α-Halo Sulfones. XII. The Chlorination of Bridgehead Sulfides and Sulfones. Transannular Double-Bond Formation in the Base-Induced Rearrangement of Bridgehead α-Chloro Sulfones[1]

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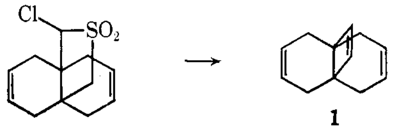
Abstract: Direct chlorination–oxidation of 9-thiabicyclo[3.3.1]nonane (**2**) and 8-thiabicyclo[3.2.1]octane (**11**) did not result in the expected introduction of an α-chloro substituent. Rather, *endo*-2-chloro sulfones were produced; these unprecedented reactions very likely proceed *via* a cleavage–recombination mechanism involving intermediate sulfenyl chlorides. Treatment of the 2-chloro sulfones with potassium *t*-butoxide led to replacement of halogen by *t*-butoxy with retention of configuration, the stereochemical outcome requiring the intervention of highly strained α,β-unsaturated sulfones in which the double bonds occupy bridgehead positions. The sulfones derived from **2** and **11** lent themselves to facile bridgehead carbanion formation. Treatment of such carbanions with sulfuryl chloride and thermal desulfonylation of the resulting bridgehead sulfonyl chlorides permitted synthetic entry to the required bridgehead α-chloro sulfones, the base-induced rearrangement of which was examined as a method for the controlled introduction of transannular double bonds.

The base-induced rearrangement of acyclic α-halo sulfones possessing at least one α′ hydrogen atom results in clean and unequivocal replacement of the halogen and sulfonyl groups by a carbon–carbon double bond.[3] Although the application of this reaction to cyclic α-halo sulfones has been much less studied, the examples reported to date appear to follow the same course despite adverse conformational and strain factors in certain cases. Most noteworthy among these latter rearrangements is the recently reported application to the synthesis of cyclobutenes such as **1**.[4] In an extension of our earlier work,[1,5] we have considered the possibility of applying the α-halo sulfone rearrangement to sulfur-bridged carbocycles with the intent of uncovering a valuable synthetic method for the controlled formation of a transannular double bond. In view of the several reaction techniques now available for the convenient preparation of sulfur-bridged carbocycles,[6–10] the intended transformation assumes added significance and general utility. Furthermore, the investigation of such systems was expected to provide revealing information about the stereochemistry of the 1,3 elimination of hydrogen chloride in α-chloro sulfones and the mechanism of chlorination of divalent organosulfur compounds.[11]



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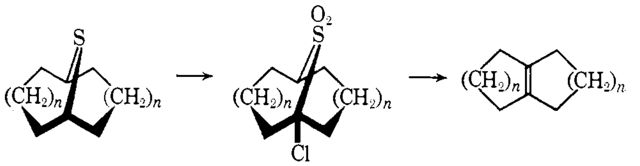

Chlorination of Thiabicycloalkanes. The reaction of sulfides with chlorine,[12] thionyl chloride,[13] sulfuryl chloride,[14] or N-chlorosuccinimide[15] are well-known methods for the preparation of α-chloro sulfides. Since these chlorinations proceed by way of a sequence of steps involving intermediate S-chlorosulfonium salts and ylides or sulfocarbonium ions, they appear to be related mechanistically to the Pummerer rearrangement.[16] Only in isolated cases has carbon–sulfur bond cleavage in a halosulfonium salt been observed, the known examples proceeding because of the fragmentation of a stable carbonium ion.[17] For this

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(1) For previous paper in this series, see L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **90**, 6790 (1968).

(2) NDEA Fellow, 1967 to present.

(3) For recent reviews of this subject, see (a) L. A. Paquette, *Accounts Chem. Res.*, 1, 209 (1968); (b) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1968, pp 121–156.

(4) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); J. C. Philips, unpublished observations.

(5) L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **90**, 6783 (1968), and earlier papers in this series.

(6) (a) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **22**, 1590 (1957); (b) S. F. Birch, R. A. Dean, and N. J. Hunter, *ibid.*, **23**, 1026 (1958).

(7) (a) V. Horak, J. Zavada, and A. Piskala, *Chem. Ind.* (London), 1113 (1958); (b) V. Horak, *Collect. Czech. Chem. Commun.*, **28**, 1614 (1963); (c) V. Horak, J. Zavada, and A. Piskala, *Acta Chim. Acad. Sci. Hung.*, 21, 97 (1959).

(8) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966); (c) F. Lautenschlager, *ibid.*, 31, 1679 (1966); (d) F. Lautenschlager, *Can. J. Chem.*, **44**, 2813 (1966); (e) F. Lautenschlager, *J. Org. Chem.*, 33, 2627 (1968); (f) P. Y. Blanc, P. Diehl, H. Fritz, and P. Schlaepfer, *Experientia*, **23**, 896 (1967).

(9) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3065, 3073 (1965).

(10) T. W. Craig, G. R. Harvey, and G. A. Berchtold, *J. Org. Chem.*, 32, 3743 (1967).

(11) L. A. Paquette, L. S. Wittenbrook, and K. Schreiber, *ibid.*, **33**, 1080 (1968), and references cited therein.

(12) (a) W. E. Lawson and T. P. Dawson, *J. Amer. Chem. Soc.*, **49**, 3119 (1927); (b) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949); (c) H. Böhme and H.-J. Gran, *ibid.*, **577**, 68 (1952); (d) H. Richtzenhain and B. Alfredsson, *Chem. Ber.*, **86**, 142 (1953); (e) H. Böhme and H.-J. Gran, *Ann.*, **581**, 133 (1953).

(13) W. E. Truce, G. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, 74, 3594 (1952).

(14) (a) F. G. Bordwell and B. M. Pitt, *ibid.*, 77, 572 (1955); (b) L. A. Paquette, *ibid.*, **86**, 4085 (1964); (c) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967); (d) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).

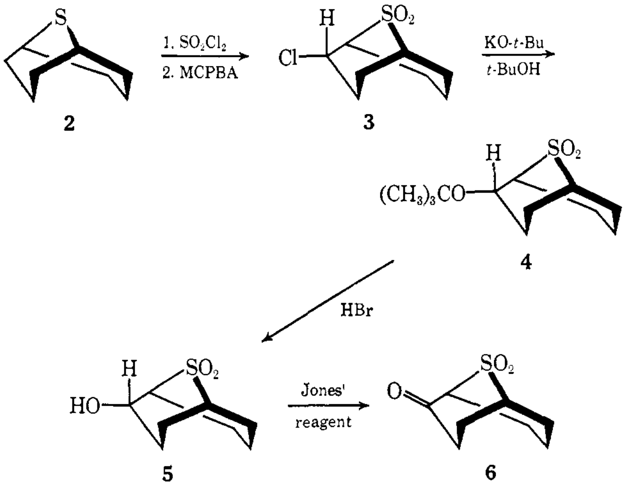
(15) (a) D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, **32**, 204 (1967); (b) D. L. Tuleen, *ibid.*, **32**, 4006 (1967); (c) D. L. Tuleen and T. B. Stephens, *Chem. Ind.* (London), 1555 (1966).

(16) G. A. Russell and G. J. Mikol, ref 3b, pp 157–207.

(17) (a) K. C. Schreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 2910 (1961); (b) D. S. Tarbell and D. P. Harnish, *J. Amer. Chem. Soc.*, 74, 1862 (1952); (c) G. E. Wilson, Jr., *ibid.*, **87**, 3785 (1965); (d) G. E. Wilson, Jr., and R. Albert, *Tetrahedron Lett.*, 6271 (1968).

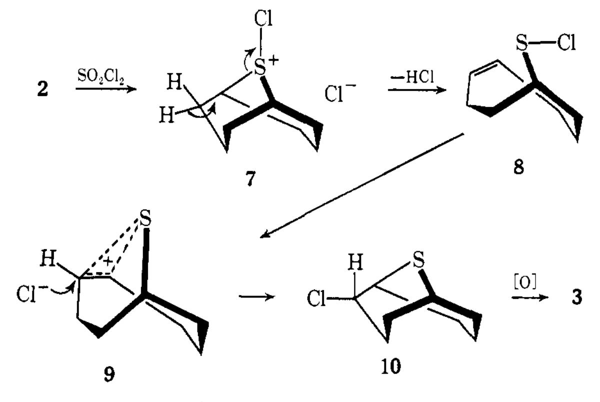
reason, it was surprising to observe that chlorination of 9-thiabicyclo[3.3.1]nonane (2)[8a,b] with sulfuryl chloride in carbon tetrachloride solution and subsequent oxidation of the resulting chloro sulfide with *m*-chloroperbenzoic acid (MCPBA) led not to the anticipated α-chloro sulfone, but rather to *endo*-2-chloro-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (3) in 68% yield. The structural assignment of this product was founded upon direct comparison with an authentic sample[8a] and by conversion to the known *endo* alcohol 5[8b] (Scheme I).

Scheme I



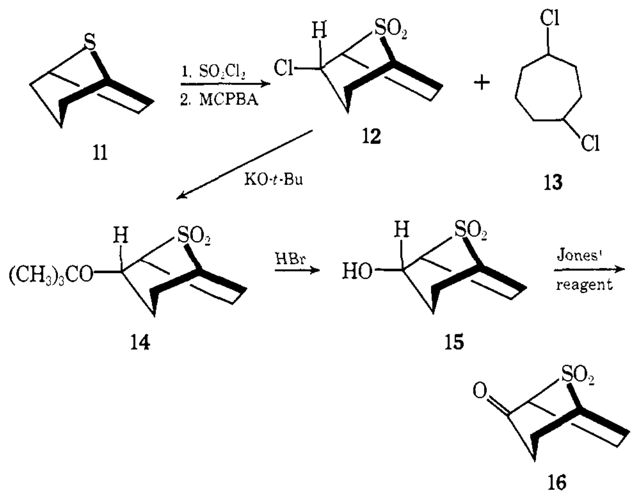
Therefore, the chlorination of 2 results in carbon–sulfur bond cleavage in which carbonium ion formation does not provide a driving force. Rather, the fragmentation in this instance appears to be governed by sulfur, probably as a result of favorable conformational effects and an advantageous stability–reactivity index in medium ring sulfenyl chloride 8 under the reaction conditions. The postulation of 8 as an intermediate best fits our observations (Scheme II).[18] Thus, attack of sulfuryl chloride on 2 can give rise initially to 7 which now can fragment with the loss of hydrogen chloride. Intramolecular attack of the sulfenyl chloride functionality in 8 upon the proximate transannular double bond is expected to be facile and to result in the formation of classical episulfonium ion 9. Subsequent attack by chloride ion with inversion of configuration at the carbon center should afford *endo* chloride 10. The contention that episulfonium ion 9 intervenes in passing from 2 to 10 is supported by the exclusive *endo* stereochemistry found of the chloro substituent in 3.

Scheme II



Similarly, chlorination–oxidation of the more strained bridged sulfide 11 led to the formation of an *endo*-2-chloro sulfone (12, Scheme III). However, the yield of 12 was only 15%, the major product in this instance being a dichloride tentatively identified as 1,4-dichlorocycloheptane (13, 80%). In the latter case, it would appear that the intermediate chlorosulfonium chloride or sulfenyl chloride is intercepted by a side reaction which proceeds at a rate competitive with the expected slower rate of cyclization of the sulfenyl chloride. Apart from the spectral confirmation of structure 12 (see Experimental Section), this chloro sulfone has demonstrated a reactivity exactly paralleling that of 3. For example, treatment of 12 with a solution of potassium *t*-butoxide in *t*-butyl alcohol afforded *endo-t*-butoxy sulfone 14, cleavage of which with concentrated aqueous hydrobromic acid gave *endo*-hydroxy sulfone 15. Oxidation of 15 with Jones' reagent led to keto sulfone 16 which exhibits carbonyl absorption at 1727 cm^{-1} characteristic of six-membered β-keto sulfones.[19] The *endo* stereoalignment of the β-sulfonyl substituents in 12–15 was derived by direct comparison of the relevant nmr spectra with those of 3–5 whose stereochemistry has been previously established.[8a,b] The excellent correspondence in chemical shifts and coupling constants for H-1 and H-2 in the two series is consistent only with the indicated assignments.

Scheme III



The mechanism of displacement of the chlorine substituent in 3 and 12 by *t*-butoxide is of interest. Since these substitutions proceed with *retention* of configuration, an SN2 pathway cannot be invoked. Nor is an SN1 process favored by theoretical considerations. Rather, a sequence involving base-catalyzed elimination of hydrogen chloride followed by Michael addition of *t*-butoxide ion satisfactorily accommodates the stereochemical features of the replacement reaction. It is significant that this mechanistic scheme requires the intervention of α,β-unsaturated sulfones 17 and 18 in which the double bonds occupy bridgehead positions. Despite the fact that such sulfones were expected to be

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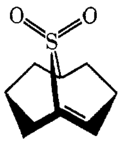
(18) For a recent review of the chemistry of sulfenyl halides, see N. Kharasch, Z. S. Ariyan, and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, 1, 93 (1966).

(19) Several such compounds which have been prepared in this laboratory show the same carbonyl stretching band at 1718–1727 cm^{-1}: 6, $\nu_{max}^{CHCl_3}$ 1718 cm^{-1}; 2-benzenesulfonylcyclohexanone, $\nu_{max}^{CHCl_3}$ 1720 cm^{-1}.

extremely reactive toward *t*-butoxide ion, several attempts were made to isolate and characterize **17**; not unsurprisingly, however, **4** was always the only product obtained under the conditions employed. It is entirely plausible that in this instance the rate of Michael addition very likely exceeds the rate of the elimination reaction so that only the product of kinetic control is isolatable. The *endo* stereoselectivity which obtains in the addition of *t*-butyl alcohol to **17** and **18** follows from the substantial shielding exerted by the sulfonyl group on the *exo* surface.



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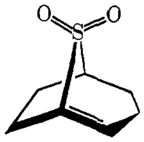

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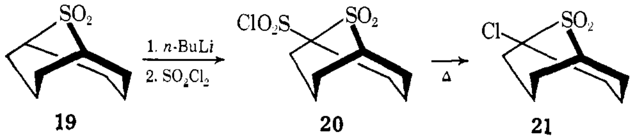
Recent work has established that the practical limit of Bredt's rule in an unsaturated hydrocarbon is $S = 7$.[20,21] The above findings suggest that when one of the bridges consists of a sulfur atom, the molecule will more readily tolerate the placement of a double bond at a bridgehead position. Apparently, the greater van der Waals radius of sulfur (1.04 Å)[22] is sufficient to reduce the torsional forces imposed on the π orbital, thereby permitting the parallel condition required for overlap *even when* $S = 6$. Reviewing these facts, we can conclude that **18**, although only a transient intermediate, very likely is now the most flagrant known violator of Bredt's rule.

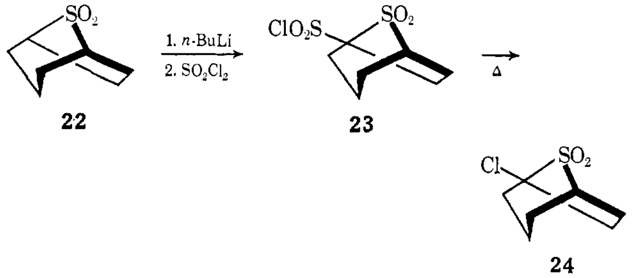
Chlorination of Bridgehead α-Sulfonyl Carbanions. In view of the fact that the desired bridgehead chlorinated sulfones were not available by direct chlorination–oxidation of the parent sulfur-bridged carbocycles, the feasibility of chlorinating bridgehead α-sulfonyl carbanions was examined. Assurance that the sulfonyl group would be capable of stabilizing an adjacent bridgehead carbanion was gained some years ago by Doering and Levy.[23] In the present work, sulfone **19** was found to react readily with *n*-butyllithium to yield the related α-sulfonyl carbanion which when treated with excess sulfuryl chloride at 0° gave rise to bridgehead sulfonyl chloride **20** (Scheme IV). This sulfonyl chloride underwent smooth thermal decomposition at 160° (0.05 mm) with evolution of sulfur dioxide and formation of the desired α-chloro sulfone (**21**).

Scheme IV



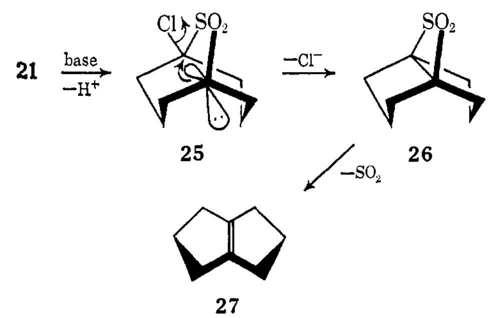
1-Chloro-8-thiabicyclo[3.2.1]octane 1,1-dioxide (**24**) was likewise conveniently prepared from the corresponding sulfone (**22**, Scheme V).

Scheme V



Base-Induced Rearrangements. Reaction of **21** with aqueous potassium hydroxide at 100° was observed to result in the gradual liberation of chloride ion and the formation of a volatile hydrocarbon. Processing of the reaction mixture after 48 hr led to the isolation of the desired hydrocarbon, $\Delta^{1,5}$-bicyclo[3.3.0]octene (**27**), in 75% yield. Thus, through a series of convenient steps, the interesting hydrocarbon **27** can now be prepared in large quantities. Although certain symmetrical 3,7-substituted derivatives of $\Delta^{1,5}$-bicyclo[3.3.0]octene have been described,[24] the only previous synthesis of the unsubstituted olefin is a low yield multistep sequence with cyclobutanone as starting material.[25] Since a substantial number of derivatives of sulfide **21** are now readily available,[8] synthetic entry to a wide variety of substituted $\Delta^{1,5}$-bicyclo[3.3.0]octenes with known stereochemistry should now be capable of realization.

Scheme VI



Treatment of chloro sulfone **24** with KO-*t*-Bu–*t*-BuOH (no reaction observed with KOH–H_2O) led to the disappearance of starting material, but none of the expected hydrocarbon $\Delta^{1,5}$-bicyclo[3.2.0]heptene (**28**) was produced. Rather, a viscous inhomogeneous oil was obtained whose mass spectrum indicated it to be approximately trimeric in nature. Because an authentic sample of **28**[26,27] proved to be stable to the reaction conditions, it may be concluded that the successful outcome of the rearrangement was intercepted at some intermediate step.

The course of the novel transannular 1,3 elimination depicted in Scheme VI deserves further comment. Firstly, attention should be called to the fact that the acidic proton and chlorine substituent in **21** are rigidly held in a W-plan relationship to each other.[28] It

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(20) (a) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967); (b) J. R. Wiseman, *ibid.*, **89**, 5968 (1967).

(21) S, the strain number for a bicyclo[x,y,z] compound, is defined as $x + y + z$ (x, y, and $z = 0$): F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

(22) By comparison, the single-bond van der Waals radius of carbon is 0.77 Å: J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 28.

(23) W. von E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, **77**, 509 (1955).

(24) A. C. Cope and F. Kagan, *ibid.*, **80**, 5499 (1958); A. C. Cope and W. J. Keller, *ibid.*, **80**, 5502 (1958).

(25) E. Vogel, *Chem. Ber.*, **85**, 25 (1952).

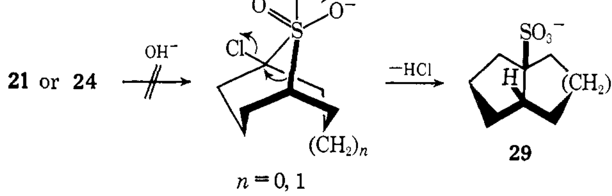
(26) W. Kirmse and K. H. Pook, *Angew. Chem. Int. Ed. Engl.*, **5**, 594 (1966).

(27) We thank Professor P. G. Gassman for making available to us the authentic specimen of **28**.

(28) In this analysis, the SO_2 group is employed as atom 3. For an analysis of this classification system, see A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967).

follows that the transition state of the observed 1,3 elimination must also adopt this topological arrangement because of the existing molecular constraint. Therefore, the cyclization of **21** to intermediate episulfone **26** corresponds to the first authenticated example of a base-initiated 1,3 elimination from an α-halo sulfone which must necessarily proceed both by way of the W-plan mechanism and inversion of configuration at the two reacting centers. Previously, this mechanism has been invoked to explain the preferential formation of *cis*-alkenes from acyclic α-halo sulfones.[3a,5] Also, Bordwell and coworkers recently provided compelling evidence that triphenylphosphine-induced 1,3 elimination of bromine from *dl*- and *meso*-$PhCHBrSO_2CHBrPh$ occurs with double inversion at C-1 and C-3.[29] The closely analogous nature of these systems suggests that the concepts proposed earlier[3a,5] are not implausible. Perhaps the most remarkable aspect of the conversion of **21** to **26** is the apparent ease with which the α-sulfonyl carbanion undergoes inversion of configuration despite the fact that the negatively charged orbital is situated at a bridgehead position.

Because it is well established that the Favorskii reaction of carbonyl-bridged α-halo ketones can proceed by either a cyclopropanone or semibenzilic mechanism,[30] we have searched carefully for semibenzilic-type behavior in the case of **21** and **24**. Careful work-up of the alkaline aqueous layers from these rearrangements gave no evidence that sulfonates of structure **29** had been produced. It would appear, therefore, that direct attack of hydroxide ion at tetravalent sulfur is not a competitive reaction in these sulfur-bridged systems.



Experimental Section[31]

Chlorination–Oxidation of 9-Thiabicyclo[3.3.1]nonane (2). To a stirred solution of 8.0 g (0.056 mol) of **2**[8a,b] in 190 ml of carbon tetrachloride was added dropwise under a nitrogen atmosphere a solution of 8.38 g (0.062 mol, 10% excess) of sulfuryl chloride in 10 ml of the same solvent. The reaction mixture was refluxed until all of the precipitated salt dissolved. The solvent was evaporated and the residue was dissolved in 200 ml of anhydrous ether. To this cold (0°) solution was added with stirring a solution of 24.4 g (0.113 mol) of 80% *m*-chloroperbenzoic acid in 125 ml of ether and the reaction mixture was allowed to stir overnight at room temperature. The solution was washed with 50 ml of saturated sodium bisulfite solution and with four 100-ml portions of saturated sodium bicarbonate solution and dried. There was obtained 8.0 g (68%) of **3** as white crystals, mp 180–183° (from cyclohexane). This sample was found to be identical with an authentic sample of *endo*-2-chloro-9-thiabicyclo[3.3.1]nonane 9,9-dioxide (lit.[8b] mp 186–187.5°).

Anal. Calcd for $C_8H_{13}ClO_2S$: C, 46.04; H, 6.28; S, 15.36. Found: C, 46.06; H, 6.35; S, 15.40.

Reaction of 3 with Potassium *t*-Butoxide. To a potassium *t*-butoxide solution [prepared for 0.82 g (0.03 g-atom) of potassium metal and 20 ml of dry, freshly distilled *t*-butyl alcohol] was added 722 mg (3.5 mmol) of **3** and the solution was refluxed for 12 hr. After the addition of 50 ml of water, the aqueous suspension was extracted with two 100-ml portions of ether. The combined ether extracts were washed with three 50-ml portions of water and dried. Removal of the solvent *in vacuo* and trituration of the remaining oil with benzene–hexane afforded 700 mg (81.5%) of **4**, mp 120–125°. Three recrystallizations from pentane gave pure *endo*-2-(*t*-butoxy)-9-thiabicyclo[3.3.1]nonane 9,9-dioxide, mp 123–125°; $\delta_{\max}^{\mathrm{CDCl_3}}$ 4.36 (multiplet, 1 H, >C*H*O–), 2.87 (broad absorption, 2 H, >C*H*SO₂–), 2.10 (multiplet, 10 H, $-CH_2-$), and 1.21 (singlet, 9 H, *t*-butyl group).

Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.51; H, 9.00; S, 12.99. Found: C, 58.69; H, 8.98; S, 12.81.

***endo*-2-Hydroxy-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (5).** To 50 ml of 47–49% hydrobromic acid was added 1.91 g (7.8 mmol) of **4** and the resulting solution was refluxed for 100 min. Water (100 ml) was added and the solution was continuously extracted with ether for 24 hr. The ether extract was dried and evaporated to provide 610 mg of white solid. The acid solution was made alkaline and again extracted with ether. An additional 530 mg of the same solid was obtained (total yield, 77.5%). The combined solids were sublimed (145° (0.08 mm)) and recrystallized from ethyl acetate; white crystals, mp 326–328° (lit.[8b] 329–330°). A mixture melting point with authentic **5** was undepressed and the respective spectra were identical.

2-Oxo-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (6). A solution of 70 mg (0.39 mmol) of **5** in 5 ml of acetone was treated with 2.5 mmol of Jones' reagent.[32] After being stirred for 30 min, the excess reagent was decomposed with methanol. The solution was decanted from the sludge and 25 ml of ether was added. The resulting organic phase was washed with water and saturated sodium bicarbonate solution and dried. Evaporation of the ether yielded 35 mg (47%) of **6**, mp 275–278° (from chloroform–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1718 (>C=O), 1310 and 1120 cm⁻¹ ($-SO_2-$).

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.07; H, 6.38; S, 17.04. Found: C, 51.90; H, 6.25; S, 16.85.

8-Thiabicyclo[3.2.1]octane (11). To a solution of 24.4 g (0.173 mol) of 3-oxo-8-thiabicyclo[3.2.1]octane[7] and 3 g of potassium hydroxide in 200 ml of diethylene glycol was added 30 ml of 98% hydrazine hydrate. The mixture was heated to reflux and the water and excess hydrazine were removed by means of a take-off condenser. After all the water had been removed, the solution was allowed to reflux for 15 min during which time the hydrazone was seen to collect in the take-off condenser and to be returned by hot solvent into the flask. A distillation head was placed on top of the take-off condenser and sulfide **11** was slowly allowed to distil and solidify in an ice bath. The solid was washed with water and dried to give 15.2 g (68.5%) of **11**, mp 175–177° (sealed tube) (lit.[6a] mp 176.5–178.5°).

Chlorination–Oxidation of 11. Treatment of 6.8 g (0.053 mol) of **11** with 8.0 g (0.058 mol) of sulfuryl chloride in 300 ml of carbon tetrachloride as above, followed by oxidation with 0.25 mol of monoperphthalic acid[33] in ether, gave 10.3 g of yellow oil. Chromatography of this oil on neutral alumina and elution with pentane gave 7.0 g (79.5%) of 1,4-dichlorocycloheptane, bp 74–76.5° (1 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.30 (broad singlet, 2 H, >C*H*Cl) and 2.10 (multiplet, 10 H, methylene groups).

Anal. Calcd for $C_7H_{12}Cl_2$: C, 50.35; H, 7.17. Found: C, 50.59; H, 7.20.

Elution with ether–hexane (1:1) gave 1.5 g (14.6%) of *endo*-2-chloro-8-thiabicyclo[3.2.1]octane 9,9-dioxide, mp 164–165° (from ethyl acetate); $\nu_{\max}^{\mathrm{CCl_4}}$ 1310, 1160, and 1110 cm⁻¹ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.50 (multiplet, 1 H, >C*H*Cl), 3.00 (multiplet, 2 H, >C*H*SO₂–), and 2.10 (multiplet, 8 H, $-CH_2-$).

Anal. Calcd for $C_7H_{11}ClO_2S$: C, 43.20; H, 5.65; Cl, 18.22; S, 16.44. Found: C, 42.95; H, 5.87; Cl, 17.91; S, 16.12.

***endo*-2-(*t*-Butoxy)-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (14).** To a solution of 720 mg (3.7 mmol) of **12** in 30 ml of freshly distilled

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(29) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, 90, 5298 (1968).

(30) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *ibid.*, 90, 514 (1968).

(31) All melting points are corrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer and nmr spectra were recorded with Varian A-60 or A-60A spectrometers. The mass spectrum was measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

(32) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(33) H. Böhme, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 619.

t-butyl alcohol was added 2.25 g (0.02 mol) of powdered potassium *t*-butoxide, and the resulting mixture was heated at reflux for 12 hr. After the addition of 100 ml of ether, the solution was washed with two 50-ml portions of water and dried. The solvent was evaporated to give 365 mg (42.5%) of **14**, mp 75–78° (from pentane); $\nu_{\max}^{\mathrm{CCl_4}}$ 1300, 1165, and 1110 cm^{-1} ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CHCl_3}}$ 4.10 (multiplet, 1 H, >CHO–), 2.80 (broad absorption, 2 H, >C*H*SO$_2$–), 2.00 (multiplet, 8 H, $-CH_2-$), and 1.18 (singlet, 9 H, *t*-butyl group).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.40; H, 8.95; S, 13.81. Found: C, 56.25; H, 8.54; S, 13.98.

***endo*-2-Hydroxy-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (15).** A 269-mg (1.16 mmol) sample of **14** was refluxed in 10 ml of hydrobromic acid (47–49%) for 10 hr. Work-up in the predescribed manner yielded 104 mg (51%) of **15**, mp 295–297° (from ethyl acetate–pentane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3400 (–OH), 1300, 1155, and 1105 cm^{-1} ($-SO_2-$).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.73; H, 6.81; S, 18.21. Found: C, 47.73; H, 6.88; S, 18.00.

Oxidation of 50 mg of **15** with Jones' reagent as above yielded 39 mg of 2-oxo-8-thiabicyclo[3.2.1]octane 8,8-dioxide (**16**), mp 256–258° (from chloroform–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1727 (>C=O), 1320, 1150, and 1110 cm^{-1} ($-SO_2-$).

1-Chlorosulfonyl-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (20). To a solution of 5.0 g (0.029 mol) of **19**[8a,b] in 200 ml of ether was added dropwise with stirring under nitrogen 28 ml of 1.6 *M* (0.045 mol) *n*-butyllithium in hexane. The yellow solution was stirred at room temperature for 10 min and was then added to 25 ml of sulfuryl chloride cooled to 0°. The resulting mixture was stirred at room temperature for 1 hr and the ether and excess sulfuryl chloride were removed *in vacuo*. Methylene chloride (200 ml) was added and the organic phase was washed with water (two 100-ml portions), dried, and concentrated to a volume of 50 ml. An equal volume of hexane was added and the solution was cooled overnight at 0°. There was obtained 2.3 g (28.4%) of **20** as white crystals, mp 163–165°, from chloroform–hexane; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1380, 1170 ($-SO_2Cl$), 1325, and 1135 cm^{-1} ($-SO_2-$).

1-Chloro-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (21). A 1.5-g (7.2 mmol) sample of **20** was placed in a sublimation apparatus and was heated at 160° (0.05 mm). As decomposition occurred, the chloro sulfone (660 mg, 59%) sublimed. Recrystallization of this material from ethyl acetate provided the analytical sample, mp 229–231° (sealed tube); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1312, 1120, and 1110 cm^{-1} ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.30 (multiplet, 1 H, >C*H*SO$_2$–) and 2.40 (multiplet, 12 H, $-CH_2-$).

Anal. Calcd for $C_8H_{13}ClO_2S$: C, 46.05; H, 6.23; Cl, 17.00; S, 15.37. Found: C, 45.96; H, 6.27; Cl, 17.04; S, 15.35.

$\Delta^{1,5}$-Bicyclo[3.3.0]octene (27). To a solution of 2.0 g (0.036 mol) of potassium hydroxide in 100 ml of water was added 1.25 g (6.0 mmol) of **21** and the mixture was refluxed for 48 hr. The reaction mixture was cooled, pentane (50 ml) was added, and the precipitate was filtered and dried. There was recovered 310 mg (25%) of **21**. The pentane layer was dried and carefully fractionated to give 490 mg (75%) of **27**, whose spectra were identical with those of an authentic sample.[34]

1-Chlorosulfonyl-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (23). A 5.9-g (0.037 mol) sample of **22** in 200 ml of ether was treated with 30 ml of 1.6 *M* *n*-butyllithium in hexane and then 35 ml of sulfuryl chloride as previously described. There was obtained 5.8 g (62%) of **23**, mp 133–135° (from ethyl acetate–pentane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1380, 1170 ($-SO_2Cl$), 1150, and 1117 cm^{-1} ($-SO_2-$).

Anal. Calcd for $C_7H_{11}ClO_4S_2$: C, 32.50; H, 4.25. Found: C, 32.32; H, 4.16.

1-Chloro-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (24). A 1.0-g (3.86 mmol) sample of **23** was placed in a sublimation apparatus and was heated at 150° (0.05 mm). The solid rapidly decomposed and **24** sublimed as it was produced. There was obtained 620 mg (85%) of **24**, mp 194–196° (sealed tube) after recrystallization from ethyl acetate; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1312, 1150, and 1120 ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.25 (multiplet, 1 H, >C*H*SO$_2$–) and 2.20 (multiplet, 10 H, $-CH_2-$).

Anal. Calcd for $C_7H_{11}ClO_2S$: C, 43.20; H, 5.65; S, 16.48. Found: C, 43.27; H, 5.70; S, 16.49.

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Addition Reactions on Coordinated Olefinic Ligands. I. The Reactions of Amines with Diene Complexes of Platinum(II) and Palladium(II)

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Abstract: A new nucleophile addition reaction to dienes coordinated to platinum(II) or palladium(II) was studied. Ammonia and aliphatic primary and secondary amines reacted smoothly with the diene π complexes to give derivatives containing carbon–metal σ bonds. The behavior of 1,5-cyclooctadiene, norbornadiene, 1,5-hexadiene, and 4-vinylcyclohexene complexes was investigated. Structural assignments were made on the basis of degradative studies. Data on the stereochemistry of the addition were also obtained.

Growing interest and investigations are centered on reactions involving ligands coordinated to transition metals. In this area, peculiar interest for reactions on unsaturated ligands stems from the importance of several catalytic processes which involve alkenes and polyenes.[1] A well-known reaction, for instance, is the addition of a nucleophilic agent to coordinated dienes in platinum(II)[2] and palladium(II)[3] complexes. Actually

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