Examples of bicyclobutanes bridged by one or two hetero atoms are known. See e.g.: (a) Corey, E. J.; Pirkle, W. H. *Tetrahedron Lett.* **1967**, 5255. (b) Kobayashi, Y.; Nakano, T.; Shirashi, K.; Takeda, A.; Kumadaki, I. *Ibid.* **1980**, *21*, 4615. (c) The intermediacy of azabenzvalene(s) has been made likely: Padwa, A.; Akiba, M.; Cohen, L. A.; Gingrich, H. L.; Kamigata, N. *J. Am. Chem. Soc.* **1982**, *104*, 286.

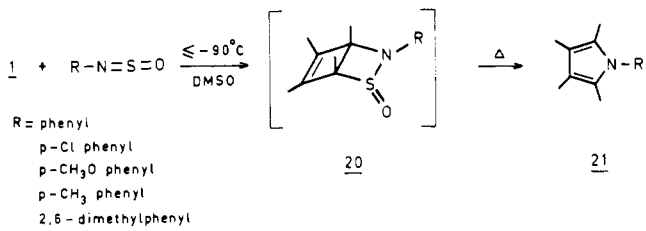
Scheme IV



Scheme V



Scheme VI



more stable than its precursors (Scheme V). Sulfinamide **15** looses "SO"[14] upon being allowed to stand in $CDCl_3$ solution at room-temperature, affording *N-tert*-butylpyrrole **19**. Compound **17** is also thermally labile and decomposes to unidentified material; addition of a protic solvent like CD_3OD gives rise to a rearrangement of **17** to **15**.

As mentioned above, the bicyclic sulfinamides **10**, **12**, and **15** appear to be good precursors for *N*-substituted tetramethylpyrroles; similar bicyclic sulfinamides derived from *N*-(*p*-methylphenyl)-, *N*-(*p*-methoxyphenyl)- and *N*-(*p*-chlorophenyl)sulfinylamine have not been observed in the direct reaction of these sulfinylamines with complex **1**. However, when a solution of Me_2SO in CH_2Cl_2 is added to a mixture of **1** and the sulfinylamines at −90 °C, at which temperature no direct reaction between **1** and the sulfinylamines is observed, the corresponding pyrroles **21** are obtained. The formation of pyrroles **21** is thought to proceed, by analogy to **12** (see above), via addition of free tetramethylcyclobutadiene to the sulfinylamines, leading to sulfinamides **20**, which due to their thermal instability cannot be isolated (Scheme VI).

Summarizing the above-described results, it has been found that the reactions of aluminum halide σ complexes of cyclobutadienes with properly N-substituted sulfinylamines offer a simple pathway to novel heterocyclic structures of the Dewar benzene and benzvalene type[15,16] as well as a route to persubstituted pyrroles.

Experimental Section

General Remarks. Melting points were determined on a Mettler FP2 apparatus. Elemental analysis were performed in the Analytical Section of our Department. Mass spectra were obtained on a AEI MS-209 mass spectrometer and IR spectra on a Perkin-Elmer 177 spectrometer. ^1H NMR spectra were recorded on a JEOL C-60-HL, a Varian XL-100, or a Nicolet NT-200 spectrometer, all equipped with a variable-temperature probe. Unless stated otherwise, the ^1H NMR spectra were recorded on solutions in $CDCl_3$, and chemical shifts are given in parts per million downfield from tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded by using a Varian XL-100 spectrometer or a Nicolet NT-200 spectrometer both equipped with a variable-temperature probe and operating at 25.16 and 50.31 MHz, respectively. Chemical shifts were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} values by using δ_{CDCl_3} = 76.91 ppm. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Solvents, except for $CDCl_3$, were distilled before use and stored over molecular sieves (3–4 Å). *N*-Phenylsulfinylamine, 2-butyne, and propyne were commercially available and used as such; $AlCl_3$ was sublimed twice before use; N-substituted sulfinylamines (except for *N*-phenylsulfinylamine) were prepared by using standard literature procedures by starting from the corresponding amines and $SOCl_2$. The reactions of aluminum halide σ complexes of cyclobutadiene and the reactions of thermally labile sulfinamides were carried out under a dry nitrogen atmosphere. Yields are (unless stated otherwise) based upon the amount of alkyne used.

Preparation of Aluminum Halide σ Complex 1.[1] A solution of 2-butyne (20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred suspension of $AlCl_3$ (1.4 g, 10.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C. Complex formation was completed by stirring for an additional 30 min at room temperature.

Preparation of Aluminum Halide σ Complexes 2 and 3.[1] A solution of 2-butyne (10 mmol) and propyne (10 mmol) or of propyne (20 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred suspension of $AlBr_3$ (5.3 g, 20 mmol) in CH_2Cl_2 (20 mL) at −90 °C. Complex formation was completed by stirring for an additional 30 min upon warming to −50 °C.

NMR Spectroscopic Measurements on Reaction Mixtures of Aluminum Halide σ Complexes of Cyclobutadienes and Sulfinylamines. Addition of 1.0 equiv of sulfinylamine in $CDCl_3$ to a solution of complex **1** (0.9 equiv), complex **2** (0.5 equiv), or complex **3** (0.5 equiv) in CH_2Cl_2 at −90 °C did not lead to a reaction according to ^1H and/or ^{13}C NMR spectroscopic measurements.

(14) Loss of SO has been encountered before. See e.g.: Dodson, R. M.; Sauers, R. F. *Chem. Commun.* **1967**, 1189. Durst, T.; Finlay, J. D.; Smith, D. J. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 950. Hogeveen, H.; Zwart, L. *J. Am. Chem. Soc.* **1982**, *104*, 4889. Aalbersberg, W. G. L.; Vollhardt, K. P. C. *Isr. J. Chem.* **1981**, *21*, 145.

(15) The denomination Dewar benzene- and benzvalene-type sulfinamides is coined for practical reasons and is not meant to indicate that the dipolar resonance structure $>N^+=S-O^-$ of the sulfinamide group is the dominant one. The observed IR frequencies at 1105, 1070, and 1070 cm^{-1} for compounds **12**, **15**, and **17** can be compared with those of acyclic sulfinamides at 1080–1105 cm^{-1}. See: Hovius, K.; Zuidema, G.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 633.

(16) See, e.g., ref 4, 6, and 13c.

NMR spectra of the solutions were recorded at various temperatures, and it was found that the reaction between the aluminum halide σ complexes and the sulfinylamines took place in the range of −60 to −20 °C.

Preparation of Tricyclic Sulfinamides of Type 4. General Procedure. Addition of the sulfinylamine (11 and 20 mmol for complexes **1** and **2**/**3**, respectively) in CH_2Cl_2 (10 mL) to a solution of the aluminum halide σ complex (10 mmol) in CH_2Cl_2 (20 mL) at −90 °C was followed by slowly warming to the temperature at which reaction occurred (determined by NMR spectroscopy). After being stirred for 30 min at this temperature, the mixture was cooled to −90 °C, and a solution of Me_2SO (2 to 5 equiv) in CH_2Cl_2 (10 mL) was added. Addition of the reaction mixture to a vigorously stirred mixture of 1 N NaOH and ether or CH_2Cl_2 (150 mL/150 mL) was followed by extraction of the organic layer with a saturated NaCl solution (twice), drying over K_2CO_3, and evaporation of the solvent. The tricyclic sulfinamides of type **4** were purified by crystallization.

***endo*- and *exo*-4,5-Benzo-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-Oxide (4).** See ref 6.

***endo*-4,5-Benzo-1,6,8-trimethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide (5)**: yield (ether/pentane) 52%; mp 137–138 °C; ^{1}H NMR 1.34 (s, 3 H), 1.53 (s, 3 H), 1.74 (d, J = 1.5 Hz, 3 H), 6.12 (s, 1 H), 6.37 (q, J = 1.5 Hz, 1 H), 6.77 (m, 1 H), 7.09 (m, 2 H), 7.29 (m, 1 H); ^{13}C NMR 12.5 (q, J = 127 Hz), 14.6 (q, J = 128 Hz), 25.4 (q, J = 128 Hz), 46.8 (s), 72.2 (s), 120.7 (d, J = 158 Hz), 123.6 (d, J = 161 Hz), 126.6 (d, J = 157 Hz), 126.9 (d, J = 161 Hz), 131.4 (s), 133.6 (s), 137.7 (d, J = 171 Hz), 143.9 (s); IR (CCl_4) 3200 (NH), 1070 cm^{-1} (S=O); MS, m/e 233 (M^+). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00; S, 13.74. Found: C, 66.69; H, 6.48; N, 5.97; S, 13.40.

***endo*-4,5-Benzo-6,8-dimethyl-2-thia-3-azabicyclo[4.2.0]-oct-7-ene 2-oxide (6)**: yield (ether/pentane) 55%; mp 161–162 °C; ^{1}H NMR 1.49 (s, 3 H), 1.83 (dd, J = 1.0, 1.4 Hz, 3 H), 3.98 (br s, 1 H), 6.38 (s, 1 H), 6.43 (q, J = 1.4 Hz, 1 H), 6.75 (m, 1 H), 7.09 (m, 2 H), 7.24 (m, 1 H); ^{13}C NMR 15.0 (q, J = 127 Hz), 28.8 (q, J = 128 Hz), 43.0 (s), 70.8 (d, J = 150 Hz), 120.9 (d, J = 160 Hz), 123.6 (d, J = 160 Hz), 126.2 (d, J = 156 Hz), 127.0 (d, J = 159 Hz), 131.6 (s), 132.2 (s), 139.1 (s), 140.1 (d, J = 172 Hz); IR (CCl_4) 3200 (NH), 1070 cm^{-1} (S=O); MS, m/e 219 (M^+). Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39; S, 14.62. Found: C, 65.39; H, 6.02; N, 6.37; S, 14.49.

***endo*-4,5-(4-Methylbenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide**: yield (toluene) 63%; mp 215 °C dec; ^{1}H NMR 1.31 (s, 3 H), 1.47 (s, 3 H), 1.64 (q, J = 1.2 Hz, 3 H), 1.89 (q, J = 1.2 Hz, 3 H), 2.29 (s, 3 H), 6.13 (s, 1 H), 6.65 (d, 1 H), 6.90 (d, 1 H), 7.09 (s, 1 H); ^{13}C NMR 9.4 (q, J = 127 Hz), 10.3 (q, J = 127 Hz), 14.4 (q, J = 127 Hz), 20.9 (q, J = 126 Hz), 23.9 (q, J = 129 Hz), 48.4 (s), 71.1 (s), 120.4 (d, J = 158 Hz), 127.5 (d, J = 160 Hz), 127.6 (d, J = 160 Hz), 129.2 (s), 132.7 (s), 132.8 (s), 135.5 (s), 146.3 (s); IR (CCl_4) 3340 (NH), 1070 cm^{-1} (S=O); MS, m/e 213 (M^+ − SO). Anal. Calcd for $C_{15}H_{19}NOS$: C, 68.93; H, 7.33; N, 5.36; S, 12.27. Found: C, 68.60; H, 7.23; N, 5.37; S, 12.20.

***endo*-4,5-(4-Methylbenzo)-6,8-dimethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide**: yield (ether) 46%; mp 175–177 °C; ^{1}H NMR 1.47 (s, 3 H), 1.82 (br s, 3 H), 2.28 (s, 3 H), 3.95 (s, 1 H), 6.42 (s, 1 H), 6.53 (s, 1 H), 6.66 (d, 1 H), 6.92 (d, 1 H), 7.06 (s, 1 H); ^{13}C NMR 15.1 (q, J = 127 Hz), 20.7 (q, J = 125 Hz), 28.7 (q, J = 128 Hz), 43.5 (s), 71.3 (d, J = 148 Hz), 120.8 (d, J = 157 Hz), 127.0 (d, J = 160 Hz), 127.9 (d, J = 160 Hz), 128.9 (s), 132.3 (s), 133.4 (s), 139.3 (s), 140.1 (d, J = 172 Hz); IR (CCl_4) 3200 (NH), 1070 cm^{-1} (S=O); MS, m/e 233 (M^+). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00; S, 13.74. Found: C, 66.77; H, 6.39; N, 5.94; S, 13.81.

***endo*-4,5-(4-Methoxybenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide**: yield (CH_2Cl_2/pentane) 61%; mp 196–198 °C; ^{1}H NMR 1.31 (s, 3 H), 1.46 (s, 3 H), 1.64 (q, J = 1.2 Hz, 3 H), 1.87 (q, J = 1.2 Hz, 3 H), 3.76 (s, 3 H), 6.33 (s, 1 H), 6.63 (m, 1 H), 6.64 (m, 1 H), 6.82 (m, 1 H); ^{13}C NMR 9.4 (q, J = 125 Hz), 10.3 (q, J = 125 Hz), 14.5 (q, J = 125 Hz), 23.8 (q, J = 125 Hz), 48.7 (s), 55.3 (q, J = 140 Hz), 71.0 (s), 111.7 (d, J = 160 Hz), 113.3 (d, J = 157 Hz), 121.3 (d, J = 160 Hz), 125.1 (s), 134.3 (s), 135.6 (s), 146.1 (s), 155.7 (s); IR (CH_2Cl_2) 3350 (NH), 1070, 1040 cm^{-1} (S=O); MS, m/e 229 (M^+ − SO). Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05; S, 11.56. Found: C, 64.56; H, 6.85; N, 4.99; S, 11.51.

***endo*- and *exo*-4,5-(4-Chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-Oxide.** The exo and endo isomers[8] were formed in the ratio 4:1 (total yield 69%).

Exo isomer: ^{1}H NMR 1.25 (q, J = 1.2 Hz, 3 H), 1.55 (s, 3 H), 1.57 (s, 3 H), 1.60 (q, J = 1.2 Hz, 3 H), 6.51 (d, J = 8.4 Hz, 1 H), 6.99 (dd, J = 2.3, 8.4 Hz, 1 H), 7.30 (d, J = 2.3 Hz, 1 H), 7.68 (s, 1 H); ^{13}C NMR 8.2, 8.8, 15.2, 17.6, 49.9, 121.6, 126.0, 126.9, 127.1, 130.7, 131.1, 137.6, 142.0; IR (CH_2Cl_2) 3300 (NH), 1065 cm^{-1} (S=O); MS, m/e 233 (M^+ − SO).

Endo isomer: ^{13}C NMR 9.4, 10.1, 14.3, 23.9, 48.3, 70.9, 121.8, 126.8, 128.2, 128.2, 131.7, 134.7, 135.8, 146.0.

4,5-(4-Chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2,2-Dioxide. To a cold, magnetically stirred solution of 450 mg (1.60 mmol) of a 1:1 mixture of the corresponding sulfinamides in 50 mL of benzene was added 325 mg (85%, technical grade) of *m*-chloroperbenzoic acid portionwise. The solution was allowed to warm to room temperature and stirred for another 10 min. After addition of 25 mL of an aqueous 1 N NaOH solution and separation of the layers, the benzene layer was washed twice with 25 mL of 1 N NaOH. The aqueous layer was extracted with 50 mL of ether and subsequently acidified with 6 N HCl to pH 1. Extraction of the water layer with CH_2Cl_2 (3 × 50 mL), drying over K_2CO_3, and evaporation of the solvent left spectroscopically pure sulfonamide. Crystallization of the product from toluene afforded 305 mg (1.02 mmol, 64%) of analytically pure sulfonamide: mp 198–200 °C; ^{1}H NMR 1.38 (q, J = 1.2 Hz, 3 H), 1.54 (s, 3 H), 1.63 (s, 3 H), 1.76 (q, J = 1.2 Hz, 3 H), 6.62 (s, 1 H), 6.82 (d, J = 8 Hz, 1 H), 7.16 (dd, J = 2, 8 Hz, 1 H), 7.30 (d, J = 2 Hz, 1 H); ^{13}C NMR 8.5 (q, J = 126 Hz), 9.2 (q, J = 126 Hz), 12.0 (q, J = 130 Hz), 17.2 (q, J = 127 Hz), 54.8 (s), 70.6 (s), 122.6 (d, J = 163 Hz), 127.1 (d, J = 162 Hz), 127.7 (d, J = 167 Hz), 130.5 (s), 132.8 (s), 135.2 (s), 136.9 (s), 142.9 (s); IR (CH_2Cl_2) 3350 (NH), 1130 cm^{-1} (br, SO_2); MS, m/e 297 (M^+). Anal. Calcd for $C_{14}H_{16}ClNO_2S$: C, 56.47; H, 5.42; Cl, 11.90; N, 4.70; S, 10.70. Found: C, 56.65; H, 5.40; Cl, 11.84; N, 4.64; S, 10.67.

3-(*p*-Nitrophenyl)-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2-Oxide (10). Sulfinamide **10** was prepared in a way similar to that for the tricyclic sulfinamides of type **4**. Attempts to purify compound **10** failed due to its thermal lability: ^{1}H NMR 1.48 (s, 3 H), 1.51 (s, 3 H), 1.70 (q, J = 1.2 Hz, 3 H), 1.85 (q, J = 1.2 Hz, 3 H), 6.8–8.2 (AA′BB′, 4 H). The structure of **10** was confirmed by oxidation to the corresponding sulfonamide **11**.

3-(2,6-Dimethylphenyl)-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2-Oxide (12). From the reaction of **1** with 2 equiv of *N*-(2,6-dimethylphenyl)sulfinylamine (see text and ref 6) was obtained a product mixture consisting the dimer of tetramethylcyclobutadiene, 2,6-dimethylaniline, and compound **12**. The aniline was removed by rapid extraction of a solution of this product mixture in CH_2Cl_2 with 1 N HCl (thus suppressing the acid-promoted decomposition of **12**), followed by extraction with 1 N NaOH. Crystallization from ether/pentane at −50 °C afforded analytically pure sulfinamide: 37% yield; ^{1}H NMR 1.41 (s, 3 H), 1.53 (s, 3 H), 1.63 (q, J = 1.2 Hz, 3 H), 1.76 (q, J = 1.2 Hz, 3 H), 2.44 (s, 6 H), 7.03 (s, 3 H); ^{13}C NMR 5.6 (q, J = 127 Hz), 9.5 (q, J = 125 Hz), 10.8 (q, J = 127 Hz), 17.1 (q, J = 127 Hz), 20.0 (q, J = 127 Hz), 71.5 (s), 81.0 (s), 127.1 (d, J = 159 Hz), 128.5 (s), 128.6 (d, J = 156 Hz), 137.9 (s), 139.2 (s), 154.0 (s); IR (CCl_4) 1105 cm^{-1} (S=O); MS, m/e 227 (M^+ − SO). Anal. Calcd for $C_{16}H_{21}NOS$: C, 69.78; H, 7.69; N, 5.09; S, 11.64. Found: C, 69.76; H, 7.76; N, 5.07; S, 11.54.

Reaction of Complex 1 with *N*-*tert*-Butylsulfinylamine. Formation of 15($AlCl_3$) and 17($AlCl_3$). A solution of 1.68 g (11 mmol) of *N*-*tert*-butylsulfinylamine in CH_2Cl_2 (10 mL) was added to a solution of complex **1** (10 mmol) in CH_2Cl_2 (20 mL) at −90 °C. ^{13}C NMR spectroscopic measurements at low temperature showed a reaction to occur at about −60 °C leading to a mixture of two products.[11] When the absorptions belonging to **1** had disappeared, the following peaks were observed: 2.2, 3.1, 6.4, 9.3, 10.3, 11.0, 13.4, and 16.7 ppm (eight CH_3), 29.4 and 30.7 ppm (two *t*-Bu groups), 34.1, 41.5, 57.2, 58.5, 70.3, 75.9, 76.6, and 80.6 ppm (eight quaternary sp^3 C), and 140.8 and 153.0 ppm (two quaternary sp^2 C).

Compounds **15** and **17** were prepared in the following way. The reaction mixture was allowed to warm from −90 to −50 °C and

was stirred for 15 min at this temperature. After the mixture was cooled again to −90 °C, a solution of 2 g of Me_2SO in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was then slowly added to a vigorously stirred, ice-cooled mixture of 150 mL of 1 N NaOH/150 mL of pentane. Separation of the layers, extraction of the organic layer with a saturated NaCl solution (twice), and drying over K_2CO_3/active carbon, followed by evaporation of the solvent (below 10 °C) left 1.75 g (77%) of slightly yellow oil. Crystallization from ca. 25 mL of pentane at −50 °C yielded sulfinamide **17**. After concentration of the filtrate to about 5 mL, sulfinamide **15** was obtained by crystallization at −50 °C. (Due to the thermal lability of the products the workup procedure had to be performed rapidly.)

4-*tert*-Butyl-1,2,5,6-tetramethyl-3-thia-4-azatricyclo[3.1.0.0^{2,6}]hexane 3-oxide (17): yield (pentane) 33%; ^{1}H NMR 1.35 (s, 9 H), 1.35 (s, 3 H), 1.50 (s, 3 H), 1.51 (s, 3 H), 1.52 (s, 3 H); ^{13}C NMR 2.4 (q, J = 129 Hz), 3.4 (q, J = 129 Hz), 6.1 (q, J = 129 Hz), 14.6 (q, J = 128 Hz), 29.5 (s), 30.8 (q, J = 126 Hz), 37.9 (s), 55.6 (s), 64.6 (s), 68.6 (s); IR (CCl_4) 1070 cm^{-1} (S=O); MS, m/e 227 (M^+). Anal. Calcd for $C_{12}H_{21}NOS$: C, 63.39; H, 9.31; N, 6.16; S, 14.10. Found: C, 63.22; H, 9.24; N, 6.20; S, 13.99.

3-*tert*-Butyl-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2-oxide (15): yield (pentane) 24%; ^{1}H NMR 1.26 (s, 3 H), 1.32 (s, 9 H), 1.39 (s, 3 H), 1.70 (q, J = 1.2 Hz, 3 H), 1.89 (q, J = 1.2 Hz, 3 H); ^{13}C NMR 9.5, 10.7, 10.7, 17.8 (4CH_3), 30.5 (t-Bu CH_3), 55.0 (s), 67.3 (s), 74.2 (s), 138.8 (s), 149.4 (s) (due to rapid decomposition no coupling constants were determined); IR (CCl_4) 1070 cm^{-1} (S=O); MS, m/e 227 (M^+). Anal. Calcd for $C_{12}H_{21}NOS$: C, 63.39; H, 9.31; N, 6.16; S, 14.10. Found: C, 63.26; H, 9.41; N, 6.32; S, 14.15.

Oxidation of Sulfinamides 10, 12, 15, and 17 to Sulfonamides 11, 13, 18, and 18, Respectively. As a typical procedure the oxidation of **17** to **18** is described. To a solution of 100 mg (0.44 mmol) of **17** in cold benzene (5 mL) was added 89 mg (1.0 equiv, 85% technical grade) of m-chloroperbenzoic acid portionwise. After the mixture warmed to room-temperature and was stirred for 5 min, 5 mL of 1 N NaOH solution was added, followed by 25 mL of saturated NaCl solution and 25 mL of CH_2Cl_2. The organic layer was extracted once more with 25 mL of a saturated NaCl solution, and after the mixture was dried over K_2CO_3 and the solvent evaporated, 98 mg (92%) of slightly yellow oil was obtained. Crystallization from pentane at −50 °C gave 78 mg (73%) of analytically pure **18**.

3-*tert*-Butyl-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2,2-Dioxide (18). Compound **18** was prepared via oxidation of **15** and **17** with m-chloroperbenzoic acid in 80% and 73% yields, respectively (yields after crystallization from pentane): mp 77–78 °C; ^{1}H NMR 1.36 (s, 9 H), 1.37 (s, 3 H), 1.52 (s, 3 H), 1.74 (q, J = 1.3 Hz, 3 H), 1.81 (q, J = 1.3 Hz, 3 H); ^{13}C NMR 7.9 (q, J = 129 Hz), 9.6 (q, J = 128 Hz), 11.3 (q, J = 127 Hz), 16.6 (q, J = 128 Hz), 29.1 (q, J = 126 Hz), 55.6 (s), 59.9 (s), 81.1 (s), 137.6 (s), 146.1 (s); IR (CCl_4) 1300, 1145 cm^{-1} (SO_2); MS, m/e 243 (M^+). Anal. Calcd for $C_{12}H_{21}NO_2S$: C, 59.22; H, 8.70; N, 5.76; S, 13.18. Found: C, 59.27; H, 8.71; N, 5.99; S, 13.09.

3-(2,6-Dimethylphenyl)-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2,2-dioxide (13): yield (from sulfinamide) >95%; mp 117–117.5 °C; ^{1}H NMR 1.31 (s, 3 H), 1.71 (q, J = 1.3 Hz, 3 H), 1.71 (s, 3 H), 1.84 (q, J = 1.3 Hz, 3 H), 2.43 (s, 3 H), 2.46 (s, 3 H), 7.0–7.2 (m, 3 H); ^{13}C NMR 8.8 (q, J= 130 Hz), 9.8 (q, J = 129 Hz), 11.1 (q, J = 128 Hz), 12.9 (q, J = 129 Hz), 18.3 (q, J = 127 Hz), 19.5 (q, J = 130 Hz), 64.3 (s), 82.1 (s), 128.3 (d, J = 160 Hz), 128.4 (d, J = 160 Hz), 128.9 (d, J = 160 Hz), 131.1 (s), 139.2 (s), 140.6 (s), 141.4 (s), 149.5 (s); IR (CCl_4) 1300, 1150 cm^{-1} (SO_2); MS, m/e 291 (M^+). Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 69.95; H, 7.26; N, 4.81; S, 11.00. Found: C, 65.99; H, 7.30; N, 4.74; S, 11.00.

3-(*p*-Nitrophenyl)-1,4,5,6-tetramethyl-2-thia-3-azabicyclo[2.2.0]hex-5-ene 2,2-dioxide (11): yield (from sulfinamide) ca. 80%; mp 122–124 °C; ^{1}H NMR 1.67 (s, 3 H), 1.70 (s, 3 H), 1.80 (q, J = 1.3 Hz, 3 H), 1.87 (q, J = 1.3 Hz, 3 H), 7.02–8.19 (AA'BB', 4 H); ^{13}C NMR 8.3 (q, J = 130 Hz), 9.8 (q, J = 128 Hz), 12.1 (q, J = 128 Hz), 14.0 (q, J = 128 Hz), 61.6 (s), 85.1 (s), 114.5 (d, J = 168 Hz), 125.3 (d, J = 165 Hz), 139.5 (s), 141.9 (s), 144.0 (s), 146.7 (s); IR (CCl_4) 1310, 1150 cm^{-1} (SO_2); MS, exact mass calcd for $C_{14}H_{16}N_2O_4S$ 308.083, found 308.086.

***N*-Substituted 2,3,4,5-Tetramethylpyrroles. General Procedures.** *N*-phenyl-, *N*-(*p*-chlorophenyl)-, *N*-(*p*-methoxyphenyl)-, and *N*-*p*-tolyl-2,3,4,5-tetramethylpyrrole were prepared directly from **1** and sulfinylamines (method A), whereas *N*-(*p*-nitrophenyl)-, *N*-(2,6-dimethylphenyl)-, and *N*-*tert*-butyl-2,3,4,5-tetramethylpyrrole were isolated as decomposition products of the bicyclic sulfinamides **10**, **12**, and **15**, respectively (method B).

Method A. To a solution of 10 mmol of complex **1** in CH_2Cl_2 (20 mL) at −90 °C was added a solution of 11 mmol of sulfinylamine in CH_2Cl_2 (10 mL), followed by a solution of 2 g of Me_2SO in CH_2Cl_2 (10 mL) (dropwise). The reaction mixture was then added to a vigorously stirred, cold mixture of 150 mL of 1 N NaOH and 150 mL of CH_2Cl_2, and the layers were separated. Extraction of the organic layer with a saturated NaCl solution (twice), drying over K_2CO_3, and evaporation of the solvent yielded the crude pyrroles. They were purified by column chromatography (Al_2O_3, basic) with pentane/CH_2Cl_2 mixtures as the eluent. Analytically pure pyrroles were obtained by crystallization from pentane at −50 °C under a dry nitrogen atmosphere.

Method B. Pure **12** and **15** and crude **10** in CH_2Cl_2 or $CDCl_3$ solutions decomposed at room temperature, yielding almost quantitatively the corresponding pyrroles. For purification of these pyrroles see method A.

***N*-Phenyl-2,3,4,5-tetramethylpyrrole (Method A).** See ref 6.

***N*-(*p*-Chlorophenyl)-2,3,4,5-tetramethylpyrrole (method A)**: yield 30%; mp 139–141 °C; ^{1}H NMR 1.97 (s, 6 H), 2.01 (s, 6 H), 7.10–7.44 (AA'BB', 4 H); ^{13}C NMR 9.2 (q, J = 125 Hz), 10.4 (q, J = 127 Hz), 114.1 (s), 123.4 (s), 129.0 (d, J = 167 Hz), 129.5 (d, J = 164 Hz), 132.9 (s), 137.9 (s); IR (CCl_4) 1490, 1395, 1380, 1365, 1090 cm^{-1}; MS, m/e 233 (M^+). Anal. Calcd for $C_{14}H_{16}ClN$: C, 71.94; H, 6.90; Cl, 15.17; N, 5.99. Found: C, 71.44; H, 6.89; Cl, 14.99; N, 5.86.

***N*-(*p*-Methoxyphenyl)-2,3,4,5-tetramethylpyrrole (method A)**: yield 64%; mp 115–116 °C; ^{1}H NMR 1.94 (s, 6 H), 2.00 (s, 6 H), 3.85 (s, 3 H), 6.92–7.13 (AA'BB', 4 H); ^{13}C NMR 9.2 (q, J = 126 Hz), 10.3 (q, J = 127 Hz), 55.1 (q, J = 143 Hz), 113.3 (s), 113.9 (d, J = 160 Hz), 123.6 (s), 129.5 (d, J = 160 Hz), 132.1 (s), 158.4 (s); IR (CCl_4) 1460, 1440, 1395, 1375, 1365, 1290, 1235, 1180, 1165, 1100, 1040 cm^{-1}; MS, m/e 229 (M^+). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.10; H, 8.33; N, 5.96.

***N*-Tolyl-2,3,4,5-tetramethylpyrrole (method A)**: yield 41%; mp 115–116 °C; ^{1}H NMR 1.95 (s, 6 H), 2.00 (s, 6 H), 2.41 (s, 3 H), 7.04–7.25 (AA'BB', 4 H); ^{13}C NMR 9.3 (q, J = 125 Hz), 10.4 (q, J = 127 Hz), 21.0 (q, J = 126 Hz), 113.5 (s), 123.6 (s), 128.1 (d, J = 160 Hz, 129.4 (d, J = 152 Hz), 136.8 (s), 136.8 (s); IR (CCl_4) 1440, 1395, 1375, 1365 cm^{-1}; MS, m/e 213 (M^+). Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.47; H, 8.96; N, 6.54.

***N*-(*p*-Nitrophenyl)-2,3,4,5-tetramethylpyrrole (method B)**: mp 120–121 °C; ^{1}H NMR 2.00 (s, 6 H), 2.00 (s, 6 H), 7.32–8.35 (AA'BB', 4 H); ^{13}C NMR 9.3 (q, J = 125 Hz), 10.7 (q, J = 127 Hz), 115.8 (s), 123.2 (s), 124.3 (d, J = 171 Hz), 128.6 (d, J = 165 Hz), 145.1 (s), 146.1 (s); IR (CCl_4) 1590, 1500, 1395, 1375, 1365, 1350 cm^{-1}; MS m/e 244 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.54; H, 6.68; N, 11.15.

***N*-(2,6-Dimethylphenyl)-2,3,4,5-tetramethylpyrrole (method B)**: mp 74–75 °C; ^{1}H NMR 1.77 (s, 6 H), 1.90 (s, 6 H), 2.00 (s, 6 H), 7.05–7.20 (m, 3 H); ^{13}C NMR 9.5 (q, J = 125 Hz), 9.7 (q, J = 127 Hz), 17.5 (q, J = 128 Hz), 113.0 (s), 121.5 (s), 127.5 (d, J = 159 Hz), 127.7 (d, J = 160 Hz), 137.3 (s), 137.8 (s); IR (CCl_4) 1470, 1435, 1355 cm^{-1}; MS, m/e 227 (M^+). Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.43; H, 9.30; N, 6.14.

***N*-*tert*-Butyl-2,3,4,5-tetramethylpyrrole (method B)**: mp 28–30 °C; ^{1}H NMR 1.67 (s, 9 H), 1.93 (s, 6 H), 2.34 (s, 6 H); ^{13}C NMR 9.7 (q, J = 128 Hz), 15.3 (q, J = 127 Hz), 32.5 (q, J = 127 Hz), 57.9 (s), 115.1 (s), 124.0 (s); IR (CCl_4) 1390, 1365, 1305, 1215, 905 cm^{-1}; MS, exact mass calcd for $C_{12}H_{21}N$ 179.167, found 179.166.

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Registry No. 1, 31886-99-4; 2, 80206-71-9; 3, 80206-70-8; *endo*-4, 81045-21-8; *exo*-4, 81129-81-9; 5, 86803-55-6; 6, 86803-56-7; 10, 86803-57-8; 11, 86803-58-9; 12, 86803-59-0; 13, 86803-60-3; 14, 86803-61-4; 15, 86803-62-5; 15($AlCl_3$), 86822-05-1; 17, 86803-63-6; 17($AlCl_3$), 86834-24-4; 18, 86803-64-7; 19, 86803-65-8; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; *N*-phenyl-2,3,4,5-tetramethylpyrrole, 1015-63-0; *N*-(*p*-chlorophenyl)-2,3,4,5-tetramethylpyrrole, 86803-66-9; *N*-(*p*-methoxyphenyl)-2,3,4,5-tetramethylpyrrole, 86803-67-0; *N*-*p*-tolyl-2,3,4,5-tetramethylpyrrole, 86803-68-1; PhN=S=O, 1122-83-4; *p*-ClPhN=S=O, 13165-68-9; *p*-(CH_3O)PhN=S=O, 13165-69-0; *p*-(CH_3)PhN=S=O, 15795-42-3; 2-butyne, 503-17-3; propyne, 74-99-7; *endo*-4,5-(4-methylbenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-69-2; *endo*-4,5-(4-methylbenzo)-6,8-dimethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-70-5; *endo*-4,5-(4-methoxybenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo-[4.2.0]oct-7-ene 2-oxide, 86803-71-6; *endo*-4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-72-7; *exo*-4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86851-44-7; 4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicicylo[4.2.0]oct-7-ene 2,2-dioxide, 86803-73-8; *N*-(2,6-dimethylphenyl)sulfinylamine, 17420-02-9; *N*-*tert*-butylsulfinylamine, 38662-39-4; *N*-(*p*-nitrophenyl)-2,3,4,5-tetramethylpyrrole, 86803-74-9.

Steric Retard of Internal Rotation in 1-Carbomethoxy-1,2-diphenylcyclopropane

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The high preference (R_A = 13) found by Chmurny and Cram for internal rotation of the hydrogen–phenyl carbon bond over the carbomethoxy–phenyl carbon bond in 1-carbomethoxy-1,2-diphenylcyclopropane appears to originate in a steric effect. There being nothing out of the ordinary in 1-carbomethoxy-2-phenylcyclopropane (R_A = 1.7) vis-à-vis 1-cyano-2-phenylcyclopropane (R_A = 2.5), the ester group of itself is probably not at fault. When it is replaced by cyano in 1-cyano-1,2-diphenylcyclopropane, R_A drops dramatically to 2.2. This marked increase in rotational propensity of the cyano–phenyl carbon bond vis-à-vis the carbomethoxy–phenyl carbon bond is reasonably ascribed to the smaller steric thickness of the cyano group and a reduced steric hindrance to rotation past the hydrogen–phenyl carbon bond.

Internal rotational propensity is the key to automerization in substituted cyclopropanes[1] and cyclobutanes.[2] If the activation energies of the hypothetical reactions are accommodated by a simple model consisting of the appropriate carbon–carbon bond dissociation energy[3] decreased by full release of ring strain and by radical-stabilizing effects of any substituents on the several bonds, the stereochemistry of the products is determined by the ratio of single to double rotations and, within the set of single rotations, by the preference of one disubstituted carbon atom to rotate over another (Figure 1). This preference, the relative internal rotational propensity, is a thermodynamic quantity[1] defined (see Figure 1) as

$$R_A = R_{YZ}^{AB} = k_{TC(AB)}/k_{TC(YZ)} = k_{CT(AB)}/k_{CT(YZ)} = k_1/k_2 = k_{-1}/k_{-2}$$

Except for an example of Chmurny and Cram,[4] which provides the stimulus for the present work, magnitudes of known rotational preferences given in Table I are neither impressively large nor clearly revealing of controlling factors. A complicated 1,2,3-trisubstituted example has been omitted but indicates a significant steric influence on R_A by the substituent at C_3.[7]

Whatever effect replacement of a shorter, smaller group by a longer, larger group might have been expected to have (cf. ref 3 and 5, Table I), the effect is small and opposite to that anticipated from a change in moments of inertia. Similarly, an approximate doubling in molecular weight (cf. 1 or 2 and 3, or 4 and 6, Table I) has no significant influence on the value of R_A.

Uniquely dramatic among this collection is the relative rotational propensity calculable from the experimental results of Chmurny and Cram[4] (Figure 2, **2t** and **2c**) on 1-carbomethoxy-1,2-diphenylcyclopropane. Its exceptionally high value (R_A = 13.3) begged for an explanation, which, it might be hoped, would give insight into the origins of rotational propensity. The present experiments were designed to determine whether an ester group might be peculiar by itself or whether the special environment of the Chmurny–Cram example might be responsible. Replacement of the ester group by the sterically narrower cyano group offered promise of useful information.

Results

Methyl 1,2-Diphenylcyclopropanecarboxylate. The starting point is the mixture of **1t** and **1c** prepared following Chmurny and Cram with minor modifications.[4] Convenient separation is effected either by crystallization or by partial saponification of the methyl esters, wherein **2c** hydrolyzes about 8 times faster than **2t**. This observation is fully consistent with the configurational assignments of Chmurny and Cram, which are based on an upfield shift in the NMR spectrum of the methyl group in **2t**, comparison of the pK_a values of **1t** and **1c** with those

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