having spectral properties consistent with those described above.

(B) Cyclohexene (34). To 20 mL of methanol in a 25-mL round-bottomed flask containing a magnetic stirring bar were added 130 mg (1.60 mmol) of cyclohexene (**34**), 30.4 mg of tetradecane, 300 mg (1.20 mmol) of iodine, and 700 mg (3.50 mmol) of 3-chloroperoxybenzoic acid. After being stirred for 3 h, the reaction mixture was worked up as described above. Preparative gas chromatography afforded iodide **21** (72%) and diether **22** (27%) as colorless liquids having spectral properties consistent with those described above.

(C) 2,4-Dimethyl-2,3-pentadiene (35). To 20 mL of methanol in a 25-mL round-bottomed flask containing a magnetic stirring bar were added 85 mg (0.89 mmol) of diene **35**, 20.6 mg of hexadecane, 120 mg (0.47 mmol) of iodine, and 400 mg (1.97 mmol) of 3-chloroperoxybenzoic acid. After being stirred for 3 h, the reaction mixture was worked up as described above. Preparative gas chromatography afforded iodide **30** (71%) as colorless crystals having spectral properties consistent with those described above.

Independent Synthesis of *trans*-1,2-Dimethoxycyclohexane (22).[34] To a solution of 1.16 g (10.0 mmol) of *trans*-1,2-cyclohexanediol in 20 mL of freshly distilled dimethoxyethane was added 48 mg (20 mmol) of sodium hydride, and resulting mixture was stirred for 4 h at room temperature under an atmosphere of nitrogen. Methyl iodide (2.8 g, 20 mmol) was added in one portion, and the solution was maintained at 40 °C for 24 h. Dilution with an equal volume of water and continuous extraction for 24 h with pentane, followed by distillation of the organic layer, afforded 75 mg of a colorless oil [bp 75 °C (32–34 mm)] which had spectral properties identical with those described above for ether **22**.

(34) We are indebted to P. R. Worsham for this preparation.

Acknowledgment. Generous financial support by the National Science Foundation and the University Research Council of the University of North Carolina is gratefully acknowledged.

Registry No. 1, 629-27-6; 2 (Y = OCH_3), 929-56-6; 2 (Y = OPr-i), 30983-85-8; 2 (Y = OBu-t), 51323-70-7; 2 (Y = Br), 111-83-1; 2 (Y = Cl), 111-85-3; 3, 30983-85-8; 4 (Y = OCH_3), 10395-53-6; 4 (Y = Cl), 765-91-3; 5, 18971-91-0; 6, 19066-23-0; 7, 768-93-4; 8 (Y = OCH_3), 6221-74-5; 8 (Y = OH), 768-95-6; 9, 930-80-3; 10 (Y = OCH_3), 57901-28-7; 10 (Y = OH), 51566-98-4; 10 (Y = Cl), 765-67-3; 11, 80754-45-6; 12 (Y = OCH_3), 13921-80-7; 12 (Y = Cl), 80754-46-7; 13, 34300-08-8; 14, 80754-47-8; 15 (isomer 1), 80754-48-9; 15 (isomer 2), 80754-49-0; 16, 80754-50-3; 17, 1809-04-7; 18 (Y = OCH_3), 56711-42-3; 18 (Y = Cl), 18651-57-5; 19, 626-62-0; 20, 931-56-6; 21, 54826-41-4; 22, 29887-60-3; 23, 80754-51-4; 24 (Y = OCH_3), 54583-18-5; 24 (Y = Cl), 34786-17-9; 25, 15501-33-4; 26, 62016-49-3; 27, 4206-67-1; 28 (Y = OCH_3), 14704-14-4; 28 (Y = Cl), 2344-80-1; 29, 35895-37-5; 30, 80754-52-5; 31, 591-50-4; 32, 696-33-3; 33, 20145-40-8; 34, 110-83-8; 35, 1000-87-9; bicyclo[2.2.1]hept-2-ene, 498-66-8; 1-octene, 111-66-0; *trans*-1,2-cyclohexanediol, 1460-57-7.

Synthesis of Strained Heterobicycles from Alkynes and Heterocumulenes

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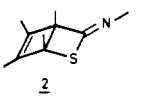
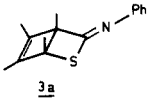
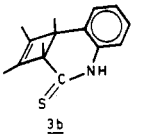
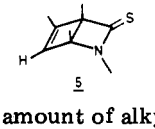
Received October 8, 1981

A one-pot synthesis of strained heterobicycles such as 2-thia(or 2-aza)-3-iminobicyclo[2.2.0]hex-5-enes and 2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxides from alkynes, aluminum halides, and heterocumulenes (isothiocyanates, carbodiimides, *N*-sulfinylaniline) is described. The thermal and acid-promoted reactions of the permethylated 2-thia-3-iminobicyclo[2.2.0]hex-5-ene **2** to monocyclic isomers are reported.

In addition to the use of aluminum halide σ complexes of cyclobutadienes for the synthesis of four-, five-, and six-membered-ring compounds[1] such as Dewar benzenes, cyclopentadienes, and pyridines, a new method of preparation of Dewar pyridones with these σ complexes and isocyanates[2] was recently introduced. In this paper it will be shown that isothiocyanates, carbodiimides, and *N*-sulfinylaniline react in a similar way with the aluminum halide σ complexes, affording strained heterobicyclic compounds. In the case of isothiocyanates and carbodiimides a difference is observed with comparable reactions involving organotransition-metal complexes, alkynes, and isothiocyanates[3] or carbodiimides:[4] under these circumstances monocyclic six-membered-ring compounds are formed.

Table I. Reactions of Aluminum Halide σ Complexes of Cyclobutadienes with Isothiocyanate

complex	isothiocyanate (RN=C=S)	product(s)	yield,[a] %
1 ($AlCl_3$)	R = Me	 **2**	66
1 ($AlCl_3$)	R = Ph	 **3a**  **3b**	35 (1/1 **3a**/**3b**)
4 (Al_2Br_6)	R = Me	 **5**	70

[a] Yields are based on the amount of alkyne used.

Dewar pyridones are easily converted to 2-pyridones either thermally[2,5] or by acid.[2] A similar investigation of

(1) (a) Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265. (b) Van Rantwijk, F.; Van der Stoel, R. E.; Van Bekkum, H. *Tetrahedron* **1978**, *34*, 569. (c) Hogeveen, H.; Kok, D. M. "The Chemistry of Acetylenes"; Patai, S., Ed.; Wiley: New York, in press; Supplement C.

(2) Hogeveen, H.; Kok, D. M., *J. Org. Chem.* **1982**, *47*, 997. Kok, D. M. Thesis, University of Groningen, 1981.

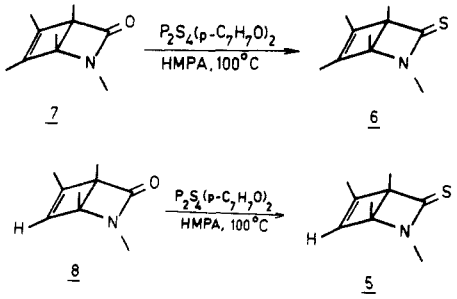
(3) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280.

(4) (a) Hong, P.; Yamazaki, H. *Tetrahedron Lett.* **1977**, 1333. (b) Hoberg, H.; Burkhart, G. *Synthesis* **1979**, 525.

(5) Fürrer, H. *Chem. Ber.* **1972**, *105*, 2780.

0022-3263/82/1947-1909$01.25/0

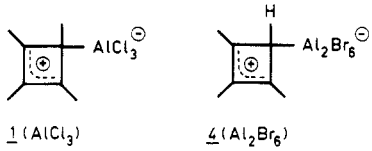
Scheme I



1,4,5,6-tetramethyl-2-thia-3-(methylimino)bicyclo[2.2.0]-hex-5-ene (2) shows a different behavior in both reactions.

Results and Discussion

Reactions with Isothiocyanates. Reaction of complex 1 ($AlCl_3$)[6] at 0 °C or at room temperature with methyl



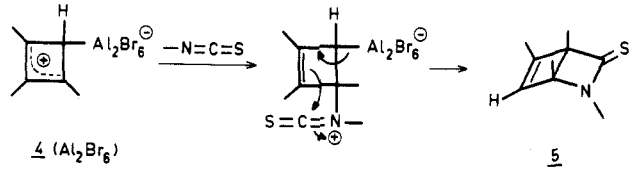
isothiocyanate affords compound **2**, a substituted 2-thia-3-iminobicyclo[2.2.0]hex-5-ene, in 66% yield (Table I). Similarly, with phenyl isothiocyanate a 1:1 mixture of compounds **3a** and **3b** is isolated in 35% yield. When complex **4** (Al_2Br_6) is allowed to react with methyl isothiocyanate below −30 °C, compound **5** is obtained in 70% yield.[7] A remarkable difference is apparent in products **2** and **5**: product **2** contains a carbon–nitrogen double bond and compound **5** a carbon–sulfur double bond. Both types of four-membered heterocycles are known, although much less frequently encountered than β-lactams. For example, 2-iminothietanes are easily prepared by cycloaddition of thioketones and ketenimines,[8a] and β-thio lactams are known from the reaction of thioketenes and imines.[8b]

Structure Assignment of Compounds 2, 3a,b, and 5. The ^{13}C NMR spectra of compounds **2**, **3a,b**, and **5** show, similar to the Dewar pyridones,[2] typical chemical shift values for the carbon atoms of the cyclobutene (see Experimental Section). Furthermore, the presence of a carbon–nitrogen double bond in compounds **2** and **3a** is revealed by an absorption at 169.4 and 170.3 ppm in the ^{13}C NMR spectrum and a strong infrared absorption at 1680 and 1660 (and 1645) cm^{-1}, respectively.[8a] An additional argument for the structure of **2** is found in the fact that it differs from the isomeric compound **6**, which contains a carbon–sulfur double bond and which was synthesized by reaction of Dewar pyridone **7** with the dimer of (*p*-methoxyphenyl)thionophosphine sulfide[9] (Scheme I). In addition to the presence of cyclobutene-skeleton carbon atoms in the ^{13}C NMR spectrum, the absorption of the $^{13}C{=}S$ carbon atom in **6** is found at 206.8 ppm, a common value for thioamide carbon atoms.[9] Similarly, compounds **3b** and **5** show a $^{13}C{=}S$ absorption at 203.5 and 205.8 ppm, respectively. Futher evidence for the structure of **3b** is revealed by the N–H absorption in the IR spectrum at 3360 cm^{-1} and by the presence of two phenyl quaternary carbon atoms in the ^{13}C NMR spectrum.

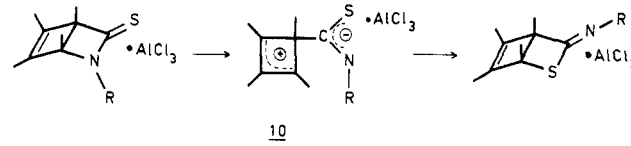
Finally, the position of the hydrogen atom on the alkene moiety of compound **5** has been determined by showing that compound **5** is identical with the one obtained on reaction of Dewar pyridone 8[2] with dimeric (*p*-methoxyphenyl)thionophosphine sulfide (Scheme I).

Mechanism of the Isothiocyanate Addition to Complexes 1 ($AlCl_3$) and 4 (Al_2Br_6). From the formation of compound **5** by reaction of complex **4** (Al_2Br_6) and methyl isothiocyanate it is concluded that, similar to the isocyanate addition to complex **4** (Al_2Br_6),[2] nucleophilic attack of the nitrogen atom of the isothiocyanate takes place at the 2(4)-carbon atom of the allylic cation, followed by a cyclization on the 3-position (Scheme II). In contrast, the adduct of complex **1** ($AlCl_3$) and methyl isothiocyanate (**2**) contains a carbon nitrogen double bond. However, the synthesis of **5** is carried out below −30 °C and that of compound **2** under otherwise identical conditions at 0 °C or higher. It is therefore conceivable that in the latter case the temperature is high enough to induce a rearrangement by $AlCl_3$ of the initial addition product **6** to the observed product **2** (Scheme III). This is comparable with the observation that both compounds **5** and **6**, rearrange under the influence of trifluoroacetic acid at room temperature to compounds **9** (69%) and **2** (48%), respectively (Scheme IV). The zwitterionic intermediate **10** bears some resemblance to the supposed intermediacy of **11** in the reaction of β-lactone anions with phenyl isothiocyanate to a 2-im-

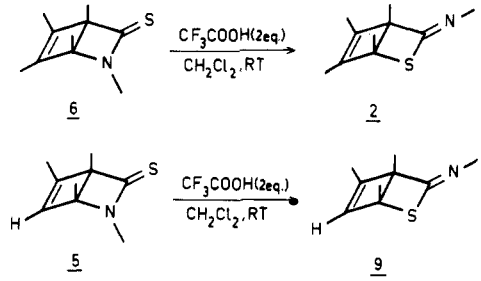
Scheme II



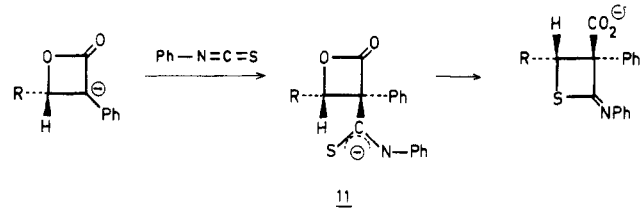
Scheme III



Scheme IV



Scheme V



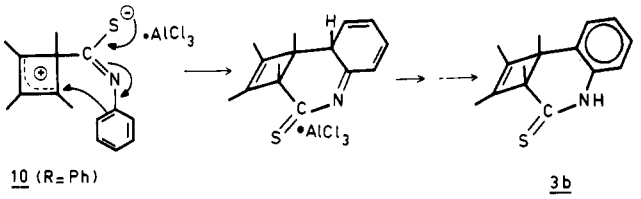
(6) The aluminum halide between parentheses indicates the Lewis acid which is attached to the cyclobutadiene moiety.

(7) When complex 1 (Al_2Cl_6) or 1 (Al_2Br_6) is treated with methyl isothiocyanate below −30 °C, a mixture of unidentified products is obtained after quenching which does not contain **2** or **6**, according to the ^1H NMR spectrum.

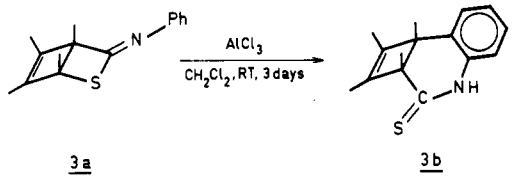
(8) (a) Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1177. (b) Schaumann, E.; Ehlers, J.; Grabley, F. F. *Chem. Ber* **1980**, *113*, 3010, 3024.

(9) Scheibye, S.; Pederson, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

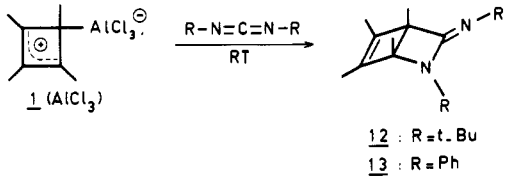
Scheme VI



Scheme VII



Scheme VIII



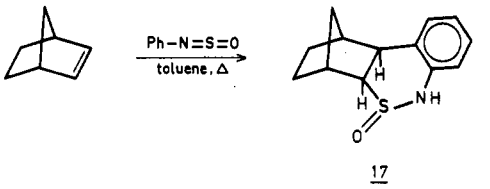
inothietane[10] (Scheme V). Apparently, a four-membered ring containing a sulfur atom (and an exocyclic C=N) is more stable than one which contains a nitrogen atom (and an exocyclic C=S). This might be due to the fact that a sulfur atom, by involvement of the unoccupied 3d orbitals, is more flexible and induces less strain in a four-membered ring than a nitrogen atom. Such an explanation has also been given for the exception of sulfur in the Baldwin rules for ring closure.[11]

Similar to the formation of compound **2**, compound **3a**, from the reaction of complex 1 ($AlCl_3$) with phenyl isothiocyanate, can be explained by the mechanism shown in Scheme III. Moreover, the formation of compound **3b** can be explained by starting from the same intermediate **10** (R = Ph): an electrophilic substitution reaction of the allylic cation of **10** (R = Ph) on the ortho position of the phenyl ring followed by a shift of the hydrogen atom leads to the formation of **3b** (Scheme VI). A related intermolecular reaction has been observed with fluorine-substituted cyclobutenyl cations, which exhibit an electrophilic substitution reaction at benzene.[12]

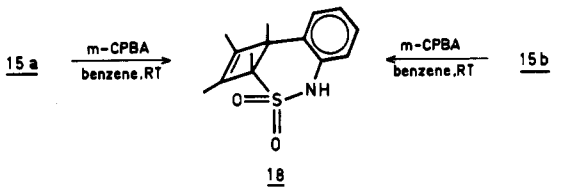
Finally, it is worth mentioning that when compound **3a** is treated with 1 equiv of aluminum trichloride at room temperature, a small amount of compound **3b** is isolated (12% yield, Scheme VII).

Reactions with Carbodiimides. On using di-*tert*-butyl- and diphenylcarbodiimide as heterocumulenes in reaction with complex 1 ($AlCl_3$), the substituted 2-aza-3-iminobicyclo[2.2.0]hex-5-enes **12** (47% yield) and **13** (68% yield) are obtained, respectively (Scheme VIII). Evidence for the bicyclic structure of compounds **12** and **13** has been obtained from the ^{13}C NMR spectra which show the presence of cyclobutene skeleton carbon atoms (see Experimental Section) and a carbon–nitrogen double bond (C=N absorption of **12** and **13** at 156.8 and 159.5 ppm, respectively). A strong infrared absorption at 1660 cm^{-1} in both cases indicates the presence of a carbon–nitrogen double bond.[13]

Scheme IX



Scheme X



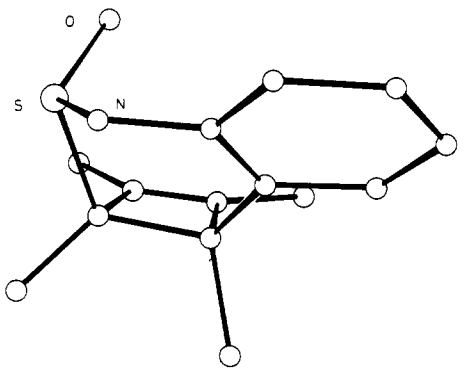


Figure 1. Representation of the spatial structure of **15a** (enantiomeric form shown).

Azetidin-2-imines are rarely encountered compounds. Recently, a novel synthesis of these four-membered heterocycles was reported by cycloaddition of *N*-tosylketenimines and imines.[14]

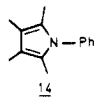
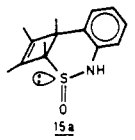
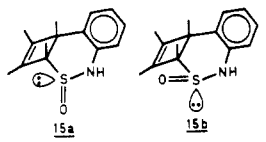
Reactions with *N*-Sulfinylaniline. When complex 1 ($AlCl_3$) is allowed to react with *N*-sulfinylaniline it is found that the nature of the product is strongly dependent on the temperature at which the reaction is carried out. When a mixture of complex 1 ($AlCl_3$) and *N*-sulfinylaniline at −80 °C (^{13}C NMR spectroscopic measurements reveal that no reaction occurs at this temperature) is quenched in alkaline water, pyrrole **14** is isolated in 30% yield (Table II). When the reagents are allowed to react at −60 °C, ^{13}C NMR spectroscopic measurements reveal the formation of **15a**, which is isolated in 74% yield. When the reaction is performed at room temperature, a 2:1 mixture of isomers **15a** and **15b** is obtained in 49% yield.

N-Sulfinylaniline is known to undergo 1,4-cycloadditions across the nitrogen–sulfur double bond with a variety of dienes to afford six-membered heterocycles.[15] In our case a similar reaction would have led to **16** which has not been observed, however. On the other hand, the reaction products **15a** and **15b** show a great resemblance to the products obtained from cycloaddition of *N*-sulfinylaniline to alkenes. For example, norbornene reacts with *N*-sulfinylaniline to give **17**[16] (Scheme IX).

Structure Assignment of Compounds 14 and 15a,b. The structure of pyrrole **14** has been established by a

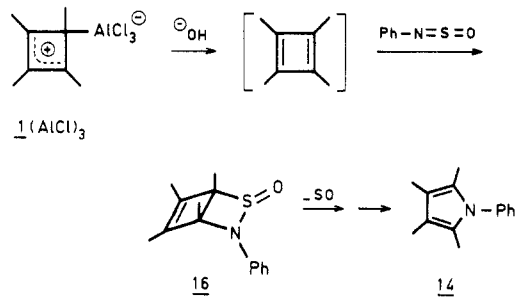
(10) Mulzer, J.; Kerkmann, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 466.
(11) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736.
(12) Smart, B. E.; Reddy, G. S. *J. Am. Chem.* **1976**, *98*, 5593.
(13) Reactions of other aluminum halide σ complexes with carbodiimides are currently being investigated and indicate that the addition of carbodiimides is similar to the addition of isocyanates.[2] Fongers, K. S., unpublished results.
(14) Van Camp, A.; Goossens, D.; Moya-Portuguez, M.; Marchard-Brynaert, J.; Ghosez, L. *Tetrahedron Lett.* **1980**, 3081.
(15) Ulrich, H. "Cycloaddition Reactions of Heterocumulenes"; Academic Press: London, 1967.
(16) Collins, G. R. *J. Org. Chem.* **1964**, *29*, 1688.

Table II. Reactions of Complex 1 ($AlCl_3$) with *N*-Sulfinylaniline

temp,[a] °C	product(s)	yield,[b] %
−80	 14	30
−60	 15a	74
−20	 15a 15b	49 (2/1 15a/15b)

[a] See text. [b] Yields are based on the amount of alkyne used.

Scheme XI

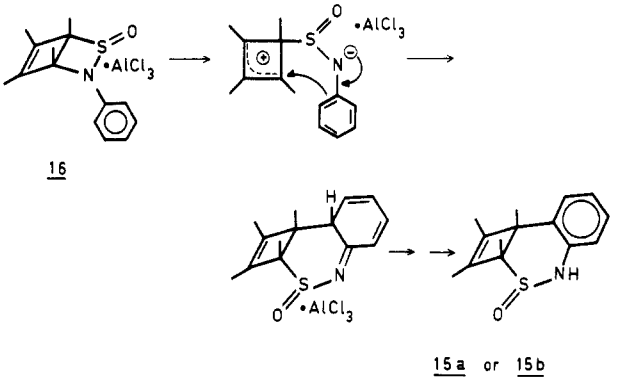


comparison with authentic material, prepared by reaction of *trans*-3,4-dichloro-1,2,3,4-tetramethylcyclobut-1-ene and aniline.[17] The structure of isomers **15a** and **15b** has been established on the basis of the ^{13}C NMR spectra showing the presence of the cyclobutene skeleton carbon atoms and the presence of two quarternary carbon atoms of the phenyl ring. In both cases the infrared spectrum exhibits absorptions at 3360 and 1050 cm^{-1}, which are due to a N—H and S=O bond, respectively. The configuration of the S=O in **15a** and **15b** could not be established, however, by common spectroscopic methods and has therefore been elucidated by an X-ray structure analysis of **15a** performed by Van Bolhuis[18] (Figure 1). The relationship between **15a** and **15b** has been unambiguously established by the fact that both **15a** and **15b** are oxidized with *m*-chloroperbenzoic acid to sulfonamide 18 in 94% and 91% yields, respectively (Scheme X).

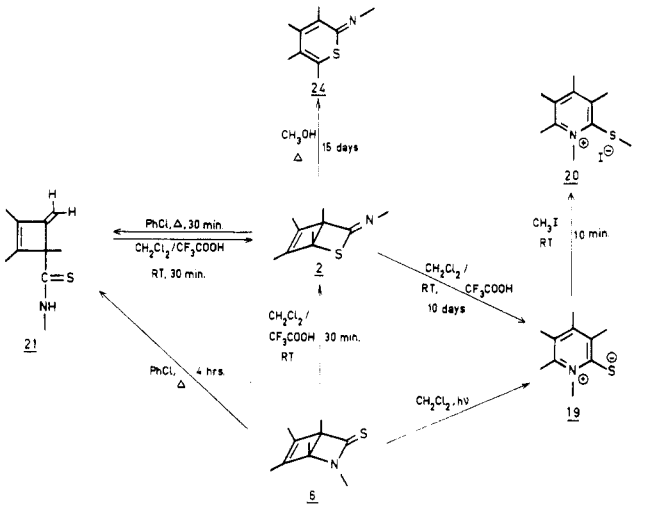
Mechanism of the Addition of *N*-Sulfinylaniline to Complex 1 ($AlCl_3$). ^{13}C NMR spectroscopic measurements have indicated that no reaction takes place within 2 h between complex 1 ($AlCl_3$) and *N*-sulfinylaniline at −80 °C. However, the isolation of pyrrole **14** upon alkaline hydrolysis means that they react on quenching of the solution with alkaline water (room temperature). This observation may be explained by assuming the intermediate generation of tetramethylcyclobutadiene on quenching and a subsequent reaction of the latter with *N*-sulfinylaniline to cycloadduct **16** (Scheme XI), which by loss of SO rearranges into pyrrole **14**.

At higher temperatures the ^{13}C NMR spectroscopic measurements reveal the following data: (i) At about −60 °C a reaction of complex 1 ($AlCl_3$) and *N*-sulfinylaniline takes place with the formation of (complexed) compound **15a**. When the sample is further warmed to room temperature, no conversion of **15a** into **15b** is found (within 0.5 h). (ii) At 20 °C the reaction of complex 1 ($AlCl_3$) and *N*-sulfinylaniline results in a mixture of isomers **15a** and **15b**.

Scheme XII



Scheme XIII



It is concluded, therefore, that the mixture of isomers is formed by a reaction of *N*-sulfinylaniline and complex 1 ($AlCl_3$) and not by an isomerization of **15a** and **15b** under the influence of aluminum trichloride. Analogous to the reaction of complex 1 ($AlCl_3$) with phenyl isothiocyanate, a ring opening of initially formed **16** under the influence of $AlCl_3$ and a subsequent electrophilic substitution reaction on the phenyl group can account for the observation of isomers **15a** and **15b** (Scheme XII). However, it remains uncertain in what stage of the reaction the ratio of isomers **15a** and **15b** is determined.

Thermal and Acid-Promoted Isomerizations of Bicyclic Compounds 2 and 6. The behavior of compounds **2** and **6** in thermal and acid-promoted reactions is more complex than that of the permethylated Dewar pyridone.[2]

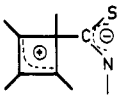
As pointed out above, compound **6** is converted into 2 within 0.5 h by using 2 equiv of trifluoroacetic acid (Scheme XIII). On being allowed to stand with 2 equiv of trifluoroacetic acid for 10 days, the latter compound rearranges to **19** (69% yield). Compound **19**, which is also obtained by a photochemical ring opening of **6** (73% yield), is rapidly methylated by methyl iodide to give **20** (almost quantitative yield).

The thermal behavior of compounds **2** and **6** differs from that of the Dewar pyridones;[2] both **2** and **6** are thermally

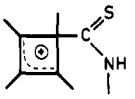
(17) Criegee, R.; Krieger, M. *Chem. Ber.* **1965**, *98*, 387.
(18) Van Bolhuis, F. Department of Chemical Physics, University of Groningen, The Netherlands.

converted into cyclobutene derivative **21** in 60% and 75% yields, respectively. A difference in reaction time is observed (according to ^1H NMR spectroscopic measurements): whereas **2** rearranges in 30 min, compound **6** requires 4 h in boiling chlorobenzene (132 °C). A possible explanation would be that compound **6** is converted into **2** in a slow reaction, followed by a rapid rearrangement of the latter compound to **21**. Indeed, when a ^1H NMR spectrum is recorded during the isomerization of **6** to **21**, small amouns of **2** are detected. Compound **21** is converted back into **2** by using 2 equiv of trifluoroacetic acid at room temperature (76% yield).

The experiments mentioned above favor the intermediacy of a dipolar structure **22** in the thermal rearrange-



22



23

ments and a protonated species **23** in the reactions with trifluoroacetic acid. An attempt to trap the zwitterionic intermediate **22** by refluxing in methanol,[19] failed and no addition of methanol was detected. Instead, after 15 days the thiacyclohexadiene **24** is formed (70% yield).

Experimental Section

General Remarks. Melting points (uncorrected) were determined on a Reichert apparatus by the Kofler method. Elemental analyses were performed in the Analytical Section of our Department. Mass spectra were obtained on an AEI MS 902 mass spectrometer and IR spectra on a Perkin-Elmer 177 spectrometer. ^1H NMR spectra were recorded on a JEOL C 60-HL spectrometer equipped with a variable temperature probe or a Varian A-60 spectrometer. 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 with a variable-temperature probe operating at 25.16 MHz with the aid of Fourier transform and were proton-noise decoupled. Proton-coupled ^{13}C NMR spectra were recorded in the gyrogate mode. Chemical shifts were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} values by using δ_{CDCl_3} = 76.9 ppm. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The solvents were distilled before use and stored over molecular sieves (3–4 Å). All reagents were commercially available and used as such with the exception of $AlCl_3$ which was sublimed before use. The reactions of the aluminum halide σ complexes of cyclobutadienes were carried out under a dry nitrogen atmosphere.

Preparation of 1,4,5,6-Tetramethyl-2-thia-3-(methylimino)bicyclo[2.2.0]hex-5-ene (2). A solution of 2.41 g of methyl isothiocyanate (33 mmol) in 15 mL of CH_2Cl_2 was added dropwise to a mechanically stirred solution of complex **1** ($AlCl_3$), prepared from 3.24 g of 2-butyne (60 mmol) and 4.38 g of $AlCl_3$ (33 mmol), in 75 mL of CH_2Cl_2 at 0 °C.[20] After warming to room temperature, the reaction mixture was poured under vigorous stirring into an aqueous 1 N NaOH/ether solution. The alkaline layer was extracted two times with ether, and the combined organic layers were dried over $MgSO_4$. After evaporation of the solvent the residue was distilled at 22 °C (0.05 mmHg) (–40 °C trap). Recrystallization from *n*-pentane at –40 °C afforded 3.72 g (66% yield) of compound **2** which was a colorless oil at room temperature: ^1H NMR 1.29 (s, 3 H), 1.45 (s, 3 H), 1.64 (s, 6 H), 2.89 (s, 3 H); ^{13}C NMR 9.1, 9.6, 10.9, 15.6 (4 q, J = 130 Hz), 41.2 (q, J = 135 Hz), 54.4 (s), 73.5 (s), 138.8 (s), 146.9 (s), 169.4 (s); IR (CCl_4) 1680 cm^{-1} (C=N); mass spectrum, molecular ion peak at m/e 181. Anal. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73; S, 17.68. Found: C, 66.3; H, 8.4; N, 7.7; S, 17.5.

Preparation of 1,4,5,6-Tetramethyl-2-thia-3-(phenylimino)bicyclo[2.2.0]hex-5-ene (3a) and 4,5-Benzo-1,6,7,8-tetramethyl-3-aza-2-thioxobicyclo[4.2.0]oct-7-ene (3b). A solution of 3.24 g of phenyl isothiocyanate (24 mmol) was added to a solution of complex **1** ($AlCl_3$), prepared from 2.16 g of 2-butyne (40 mmol) and 2.92 g of $AlCl_3$ (22 mmol), in 15 mL of CH_2Cl_2 at 0 °C.[20] After warming to room temperature, the reaction mixture was stirred for 10 h. The workup was carried out analogous to the procedure used for compound **2**. The crude residue (2.45 g) contained according to ^1H NMR integration approximately 1.8 g of isomers **3a,b**. Recrystallization from ether afforded 820 mg (17% yield) of **3b**: mp 212–214 °C; ^1H NMR (CCl_4) 1.44 (br, s, 6 H), 1.63 (br, s, 6 H), 6.63–7.25 (m, 4 H), 10.85 (s, 1 H); ^{13}C NMR 8.3, 9.3, 19.9, 20.4 (4 q, J = 125 Hz), 48.6 (s), 57.6 (s), 115.9, 124.6, 126.6, 127.0 (4 d, J = 160 Hz), 128.6 (s), 132.9 (s), 141.4 (s), 144.1 (s), 203.5 (s); IR (CCl_4) 3360 (NH), 1480 cm^{-1} (N—C=S)[8b]; mass spectrum, molecular ion peak at m/e 243. Anal. Calcd for $C_{15}H_{17}NS$: C, 74.04; H, 7.04; N, 5.75; S, 13.18. Found: C, 73.8; H, 6.8; N, 5.8; S, 13.0. Further concentration of the solution and recrystallization from ether at –50 °C afforded 900 mg (18% yield) of compound **3a**: mp 65.5–66.5 °C; ^1H NMR (CCl_4) 1.38 (s, 3 H), 1.46 (s, 3 H), 1.69 (m, 6 H), 6.61–7.33 (m, 5 H); ^{13}C NMR 9.3, 9.8 (2 q, J = 125 Hz), 11.0, 15.4 (2 q, J = 130 Hz), 56.1 (s), 74.4 (s), 120.4 (d, J = 155 Hz), 124.2 (d, J = 160 Hz), 128.2 (d, J = 160 Hz), 139.2 (s), 147.1 (s), 148.4 (s), 170.3 (s); IR (Nujol) 1645, 1660 cm^{-1} (C=N); mass spectrum, molecular ion peak at m/e 243. Anal. Calcd for $C_{15}H_{17}NS$: C, 74.04; H, 7.04; N, 5.75; S, 13.18. Found: C, 73.8; H, 7.0; N, 5.7; S, 13.1.

Preparation of 1,2,4,5-Tetramethyl-2-aza-3-thioxobicyclo[2.2.0]hex-5-ene (5). A solution of 1.61 g of methyl isothiocyanate (22 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a magnetically stirred solution of complex **4** (Al_2Br_6), prepared from 0.54 g of 2-butyne (10 mmol), 0.40 g of propyne (10 mmol), and 5.4 g of $AlBr_3$ (20 mmol), in 50 mL of CH_2Cl_2 at –85 °C.[21] The solution was warmed to –30 °C and poured into 200 mL of an aqueous 1 N NaOH solution under vigorous mechanical stirring. The alkaline layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over K_2CO_3, followed by evaporation of the solvent. The residue, a brown-red oil, was dissolved in *n*-pentane and treated with activated charcoal during 0.5 h. After filtration and evaporation of *n*-pentane, the yellow oil was recrystallized from *n*-pentane at –50 °C, affording 1.17 g (70% yield) of compound **5** (^1H NMR pure). An analytically pure sample was obtained by another recrystallization from *n*-pentane at –50 °C: mp 44–45 °C; ^1H NMR 1.35 (s, 3 H), 1.45 (s, 3 H), 1.85 (d, J = 1.5 Hz, 3 H), 3.03 (s, 3 H), 6.24 (q, J = 1.5 Hz, 1 H); ^{13}C NMR 8.1 (q, J = 130 Hz), 11.0, 11.9 (2 q, J = 125 Hz), 29.4 (q, J = 140 Hz), 67.0 (s), 72.1 (s), 130.4 (d, J = 175 Hz), 153.0 (s), 205.8 (s); IR (Nujol) 1460 cm^{-1} (N—C=S);[8b] mass spectrum, molecular ion peak at m/e 167. Anal. Calcd for $C_9H_{13}NS$: C, 64.63; H, 7.83; N, 8.37; S, 19.17. Found: C, 64.6; H, 7.7; N, 8.4; S, 19.2.

Preparation of 1,2,4,5,6-Pentamethyl-2-aza-3-thioxobicyclo[2.2.0]hex-5-ene (6) from 1,2,4,5,6-Pentamethyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (7) and Dimeric (*p*-Methoxyphenyl)thioxophosphine Sulfide. A magnetically stirred solution of 2.0 g of Dewar pyridone **7** (13 mmol) and 2.47 g of $P_2S_4(p\text{-}C_7H_7O)_2$ (6.5 mmol) in 12 mL of HMPA was heated to 90 °C. After 3 min the reaction mixture was cooled to room temperature and poured into 250 mL of water. The water layer was extracted with ether (2 × 100 mL), and the combined ether layers were dried over $MgSO_4$. After evaporation of the solvent, the solid yellow residue was recrystallized from ether (–30 °C), affording 1.54 g (70% yield) of compound **6**: mp 106–107 °C; ^1H NMR 1.30 (s, 3 H), 1.43 (s, 3 H), 1.73 (s, 6 H), 2.99 (s, 3 H); ^{13}C NMR 7.7, 8.7, 8.9, 9.6 (4 q, J = 125 Hz), 28.6 (q, J = 145 Hz), 64.8 (s), 73.1 (s), 139.3 (s), 142.7 (s), 206.8 (s); IR (CCl_4) 1480 cm^{-1} (N—C=S);[8b] mass spectrum, molecular ion peak at m/e 181. Anal. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73; S, 17.68. Found: C, 66.3; H, 8.2; N, 7.5; S, 17.4.

Preparation of Compound 5 from 1,2,4,5-Tetramethyl-3-oxo-2-azabicyclo[2.2.0]hex-5-ene (8) and Dimeric (*p*-Meth-

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(20) Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193.
(21) Hogeveen, H.; Kingma, R. F.; Kok, D. M., *J. Org. Chem.* **1982**, *47*, 989.

oxyphenyl)thioxophosphine Sulfide. A magnetically stirred solution of 604 mg of compound **8** (4 mmol) and 812 mg of $P_2S_4(p\text{-}C_7H_7O)_2$ (2 mmol) in 6 mmol of HMPA was heated to 100 °C. After 45 min the reaction mixture was cooled to room temperature and poured into water. The water layer was extracted with ether (2 × 100 mL), and the combined ether layers were dried over K_2CO_3. After evaporation of the solvent, the solid residue was dissolved in *n*-pentane and treated with activated charcoal. After filtration and evaporation of *n*-pentane, 365 mg (55% yield) of a colorless solid compound was isolated. The ^1H and ^{13}C NMR spectra of this compound were identical with those for compound **5**.

Isomerization of Compound 6 to Compound 2 by CF_3CO-OH. A solution of 2.05 g of CF_3COOH (18 mmol) in 4 mL of CH_2Cl_2 was added to a magnetically stirred solution of 1.63 g of compound **6** (9 mmol) at room temperature. After 0.5 h the ^1H NMR spectrum of a sample of the solution indicated that compound **6** had disappeared. The reaction mixture was poured into 200 mL of an aqueous 1 N NaOH solution, and the alkaline layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over K_2CO_3. After evaporation of the solvent, the oily residue was distilled (short path) at 80 °C (12 mmHg), yielding 1.12 g (69% yield) of compound **2**, according to the ^1H NMR spectrum.

Isomerization of Compound 5 to 1,4,5-Trimethyl-2-thia-3-(methylimino)bicyclo[2.2.0]hex-5-ene (9) by CF_3COOH. A solution of 228 mg of CF_3COOH (2 mmol) was added to a solution of 167 mg of compound **5** (1 mmol) in 0.5 mL of $CDCl_3$ in an NMR tube. After the tube was shaken, the reaction was followed by means of ^1H NMR spectroscopy. After 0.5 h, compound **5** had disappeared, and the reaction mixture was poured into 100 mL of an aqueous 1 N NaOH solution. The alkaline layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over K_2CO_3, and after evaporation of the solvent, 155 mg of a dark brown oil was isolated. The oil was dissolved in *n*-pentane and treated with activated charcoal. After filtration and evaporation of *n*-pentane, 83 mg (48% yield) of compound **9** (96% pure, according to the ^1H NMR spectrum) was obtained as a yellow oil: ^1H NMR 1.38 (s, 3 H), 1.63 (s, 3 H), 1.83 (d, J = 1.5 Hz, 3 H), 3.14 (s, 3 H), 6.49 (q, J = 1.5 Hz, 1 H); ^{13}C NMR 11.5, 12.5, 17.9 (3 q, J = 130 Hz), 41.9 (q, J = 140 Hz), 53.6 (s), 75.6 (s), 139.4 (d, J = 165 Hz), 149.2 (s), 169.0 (s); IR (neat) 1680 cm^{-1} (C=N); mass spectrum, molecular ion peak at m/e 167; exact mass calcd for $C_9H_{13}NS$ m/e 167.077, found m/e 167.076.

Isomerization of Compound 3a to Compound 3b by $AlCl_3$. To a magnetically stirred solution of 486 mg of compound **3a** (2 mmol) in 10 mL of CH_2Cl_2 was added at room temperature 294 mg of $AlCl_3$ (2.2 mmol). The reaction mixture turned instantly black. After 3 days the magnetically stirred solution was poured into 100 mL of an aqueous 1 N NaOH solution. The alkaline layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried over K_2CO_3. After evaporation of CH_2Cl_2, 0.42 g of a brown oil was isolated. According to the ^1H NMR spectrum of this oil both compounds **3a** and **3b** were present. Treatment with *n*-pentane gave 60 mg (12% yield) of compound **3b** as a solid.

Preparation of 2-*tert*-Butyl-1,4,5,6-tetramethyl-2-aza-3-(*tert*-butylimino)bicyclo[2.2.0]hex-5-ene (12). A solution of 1.70 g of di-*tert*-butylcarbodiimide[22] (11 mmol) in 10 mL of CH_2Cl_2 was added dropwise at 0 °C to a mechanically stirred solution of complex 1 ($AlCl_3$), prepared from 1.08 g of 2-butyne (20 mmol) and 1.46 g of $AlCl_3$ (11 mmol), in 35 mL of CH_2Cl_2.[20] After warming to room temperature, the reaction mixture was poured into 200 mL of an aqueous 1 N NaOH solution under vigorous stirring. The alkaline layer was extracted with ether (2 × 100 mL). The combined organic layer was washed with water (1 × 50 mL) and dried over $MgSO_4$. After evaporation of the ether the oily residue was distilled in a Kugelrohr apparatus at 60 °C (0.05 mmHg), affording 1.23 g (47% yield) of compound **12** as a slightly yellow oil: ^1H NMR (recorded on a Varian XL-100 spectrometer) 1.20 (s, 9 H), 1.23 (s, 3 H), 1.26 (s, 9 H), 1.27 (s, 3 H), 1.63 (distorted q, J = 1 Hz, 3 H), 1.68 (distorted q, J = 1 Hz, 3 H); ^{13}C NMR 10.1, 11.1, 12.9, 16.3, 27.5, 32.6 (6 q, J = 125 Hz), 51.8 (s), 54.0 (s), 59.7 (s), 64.7 (s), 140.0 (s), 141.5 (s), 156.8 (s); IR ($CHCl_3$) 1660 cm^{-1} (C=N); mass spectrum, molecular ion peak at m/e 262; exact mass calcd for $C_{16}H_{30}N_2$ m/e 262.241, found m/e 262.242.

Preparation of 1,4,5,6-Tetramethyl-2-phenyl-2-aza-3-(phenylimino)bicyclo[2.2.0]hex-5-ene (13). Compound **13** was prepared analogously to the procedure used for compound **12** by using 2.16 g of 2-butyne (20 mmol), 2.92 g of $AlCl_3$ (22 mmol), and 70 mL of CH_2Cl_2 for the synthesis of complex 1 ($AlCl_3$)[20] and 4.60 g of diphenylcarbodiimide[22] (24 mmol) in 20 mL of CH_2Cl_2. After the workup, 6.2 g of a solid was isolated and recrystallized from methylcyclohexane, affording 4.3 g (70%) of compound **13** as white crystals: mp 127–128 °C; ^1H NMR (CCl_4) 0.90 (s, 3 H), 1.51 (s, 3 H), 1.63 (br s, 3 H), 1.75 (br s, 3 H), 6.50–7.50 (m, 10 H); ^{13}C NMR 9.8, 10.2, 11.1, 12.2 (4 q, J = 130 Hz), 59.5 (s), 66.8 (s), 115.7, 121.1, 122.0, 122.4, 128.2, 128.6 (6 d, J = 160 Hz), 140.8 (s), 142.3 (s), 142.6 (s), 148.9 (s), 159.5 (s); IR (Nujol) 1660 cm^{-1} (C=N); mass spectrum, molecular ion peak at m/e 302. Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.41; H, 7.33; N, 9.27. Found: C, 83.5; H, 7.3; N, 9.2.

Preparation of *N*-Phenyltetramethylpyrrole (14). A solution of 3.06 g of *N*-sulfinylaniline (22 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of complex 1 ($AlCl_3$), prepared from 2.16 g of 2-butyne (40 mmol) and 2.92 g of $AlCl_3$ (22 mmol), in 70 mL of CH_2Cl_2[20] at −85 °C. After the addition the reaction mixture was poured into 200 mL of an aqueous 1 N NaOH solution under vigorous stirring. After a workup analogous to the procedure used for the synthesis of compound **2**, the oily residue was distilled (short path) at 80 °C (0.01 mmHg), affording 1.20 g of pyrrole **14**: ^1H NMR 1.90 (s, 6 H), 1.95 (s, 6 H), 6.40–7.43 (m, 5 H). The ^1H NMR spectrum was identical with the ^1H NMR spectrum of pyrrole **14** obtained by reaction of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene and aniline in refluxing nitromethane.[17]

Preparation of *endo*-4,5-Benzo-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-Oxide (15a). A solution of 1.53 g of *N*-sulfinylaniline (11 mmol) in 10 mL of CH_2Cl_2 was added dropwise at −60 °C to a solution of complex 1 ($AlCl_3$), prepared from 1.08 g of 2-butyne (20 mmol) and 1.46 g of $AlCl_3$ (11 mmol), in 35 mL of CH_2Cl_2.[20] After the mixture warmed to room temperature, the workup procedure was carried out in a manner analogous to that for pyrrole **14**, yielding a solid residue. Recrystallization from methylcyclohexane afforded 1.82 g (74% yield) of **15a**: mp 185–187 °C; ^1H NMR 1.25 (s, 3 H), 1.43 (s, 3 H), 1.59 (distorted q, J = 1.1 Hz, 3 H), 1.81 (distorted q, J = 1.1 Hz, 3 H), 6.26 (s, 1 H), 6.40–7.25 (m, 4 H). ^{13}C NMR 9.4, 10.2, 14.4, 24.0 (4 q, J = 130 Hz), 48.1 (s), 70.6 (s), 120.7, 123.0, 126.6, 126.8 (4 d, J = 160 Hz), 132.0 (s), 132.6 (s), 135.3 (s), 146.4 (s); IR (CCl_4) 3350 (NH), 1050 cm^{-1} (S=O); mass spectrum, m/e 199 ($M^+ - SO$). Anal. Calcd for $C_{14}H_{17}NSO$: C, 67.98; H, 6.93; N, 5.66; S, 12.95. Found: C, 67.8; H, 7.0; N, 5.6; S, 12.8.

Preparation of a Mixture of 15a and *exo*-4,5-Benzo-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-Oxide (15b). The preparation of the mixture was carried out analogously to the synthesis of **15a**, only *N*-sulfinylaniline was added at room temperature. After the workup, the residue contained **15a** and **15b** in a 2:1 ratio. Recrystallization from CCl_4 afforded 690 mg of **15a**. Concentration and further crystallization yielded 360 mg of **15b**: mp 225 °C dec; ^1H NMR 1.25 (distorted q, J = 1.1 Hz, 3 H), 1.58 (br s, 6 H), 1.60 (distorted q, J = 1.1 Hz, 3 H), 6.58 (br s, 1 H), 6.38–7.38 (m, 4 H); ^{13}C NMR 8.2, 8.8, 15.4, 17.7 (4 q, J = 130 Hz), 50.0 (s), 72.7 (s), 120.5, 123.0, 126.0, 127.2 (4 d, J = 160 Hz), 129.1 (s), 132.9 (s), 137.1 (s), 142.4 (s); IR (CCl_4) 3360 cm^{-1} (NH), 1050 cm^{-1} (S=O); mass spectrum, m/e 199 ($M^+ - SO$). Anal. Calcd for $C_{14}H_{17}NSO$: C, 67.98; H, 6.93; N, 5.66; S, 12.95. Found: C, 67.8; H, 6.8; N, 5.7; S, 12.8.

^{13}C NMR Spectroscopic Measurements of Solutions of Complex 1 ($AlCl_3$) and *N*-Sulfinylaniline. A solution of complex 1 ($AlCl_3$) (0.5 M) in 2 mL of CH_2Cl_2 was transferred to a 12-mm (i.d.) NMR tube, kept at −90 °C, followed by 153 mg of N-sulfinylaniline (1.1 mmol) in 2 mL of $CDCl_3$. At −90 °C the ^{13}C NMR spectrum of the solution showed no reaction within 2 h. At −80 °C reaction was observed, and the sp^3 cyclobutene skeleton carbon atoms of (complexed) **15a** appeared at 48.6 and 71.9 ppm. No changes were observed in the spectrum on warming of the sample to room temperature. When the solution of complex 1 ($AlCl_3$) and *N*-sulfinylaniline were combined at 20 °C, a ^{13}C NMR spectrum at −40 °C showed the presence of four sp^3 cy-

(22) Appel, R.; Kleinstuck, R.; Ziehn, K. D. *Chem. Ber.* **1971**, *104*, 1335.

clobutene skeleton carbon atoms at 48.8 (**15a**), 50.5 (**15b**), 72.3 (**15a**), and 73.6 (**15b**) ppm.

Oxidation of Compound 15a with *m*-Chloroperbenzoic Acid to 4,5-Benzo-1,6,7,8-tetramethyl-2-thia-3-azabicyclo-[4.2.0]oct-7-ene 2,2-Dioxide (18). *m*-Chloroperbenzoic acid (811 mg, 85%, technical grade) was added at room temperature to a magnetically stirred solution of 988 mg of **15a** (4 mmol) in 50 mL of benzene. After 5 min, 25 mL of an aqueous 1 N NaOH solution was added, the layers were separated, and the benzene layer was extracted another two times with an aqueous 1 N NaOH solution, followed by acidification of the combined alkaline layers with concentrated hydrochloric acid (pH 1). The acidic layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over K_2CO_3, and evaporation of the solvent afforded 990 mg (94% yield) of sulfonamide **18**. Analytically pure material was obtained by recrystallization from toluene: mp 201 °C; ^1H NMR 1.38 (distorted q, J = 1.5 Hz, 3 H), 1.58 (s, 3 H), 1.65 (s, 3 H), 1.78 (distorted q, J = 1.5 Hz, 3 H), 6.50–7.58 (m, 5 H); ^{13}C NMR 8.3, 9.1, 12.1, 17.2 (4 q, J = 130 Hz), 54.8 (s), 70.8 (s), 121.2, 125.0, 126.8, 127.6 (4 q, J = 160 Hz), 130.7 (s), 136.3 (s), 136.5 (s), 143.3 (s); IR ($CHCl_3$) 1150 (SO_2), 3360 cm^{-1} (NH); mass spectrum, molecular ion peak at m/e 263. Anal. Calcd for $C_{14}H_{17}NSO_2$: C, 63.80; H, 6.58; N, 5.31; S, 12.14. Found: C, 63.9; H, 6.5; N, 5.4; S, 12.2.

Oxidation of Compound 15b with *m*-Chloroperbenzoic Acid to Compound 18. The procedure was analogous to the oxidation of **15a** and used 494 mg (2 mmol) of **15b**, 405 mg of *m*-chloroperbenzoic acid (85%, technical grade), and 25 mL of benzene affording 480 mg of (91% yield) sulfonamide **18**. The melting point and ^1H and ^{13}C NMR spectra were identical with those of the compound obtained from the oxidation of **15a**.

Preparation of 1,3,4,5,6-Pentamethyl-1-aza-2-thioxocyclohexa-3,5-diene (19) from Compound 2 with 2 Equiv of CF_3COOH. A solution of 2.05 g of CF_3COOH (18 mmol) in 2 mL of CH_2Cl_2 was added at room temperature to a magnetically stirred solution of 540 mg of **2** in 8 mL of CH_2Cl_2. After 10 days the ^1H NMR spectrum of a sample of the solution indicated that **2** had disappeared. After a workup analogous to the procedure used for the synthesis of **2** from **6**, 1.52 g of a yellow solid was isolated. Recrystallization from CH_2Cl_2/ether afforded analytically pure **19**: 1.12 g (69% yield); mp 215–218 °C; ^1H NMR 2.16 (s, 3 H), 2.21 (s, 3 H), 2.49 (s, 3 H), 2.55 (s, 3 H), 4.18 (s, 3 H); ^{13}C NMR 15.7, 17.8, 18.4, 20.2 (4 q, J = 130 Hz), 42.0 (q, J = 140 Hz), 121.0 (s), 136.0 (s), 142.9 (s), 143.2 (s), 176.7 (s); mass spectrum, molecular ion peak at m/e 181. Anal. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73; S, 17.68. Found: C, 66.0; H, 8.2; N, 7.6; S, 17.7.

Preparation of 1,3,4,5,6-Pentamethyl-2-(methylthio)-pyridinium Iodide (20) from Compound 19 and Methyl Iodide. A solution of 1.4 g of methyl iodide (10 mmol) in 5 mL of CH_2Cl_2 was added to a solution of 360 mg (2 mmol) of **19** at room temperature. After 10 min the ^1H NMR spectrum of a sample of the solution showed that **19** had disappeared. Evaporation of CH_2Cl_2 and CH_3I, under high vacuum [20 °C (0.005 mmHg)], afforded **20** (pure according to the ^1H NMR spectrum) as a yellow powder: 635 mg (99% yield); ^1H NMR 2.41 (s, 6 H), 2.55 (s, 3 H), 2.65 (s, 3 H), 2.88 (s, 3 H), 4.55 (s, 3 H); ^{13}C NMR 16.0 (q, J = 130 Hz), 18.0 (q, J = 145 Hz), 18.2, 18.5, 20.0 (3 q, J = 130 Hz), 44.7 (q, J = 145 Hz), 134.6 (s), 138.8 (s), 148.3 (s), 152.7 (s), 153.1 (s).

Thermal Conversion of Compound 2 to 4-[(Methylamino)thiocarbonyl]-1,2,4-trimethyl-3-methylenecyclobut-1-ene (21). Compound **2** (1.0 g, 5.5 mmol) was dissolved in 25 mL of chlorobenzene and refluxed for 30 min (**2** has disappeared according to the ^1H NMR spectrum). After evaporation of chlorobenzene, the oil residue was sublimed at 90 °C (0.005 mmHg), affording **21**: 600 mg (60% yield); mp 53–53.5 °C; ^1H NMR 1.60 (s, 3 H), 1.63 (br s, 3 H), 1.85 (br s, 3 H), 3.04 (d, J = 4.9 Hz, 2 H), 4.43 (s, 1 H), 7.6–8.5 (broad absorption, 1 H); ^{13}C NMR 8.2, 9.0, 20.7 (3 q, J = 125 Hz), 31.6 (q, J = 140 Hz), 63.4 (s), 91.7 (t, J = 160 Hz), 139.2 (s), 152.6 (s), 153.6 (s), 205.2 (s); IR 3360 (NH), 1445 cm^{-1} (N—C=S); mass spectrum, molecular ion peak at m/e 181. Anal. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73; S, 17.68. Found: C, 66.3; H, 8.3; N, 7.7, S, 17.6.

Thermal Conversion of Compound 6 to Compound 21. Compound **6** (2.0 g, 11 mmol) was dissolved in 40 mL of chlorobenzene and refluxed for 4 h (**6** had disappeared according to the ^1H NMR spectrum). After evaporation of chlorobenzene, the oily residue was sublimed at 90 °C (0.005 mmHg), yielding 1.50 g of **21** (75% yield). The melting point and ^1H NMR spectrum were identical with the data for the compound obtained by thermolysis of **2**.

Conversion of Compound 21 to Compound 2 with CF_3CO-OH. A solution of 228 mg of CF_3COOH (2 mmol) in 1 mL of CH_2Cl_2 was added to a magnetically stirred solution of 180 mg of **21** (1 mmol) in 2 mL of CH_2Cl_2. According to the ^1H NMR spectrum of a sample of the solution, compound **21** had vanished within 5 min. A workup analogous to the procedure used for the synthesis of **2** from **6** afforded 136 mg of **2** (76% yield; pure according to the ^1H NMR spectrum). The ^1H NMR spectrum of this compound was identical with the spectrum of the compound obtained by reaction of complex **1** ($AlCl_3$) with methyl isothiocyanate.

Photochemical Conversion of Compound 6 to Compound 19. A solution of 900 mg of **6** (5 mmol) in 150 mL of CH_2Cl_2 was irradiated with a Hanau Q-81 high-pressure mercury arc at room temperature during 6 h. Evaporation of the solvent left a yellow solid, which was sublimed at 140 °C (0.1 mmHg), giving 657 mg of **19** (73% yield). The ^1H NMR spectrum of this compound was identical with the spectrum of the compound obtained by reaction of **2** with CF_3COOH.

Conversion of Compound 2 to 3,4,5,6-Tetramethyl-1-thia-2-(methylimino)cyclohexa-3,5-diene (24). A solution of 150 mg of **2** (0.83 mmol) in 8 mL of methanol was refluxed for 15 days. A ^1H NMR spectrum of a sample of the solution showed that **2** had vanished. After evaporation of the solvent, 145 mg of a yellow solid was obtained, which was purified by recrystallization from *n*-hexane at −50 °C, affording 102 mg (70% yield) of **24** (pure according to the ^1H NMR spectrum) as an orange-yellow solid: mp 79–82 °C; ^1H NMR 2.05 (s, 3 H), 2.18 and 2.20 (both s, together 9 H), 3.23 (s, 3 H); ^{13}C NMR 15.2, 16.6, 18.5, 21.1 (4 q, J = 130 Hz), 39.6 (q, J = 135 Hz), 124.4 (s), 128.1 (s), 128.2 (s), 138.5 (s), 159.2 (s); mass spectrum, molecular ion peak at m/e 181; exact mass calcd for $C_{10}H_{15}NS$ m/e 181.093, found 181.091.

Registry No. 1, 31886-99-4; **2**, 81045-13-8; **3a**, 81045-14-9; **3b**, 81045-15-0; **4**, 80206-71-9; **5**, 81045-16-1; **6**, 81045-17-2; **7**, 38052-13-0; **8**, 80206-55-9; **9**, 81045-18-3; **12**, 81045-19-4; **13**, 81045-20-7; **14**, 1015-63-0; **15a**, 81045-21-8; **15b**, 81129-81-9; **18**, 81045-22-9; **19**, 81045-23-0; **20**, 81045-24-1; **21**, 81045-25-2; **24**, 81045-26-3; methyl isothiocyanate, 556-61-6; 2-butyne, 503-17-3; phenylisothiocyanate, 103-72-0; di-*tert*-butylcarbodiimide, 691-24-7; ciphenylcarbodiimide, 622-16-2; *N*-sulfinylaniline, 1122-83-4.