This substance is 2-ethoxy-3-methyl-4-pyrimidinone, as its hydrolysis (1 *N* hydrochloric acid, 1 hr boiling) gave 3-methyluracil; the identity was established by paper chromatography and ir spectra. The mother liquor from the recrystallizations from cyclohexane were evaporated, dissolved in ligroin, and left at 0° overnight. The crystals which formed were separated, the liquid was evaporated, the residue was distilled *in vacuo* (80° bath temperature, 10 mm); and 120 mg of oily distillate resulted, which remained as a liquid even after long standing at room temperature.

Anal. Calcd for $C_7H_{10}N_2O_2$: N, 18.17. Found: N, 17.88.

This substance is apparently 2-ethoxy-4-methoxypyrimidine, as reaction with excess methyl iodide at room temperature gave 1-methyl-4-methoxy-2-pyrimidinone. The identity of the product was established by the ir spectrum.

Preparation of 1-Vinyl-2-ethoxy-4-pyrimidinone.—A solution of 0.1 ml of concentrated sulfuric acid in 2 ml of ethyl acetate was added to a suspension of 0.5 g of mercuric acetate in 250 ml of vinyl acetate in a pressure flask. A clear solution resulted; 1.5 g of 2-ethoxy-4-pyrimidinone was then added. Nitrogen was bubbled through the solution and kept in a 50° bath for 2 days. Dry sodium acetate was then added, and the solution was stirred for 10 min and filtered. The filtrate was evaporated *in vacuo* and the residue was dissolved in chloroform. The chloroform solution was extracted five times with cold 1 *N* NaOH; the emulsion formed was separated by centrifugation. After drying, the chloroform fraction was evaporated *in vacuo;* yellow crystals and an oil remained. The crystals were first recrystallized from carbon tetrachloride and then from a large volume of cyclohexane, and sublimed *in vacuo* (0.05 mm). White crystals were obtained (200 mg, 10%): mp 97–99°; λ_{max} (0.05 *M* phosphate buffer, pH 7) 266 mμ (ϵ 12,800) and 240 (side band, 10,400); λ_{min} 222 mμ.

Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.81; H, 6.05; N, 16.88.

Hydrogenation of 1-Vinyl-2-ethoxy-4-pyrimidinone.—The vinyl compound (150 mg) was dissolved in 15 ml of ethanol and 15 ml of water, 75 mg of catalyst (5% Pd on carbon) was added, and the solution was hydrogenated at room temperature and atmospheric pressure. After 70 min, hydrogen corresponding approximately to one double bond had been consumed. The mixture was then filtered with Celite and the solution was evaporated, yielding crystals, mp 81–93° after recrystallization from a small volume of carbon tetrachloride and vacuum sublimation. Spectral properties indicated that 1-ethyl-2-ethoxy-4-pyrimidinone was the main component, but further purification was difficult. Attempted separation of impurities by extraction with alkali gave low yields, apparently owing to hydrolysis. Gas–liquid partition chromatography separation requires a high temperature (200°, Hewlett-Packard 700 laboratory chromatograph, 10% silicon fluid S-96 column), causing a partial isomerization. Finally, a pure compound was obtained through fractional vacuum sublimation. At 0.1-mm pressure and 65° (bath temperature) the sublimed fractions were monitored by disappearance of the ir band at 1680 cm^{-1}, which represents an impurity subliming before the desired compound. Fractions not having this absorption (60%), mp 94–97°, were recrystallized from tetrahydrofuran and resublimed, mp 99.5–100°; these operations did not change the ir spectrum.

Anal. Calcd for $C_8H_{12}N_2O_2$: N, 16.66. Found: N, 16.50.

Hydrogenation and Hydrolysis of 1-Vinyl-2-ethoxy-4-pyrimidinone.—The vinyl compound was hydrogenated in the same way as in the previous experiment. The residue after evaporation was dissolved in 10 ml of 1 *N* hydrochloric acid and left overnight. The solution was evaporated and the residue was resublimed *in vacuo* (0.05 mm), yielding 70 mg of white crystals, mp 130–140°, apparently a mixture. This product was dissolved in 80 ml of water, 40 mg of catalyst (5% Rh on $Al_2O)_3$ was added, and the solution was hydrogenated in the same way as described earlier. After filtration, the solution was evaporated and the resulting crystals were sublimed *in vacuo,* giving 50 mg of sublimate which, according to the ir spectrum, is identical with 1-ethyl-5,6-dihydrouracil.

Registry No.—**1b,** 20541-38-2; **2b,** 23220-30-6; 2-ethoxy-4-methoxypyrimidine, 23220-28-2; 1-vinyl-2-ethoxy-4-pyrimidinone, 23220-29-3.

Acknowledgment.—This work was made possible through the kind interest and support of Dr. G. L. Eichhorn. Further, I would like to thank Dr. D. M. Brown and Dr. D. J. Brown for samples **2c** and **4**, respectively, and Dr. J. J. Butzow, Dr. J. J. Fox, Dr. P. J. Krueger, and Dr. C. H. Robinson for comments on the manuscript.

Cycloaddition Reactions of Thiete 1,1-Dioxides. The Preparation of 2-Thiabicyclo[2.2.0]hexane Derivatives[1]

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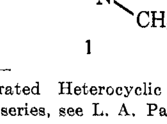
The reaction of thiete 1,1-dioxide and its 2,2-dimethyl derivative with typical enamines, ynamines, and dienamines has been studied. Cycloaddition resulted in the examples reported to give derivatives of the previously unknown 2-thiabicyclo[2.2.0]hexane system and of 7-thiabicyclo[4.2.0]oct-3-ene. Such condensations provide a ready synthetic entry to such molecules. The nmr spectra of the adducts are discussed.

In contrast with the recent surge of interest in bicyclo[2.2.0]hexane chemistry,[3] little attention has been paid to monoheteroatomic analogs of this strained bicyclic ring system. The only successful synthesis of a 2-azabicyclo[2.2.0]hexane derivative (1) was reported by Corey and Streith[4] in 1964. 1-Azabicyclo[2.2.0]hexane (2) is recognized at this time only as a transitory intermediate.[5] Several 2-oxabicyclo[2.2.0]hexanes, such as 3[4] and 4,[6] are recognized to result from



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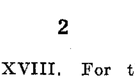

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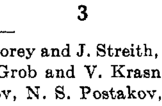

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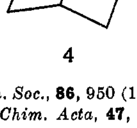

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[1] Unsaturated Heterocyclic Systems. LXVIII. For the previous paper in this series, see L. A. Paquette, T. Kakihana, and J. F. Hansen, *Tetrahedron Lett.*, in press.

[2] NDEA Fellow, 1967–present.

[3] K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968).

[4] E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

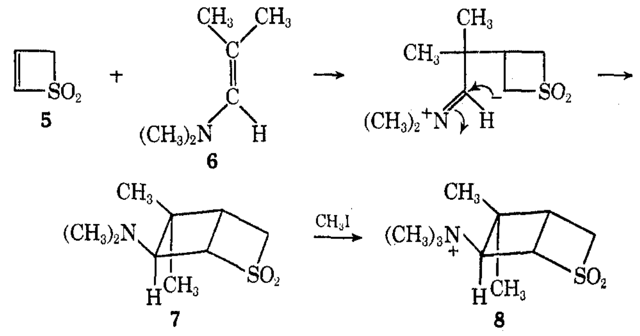
[5] C. A. Grob and V. Krasnobajew, *Helv. Chim. Acta*, **47**, 2145 (1964); I. N. Nazarov, N. S. Postakov, N. N. Mikhelva, and N. A. Tradkina, *J. Gen. Chem. USSR*, **29**, 2573 (1959); V. Prelog, E. Cerkovnikov, and G. Ustricev, *Justus Jiebigs Ann. Chem.*, **535**, 37 (1938).

[6] R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 775 (1960).

certain intramolecular photochemical cycloadditions.[7]

With the twofold objective of preparing simple derivatives of the unknown 2-thiabicyclo[2.2.0]hexane system and of exploring further the cycloadditive propensity of thiete 1,1-dioxides, we have briefly investigated the reactions of **5** and **12** with a number of different types of electron-rich olefins. It was anticipated that the proven dienophilic capability of thiete 1,1-dioxides[8] would be increasingly evident in such condensations.

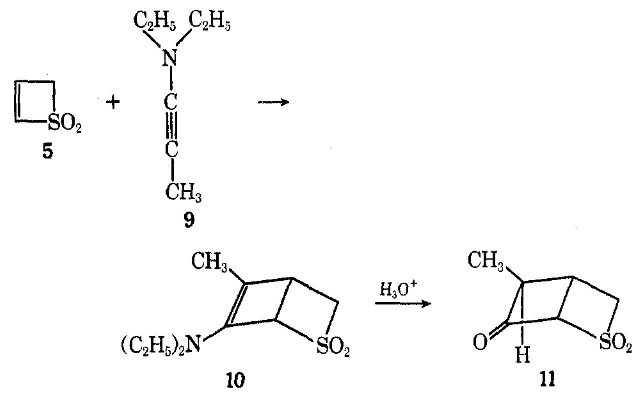
Enamines.—When thiete 1,1-dioxide (**5**) and 2-methyl-1-dimethylamino-1-propene (**6**) were refluxed in benzene solution for 24 hr, the 1:1 crystalline adduct **7** was obtained in 60% yield. That this substance was a 2-thiabicyclo[2.2.0]hexane derivative was clearly revealed by its nmr spectrum. Thus, in addition to the two six-proton singlets at δ 1.20 and 2.10 due to the methyl groups bonded to C_5 and nitrogen, respectively, there was seen a multiplet at 2.17–2.47 assigned to the H_4 proton, a doublet (J = 6 Hz) centered at 3.00 due to H_6, and a second multiplet at 3.87–4.42 ascribed to the three α-sulfonyl protons. Alternative structures for this product can be eliminated since they would be expected to exhibit either vinyl absorption or fewer α-sulfonyl protons.



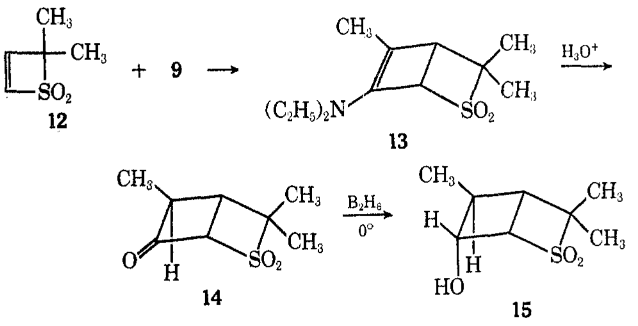
The *exo* orientation of the dimethylamino group in **7** was assigned initially on the basis of the customary minimization of nonbonded steric interactions expected in the transition state for C_1C_6 bond formation. Substantiation of this assignment is seen in the magnitude of the H_1H_6 coupling constant (6 Hz) which is convincingly accommodated by the existing dihedral angle.[6,7a]

Although **7** readily afforded a methiodide (**8**), attempts to degrade this quaternary salt under a variety of Hofmann elimination conditions failed to yield a characterizable product.

Ynamines.—A similar condensation of **5** with diethyl-1-propynylamine (**9**) in refluxing benzene led in this instance to the unsaturated 2-thiabicyclo[2.2.0]hexane derivative **10.** However, this cycloaddition product was not characterized *per se* because of its instability in air. Instead, the residual enamine moiety in **10** was hydrolyzed in acid and keto sulfone **11** could be isolated consistently in 45% overall yield. This substance exhibited principal infrared peaks in chloroform solution at 1785 (C=O), 1332, and 1145 cm^{-1} (SO_2). In its nmr spectrum ($CDCl_3$), the methyl group is seen as a doublet (J = 7.5 Hz) at δ 1.37 and H_1 appears at δ 5.68 as a quartet of triplets ($J_{1,4}$ = 7.0 Hz; $J_{1,5}$ = 3.0 Hz; $J_{1,3}$ = 1.0 Hz); the complex multiplet ascribed to the two remaining α-sulfonyl protons is centered at δ 4.42, whereas the complex patterns due to H_4 and H_5 are seen at δ 3.40 and 3.90, respectively. The stereochemical assignment of the 5-methyl group in **11** derives principally from the strong *exo* preference anticipated from this substituent under the equilibrating conditions employed and from the nmr coupling constants, but depends further upon recognition of the fact that there exists a very close spectral correlation with **14** (see below) in which an *endo*-5-methyl group is considered very unlikely because of prohibitive steric crowding.



Ynamine **9** also underwent 2 + 2 cycloaddition to 2,2-dimethylthiete 1,1-dioxide (**12**). Acid hydrolysis of the intermediate enamine **13** led in this instance (43% overall yield) to keto sulfone **14** which likewise exhibited an intense cyclobutanone carbonyl stretching mode at 1795 cm^{-1}. As expected, the nmr spectrum of **14** was considerably simplified relative to that of **11** because of the presence of the *gem*-dimethyl groups at C_3 (sharp singlets at δ 1.62 and 1.72). Thus, whereas both H_1 ($J_{1,4}$ = 7.0 Hz; $J_{1,5}$ = 2.5 Hz) and H_4 ($J_{1,4}$ = 7.0 Hz; $J_{4,5}$ = 4.5 Hz) appear as doublets of doublets at δ 5.47 and 2.53, respectively, H_5 is seen as a pair of overlapping quartets centered at δ 3.80 and the 5-methyl substituent as an upfield doublet (δ 1.23; J = 7.5 Hz).



Diborane reduction of the carbonyl group in **14** proceeded readily and in high yield to give *endo* hydroxy sulfone **15**. The latter displayed strong hydroxyl absorption in the infrared at 3450 cm^{-1} and an nmr spectrum in full agreement with the assigned structure (see Experimental Section). This secondary alcohol proved to be labile to bases, *e.g.*, aluminum isopropoxide, etc.,

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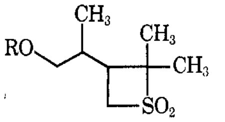
(7) For other examples of intramolecular bicyclic oxetane formation, see (a) H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965); (b) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965); (c) J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, **34**, 2814 (1969).

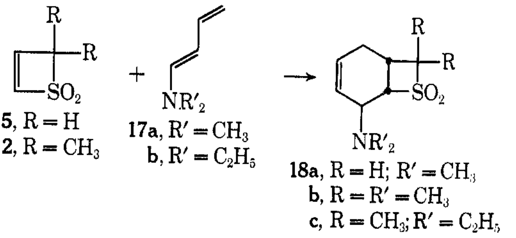
(8) (a) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962); (b) D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964); (c) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); (d) L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

even under mild conditions. For example, upon standing overnight at room temperature in the presence of diborane, **15** undergoes reductive cleavage to **16a**. This behavior is not unexpected since it derives considerable driving force from the relief of ring strain and the transient intervention of an α-sulfonyl carbanion. Alcohol **16a** was further characterized as its crystalline tosylate **16b**.



16a, R = H
b, R = $SO_2C_6H_4CH_3$-*p*

Dienamines.—Preparation of 7-thiabicyclo[4.2.0]-oct-3-enes was effected by a related cycloaddition of dienamines to thiete 1,1-dioxides. 1-Dimethylamino-1,3-butadiene (**17a**) was subjected to reaction with both **5** and **12** to give adducts **18a** and **18b**, respectively.



5, R = H
12, R = CH_3

17a, R′ = CH_3
b, R′ = C_2H_5

18a, R = H; R′ = CH_3
b, R = R′ = CH_3
c, R = CH_3; R′ = C_2H_5

As observed earlier, **12** is more sluggish to react than **5** because of the steric effect generated by the *gem*-dimethyl functionality on the adjacent sp² carbon atom which, in this instance, is a neopentyl center. 1-Diethylamino-1,3-butadiene (**17b**) behaved similarly.

The nmr spectra of adducts **18a–c** were in complete agreement with the assigned structures. In these examples, however, it did not prove possible unequivocally to assign stereochemistry to the dialkylamino group.

In conclusion, the present research reveals that simple cycloaddition reactions of electron-rich olefins to thiete 1,1-dioxides provide a ready means of preparing derivatives of 2-thiabicyclo[2.2.0]hexane and 7-thiabicyclo[4.2.0]octane. However, preliminary studies have also indicated that 1,1-di(1-piperidinyl)ethylene, N,N-dimethyl-2-phenylethynylamine, and N,N,N′,N′-tetramethyl-1,3-butadiene-1,4-diamine do not react with **5** and **12**. Therefore, this particular cycloaddition is not entirely general.

Experimental Section

Melting points are corrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

5,5-Dimethyl-6-*exo*-dimethylamino-2-thiabicyclo[2.2.0]hexane 2,2-Dioxide (7).—A solution of 3.0 g (0.039 mol) of thiete 1,1-dioxide (**5**)[9] and 3.9 g (0.039 mol) of 2-methyl-1-dimethylamino-1-propene (**6**)[10] in 5 ml of dry benzene was refluxed for 24 hr under a nitrogen atmosphere. Chromatography of the concentrated reaction mixture on neutral alumina afforded, on elution with ether–petroleum ether (1:3), 3.5 g (60%) of **7**: mp 102–103° further recrystallization from ether–petroleum ether did not improve the melting point); $\nu_{max}^{CCl_4}$ 1335, 1220, 1210, 1185, and 1145 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.20 [s, 6 H, $C(CH_3)_2$], 2.10 [s, 6 H, $N(CH_3)_2$], 2.17–2.47 (m, H_4), 3.00 (d, J = 6.0 Hz, H_6), and 3.87–4.42 (m, 3 H, α-sulfonyl).

Anal. Calcd for $C_9H_{17}NO_2S$: C, 53.17; H, 8.43; S, 15.77. Found: C, 53.43; H, 8.45; S, 15.76.

A methiodide of **7** was prepared in the usual way in 83% yield. Recrystallization from methanol–ether gave pure **8**, mp 225° dec.

Anal. Calcd for $C_{10}H_{20}INO_2S$: C, 34.79; H, 5.84; S, 9.29. Found: C, 34.86; H, 5.86; S, 8.90.

***exo*-5-Methyl-2-thiabicyclo[2.2.0]hexan-6-one 2,2-Dioxide (11).**—A solution of 8.73 g (0.087 mol) of **5** and 12.0 g (0.107 mol) of diethyl 1-propynylamine (**9**, Fluka) in 150 ml of dry benzene was heated at reflux under nitrogen for 24 hr. The benzene was evaporated and the residual red oil was dissolved in 100 ml of 6 *M* HCl and extracted continuously with ether overnight. Evaporation of the dried ether solution yielded 6.30 g (45%) of **11** which was twice recrystallized from benzene–hexane: mp 75–78°; $\nu_{max}^{CHCl_3}$ 1785 (C=O), 1332, 1188, and 1144 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.37 (d, J = 7.5 Hz, methyl), 3.40 (m, H_4), 3.90 (m, H_5), 4.42 (m, 2 H), (remaining α-sulfonyl), and 5.68 (q of t, J = 7.0, 3.0, and 1.0 Hz, H_1).

Anal. Calcd for $C_6H_8O_3S$: C, 45.00; H, 5.00; S, 20.02. Found: C, 44.90; H, 5.08; S, 19.74.

***exo*-3,3,5-Trimethyl-2-thiabicyclo[2.2.0]hexan-6-one 2,2-Dioxide (14).**—A solution of 7.0 g (0.053 mol) of 2,2-dimethylthiete 1,1-dioxide (**12**)[10] and 7.0 g (0.063 mol) of **9** in 100 ml of dry benzene was refluxed under nitrogen for 48 hr. The benzene was evaporated and the residual red oil was hydrolyzed as above to give 4.23 g (42.5%) of **14**: mp 118–119° after two recrystallizations from benzene–hexane; $\nu_{max}^{CHCl_3}$ 1795 (C=O), 1325, 1170, and 1115 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.23 (d, J = 7.5 Hz), 1.62, 1.72 (s, *gem*-dimethyl), 2.53 (d of d, J = 7.0 and 4.5 Hz, H_4), 3.80 (overlapping quartets, H_5), and 5.47 (d of d, J = 7.0 and 2.5 Hz, H_1).

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.07; H, 6.38; S, 17.04. Found: C, 51.18; H, 6.49; S, 16.86.

***exo*-3,5,5-Trimethyl-*endo*-4-hydroxy-2-thiabicyclo[2.2.0]hexane 2,2-Dioxide (15).**—Into a solution of 2.87 g (0.015 mol) of **14** in 200 ml of anhydrous tetrahydrofuran cooled to 0° under nitrogen was introduced gaseous diborane, generated externally by dropping 15 g (0.11 mol) of boron trifluoride etherate into a solution of 1.5 g (0.04 mol) of sodium borohydride in 50 ml of diglyme. After completion of the diborane generation (30 min), the mixture was stirred for an additional 2 hr at 0°. Dilute hydrochloric acid (50 ml) was added cautiously, the tetrahydrofuran was evaporated, and the aqueous layer was continuously extracted overnight with ether. The dried ether solution was evaporated to afford 2.15 g (75.5%) of **15**: mp 54–55.5° (from benzene–hexane); $\nu_{max}^{CHCl_3}$ 3450 (OH), 1312, 1287, 1125, and 1110 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.21 (d, J = 7.0 Hz, 5-methyl), 1.51, 1.53 (s, *gem*-dimethyl), 1.82 (t, J = 7.0 Hz, H_4), 2.85 (m, H_5), 3.85 (broad s, H_1 and H_6), and 4.80 (broad, OH).

Anal. Calcd for $C_8H_{14}O_3S$: C, 50.53; H, 7.36; S, 16.87. Found: C, 50.51; H, 7.41; S, 16.98.

Ring Opening of 15.—A 2.50-g sample of **14** was reduced in the above manner with diborane. The reaction mixture was allowed to stir at room temperature overnight. After the same work-up, 1.59 g (63%) of **16a**, a viscous oil, was obtained. This material was molecularly distilled at 100° (0.5 mm): $\nu_{max}^{CHCl_3}$ 3510, 3400 (OH), 1305, 1153, and 1120 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 0.98 (d, J = 6.5 Hz, methyl), 1.54 (s, *gem*-dimethyl), 2.00 (m, 2 H, H_3 and adjacent proton), 3.05 (s, OH), 3.42 (d, J = 4.8 Hz, OCH_2), and 3.83 (AB, J = 10.0 and 2.5 Hz, α-sulfonyl).

This alcohol was converted into its tosylate (**16b**) with tosyl chloride in pyridine at 0°. The crystalline sulfonate ester was obtained as white prisms, mp 124.5–125.5° (from ethanol).

Anal. Calcd for $C_{15}H_{22}O_5S_2$: C, 52.02; H, 6.35; S, 18.52. Found: C, 52.26; H, 6.58; S, 18.34.

5-Dimethylamino-7-thiabicyclo[4.2.0]oct-3-ene 7,7-Dioxide (18a).—A mixture of 6.35 g (0.061 mol) of **5** and 6.0 g (0.062 mol) of 1-dimethylamino-1,3-butadiene (**17a**)[11] in 10 ml of dry benzene was left at room temperature under nitrogen for 6 days. The black solution was concentrated *in vacuo* and the residue was chromatographed on neutral alumina. Elution with petroleum ether–ether (9:1) gave 8.8 g (71.5%) of **18a** as a yellow oil. Purification through its hydrochloride salt gave a colorless oil

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[9] D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

[10] W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Lett.*, 1677 (1963).

[11] Z. Arnold, *Collect. Czech. Chem. Comm.*, **25**, 1308 (1960).

with no change in spectral properties: $\nu_{max}^{CCl_4}$ 1325, 1200, 1175, and 1130 cm^{-1} (SO_2); $\delta_{TMS}^{CCl_4}$ 1.90–2.83 (m, H_1 and H_2), 2.20, 2.34 (s, $N(CH_3)_2$), 3.33–3.74 and 4.00–4.62 (m, 2 H each, H_5 and α-sulfonyl), and 5.86 (broad s, 2 H, vinyl).

A methiodide of **18a** was obtained in 78% yield, mp 191° dec (methanol–water).

Anal. Calcd for $C_{10}H_{18}INO_2S$: C, 34.99; H, 5.29; N, 4.08. Found: C, 34.92; H, 5.35; N, 3.93.

5-Dimethylamino-8,8-dimethyl-7-thiabicyclo[4.2.0]oct-3-ene 7,7-Dioxide (18b).—A mixture of 5.0 g (0.038 mol) of **12** and 4.0 g (0.041 mol) of **17a** in 10 ml of dry benzene was left at room temperature under nitrogen for 1 week and then refluxed for 2 hr. The black solution was worked up and chromatographed as above to give an oily solid, recrystallization of which from ether–petroleum ether afforded 1.7 g (19.5%) of **18a**, mp 45–48°. An analytical sample was prepared through the hydrochloride salt, mp 215° dec (from methanol–ether), and regeneration of the free base: mp 59°; $\nu_{max}^{CCl_4}$ 1315, 1175, 1153, and 1112 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.40 and 1.65 (s, *gem*-dimethyl), 2.28 (s, $N(CH_3)_2$), 2.17 (m, 2 H, H_2), 3.65–3.86 (m, H_5), 4.25–4.60 (m, H_6), and 5.88 (broads, 2 H, vinyl).

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.61; H, 8.35; N, 6.10; S, 13.98. Found: C, 57.62; N, 8.42; N, 5.99; S, 13.84.

A methiodide salt of **18b** was prepared, mp 211° dec (methanol–water).

Anal. Calcd for $C_{12}H_{22}INO_2S$: C, 38.82; H, 5.97; S, 8.64. Found: C, 38.62; H, 5.92; S, 8.42.

5-Diethylamino-8,8-dimethyl-7-thiabicyclo[4.2.0]oct-3-ene 7,7-Dioxide (18c).—A mixture of 1.0 g (7.6 mmol) of **12** and 0.94 g (7.6 mmol) of 1-diethylamino-1,3-butadiene (**17b**)[12] in 5 ml of dry xylene was refluxed under nitrogen for 12 hr. The dark reaction mixture was concentrated and the residue was chromatographed on Florisil. Elution of the column with petroleum ether containing increasing amounts of ether gave a yellow crystalline solid. Recrystallization of this substance from petroleum ether afforded 0.4 g (19.5%) of **18c**: mp 64°; $\nu_{max}^{CCl_4}$ 1312, 1165, 1150, and 1110 cm^{-1} (SO_2). Approximately one-fourth of the starting quantity of **12** was recovered.

Anal. Calcd for $C_{13}H_{23}NO_2S$: C, 60.66; H, 9.01; N, 5.44; S, 12.46. Found: C, 60.39; H, 8.88; N, 5.40; S, 12.36.

Registry No.—**7,** 23431-18-7; **8,** 23430-88-8; **11,** 23430-89-9; **14,** 23430-90-2; **15,** 23430-91-3; **16a,** 23431-19-8; **16b,** 23431-20-1; **18a,** 23430-92-4; **18a** (methiodide), 23430-93-5; **18b,** 23430-94-6; **18b** (methiodide), 23465-13-6; **18c,** 23430-95-7.

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The Reaction of 6,6-Dibromobicyclo[3.1.0]hexane with Methyllithium. Efficient Trapping of 1,2-Cyclohexadiene by Styrene[1]

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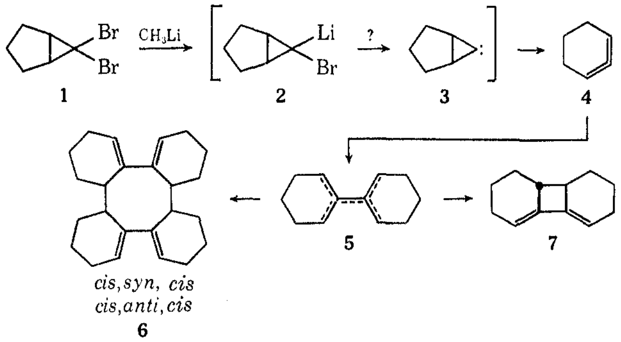
The reaction of 6,6-dibromobicyclo[3.1.0]hexane (1) with methyllithium in styrene affords a 76% yield of *exo*- and *endo*-7-phenylbicyclo[4.2.0]oct-1-ene (**8a** and **8b**) in a ratio of 2.2:1. The structures of **8a** and **8b** have been established by spectral methods, oxidative degradation, and hydrogenation to *exo*- and *endo*-7-phenylbicyclo[4.2.0]octane, which were synthesized independently. The formation of **8a** and **8b** is interpreted in terms of the generation of 1,2-cyclohexadiene, which adds to styrene to form a singlet biradical that closes to **8a** and **8b**.

The reaction of 6,6-dibromobicyclo[3.1.0]hexane (**1**) with methyllithium gives no evidence of products derived from carbene **3** (Scheme I). Rather, at −80° the major products are the stereoisomers **6**, while in refluxing ether diene **7** is formed in good yield.[3] We have interpreted[3] these results in terms of the generation of 1,2-cyclohexadiene (**4**) from either **2** or **3** (or both) and have suggested that dimerization of **4** first gives a diallylene **5**, which either cyclizes to **7** at "high" temperatures or dimerizes to **6** at low temperatures (Scheme I). In order to gain insight into the nature of 1,2-cyclohexadiene, we have investigated intercepting it with various reagents. In this paper we report the trapping of **4** with styrene and a rigorous proof of the structures of the adducts.

Scheme I



The reaction of **1** with methyllithium in isobutylene, cyclohexene, and furan under a variety of conditions produced the same products, **6** and **7**, observed when ether was employed as the sole solvent; no evidence for any "trapping products" was obtained. However, addition of methyllithium in ether to a solution of **1** in pure styrene at −15° gave, after distillation, a 76% yield of a 1:1 styrene–C_6H_8 adduct **8**. A small amount (4–5%) of **7** was formed and the total distillation residue, *ca.* one-tenth the weight of **8**, was found to consist of **6** (along with small amounts of "trimeric" material[3]). No evidence was found for the formation of any styrene polymer. The product composition was the same with methyllithium made from methyl bromide or methyl iodide. Dilution of the styrene in ether lowered the yield of **8** somewhat.

The trapping product **8** was shown by glpc to be a mixture of two compounds, in a ratio of 2.2:1. Based on the detailed evidence presented below, the major product has been shown to be *exo*-7-phenylbicyclo-

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[2] National Institutes of Health Predoctoral Fellow, 1960–1964.

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