2,4-Dimethyl-3-(β-carbomethoxyethyl)-5-carbobenzoxypyrrole: mp 99–100° (lit.[11] mp 99–100°); nmr (CCl$_4$) δ 2.15 (s), 2.25 (s), 2.48 (m), 3.56 (s), 5.23 (s), 7.27 (s); $\nu_{max}^{CHCl_3}$ 1680, 1730 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 283 nm.

Registry No.—1 (R = CH$_3$), 5408-04-8; 1 (R = C(CH$_3$)$_3$), 27332-07-6; 1 (R = p-CH$_3$OC$_6$H$_4$), 27331-97-1; 2 (R′ = CH$_3$), 13984-53-7; benzyl 2-oximinoacetoacetate, 27331-98-2.

[11] A. Hayes, G. W. Kenner, and N. R. Williams, *J. Chem. Soc.*, 3779 (1958).

Synthesis of *endo*-4-Bromo-6-thiabicyclo[3.2.1]octane and 6-Thiabicyclo[3.2.1]oct-3-ene[1]

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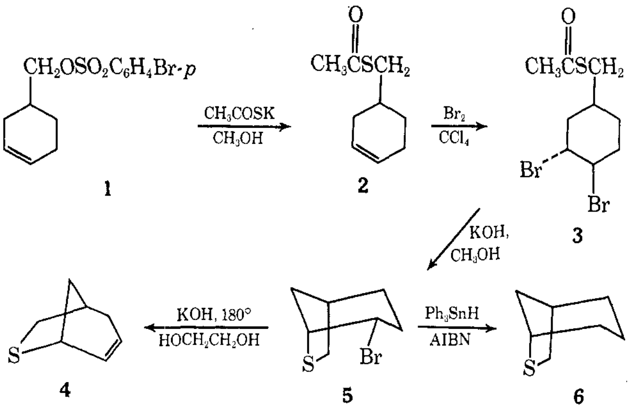
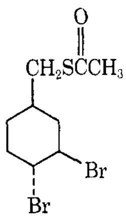
Received June, 4, 1970

As part of a continuing program of investigation of stereochemical aspects of cyclic and bicyclic sulfur compounds, we have developed syntheses of *endo*-4-bromo-6-thiabicyclo[3.2.1]octane (**5**) and 6-thiabicyclo[3.2.1]oct-3-ene (**4**). The synthetic sequences beginning with 3-cyclohexenylmethyl *p*-bromobenzenesulfonate (**1**) are summarized in Scheme I. Compound **1** was prepared by the sodium borohydride reduction of 3-cyclohexenecarboxaldehyde, followed by reaction of the alcohol with *p*-bromobenzenesulfonyl chloride in pyridine.

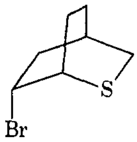
SCHEME I



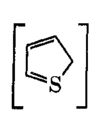
The critical step in Scheme I was the bromination of the thioacetate **2**. Trans-diaxial bromination[2] could give dibromide **3** and/or **7** depending on relative conformer populations and rates of bromination. Release of the nucleophilic thiolate by treatment of the dibromothioacetate with potassium hydroxide in methanol gave bicyclic bromide **5** in 62% yield. No material which could be identified as bromide **8** was found in the reaction product; either the bromination of **2** gave exclusively **3** or dibromothioacetate **7** failed to cyclize under the reaction conditions.



7



8



9

The structure of **5** was established by chemical and physical methods. Treatment of **5** with triphenyltin hydride[3] and azobisisobutyronitrile gave 6-thiabicyclo[3.2.1]octane (**6**), identical by infrared spectroscopy[4] with that prepared by Birch and coworkers.[5] It was significant to note that the infrared spectrum of **5** was very similar to that of **6** in the 1050–650 cm^{-1} region suggesting that rearrangement did not occur during the reduction step.

The base peak in the mass spectrum of **5** was found at *m/e* 85. We suggest that this peak is indicative of the presence of a five-membered ring[6] and corresponds to ion **9**. The nmr spectrum of **5** revealed an eight-line pattern centered at δ 4.22 with coupling constants of 12, 6, and 2 Hz. This multiplet is assigned to the axial hydrogen at C-4 with the 12-Hz coupling constant due to trans-diaxial coupling.

The dipole moment of **5** in benzene solution was found to be 3.51 D. From models and model compounds the predicted dipole moment of **5** is 3.7 D (chair conformation) or 3.8 D (boat conformation). The isomeric *exo*-4-bromo-6-thiabicyclo[3.2.1]octane would be expected to have a dipole moment of 1.0 D (chair conformation) or 2.8 D (boat conformation).

The bicyclic bromide **5** was significantly unreactive. The common methods for achieving elimination, displacement, and solvolytic reactions on secondary bromides were unsuccessful. The sodium iodide in acetone test was negative after 23 hr at reflux.[7] The bromide **5** was recovered after 2 days in refluxing acetic acid, after 4 days in refluxing *tert*-butyl alcohol containing 10 equiv of potassium *tert*-butoxide, and after attempts to make lithium and Grignard reagents. The lack of success in these and similar reactions can probably be attributed to the close proximity of the sulfur to the departing bromide. S$_N$1, S$_N$2, and elimination reactions all involve a planar or developing planar transition state at C-4. Models of such a transition state reveal severe steric crowding between the departing bromine and the sulfur.

Two reactions of bromide **5** were successful. The first of these, triphenyltin hydride reduction, has been mentioned above. Dehydrobromination to yield 40% of 6-thiabicyclo[3.2.1]oct-3-ene (**4**) was achieved using potassium hydroxide in ethylene glycol at 180° for 18 hr. The nmr of **4** revealed two vinyl hydrogens. One was a broadened doublet centered near δ 5.4. The second was a broadened triplet pattern centered near δ 6.1. The pattern exhibited by these vinyl hydrogens was remarkedly similar to that observed in the vinyl region of

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[1] Part XXVII in the series, "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 8648).

[2] K. Kozima, K. Sakashita, and S. Maeda, *J. Amer. Chem. Soc.*, **76**, 1965 (1954).

[3] E. J. Kupchik and R. E. Connolly, *J. Org. Chem.*, **26**, 4747 (1961).

[4] API Research Project 44 Catalog, in No. 1861.

[5] S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **22**, 1590 (1957).

[6] The mass spectra of a number of bicyclic sulfides will be discussed in detail in a future paper.

[7] For another example of a bicyclic sulfur compound which failed to respond to this test, see E. D. Weil, K. J. Smith, and R. J. Gniber, *J. Org. Chem.*, **31**, 1669 (1966).

bicyclo[3.2.1]oct-3-en-6-one and numerous other bicyclo[3.2.1]oct-2-ene derivatives. On the other hand, the pattern found in the vinyl region of related bicyclo[2.2.2]octene derivatives was consistently much sharper and more symmetrical.[8]

Experimental Section

3-Cyclohexenylmethyl *p*-Bromobenzenesulfonate (1).—Sodium borohydride reduction of 3-cyclohexenecarboxaldehyde in absolute ethanol gave 3-cyclohexenylcarbinol, bp 64–65° (4.8 mm), n^{25}_{D} 1.4827, in 87% yield. To a solution of 3-cyclohexene-1-carbinol (70 g, 0.625 mol) in 360 ml of anhydrous pyridine at $-10°$ was slowly added 190 g (0.745 mol) of *p*-bromobenzenesulfonyl chloride over a period of 30 min. The reaction mixture was constantly stirred in a methanol–ice bath during addition. The reaction was stirred for 2 hr at $-10°$ after addition was complete, allowed to stand in a refrigerator for 24 hr, and poured directly into a 1-l. ice solution containing 180 ml of concentrated hydrochloric acid. Vigorous stirring produced a white slushy solid. Filtration of the solid, drying over anhydrous magnesium sulfate in methylene chloride, removal of methylene chloride by vacuum distillation, and recrystallization from absolute ethanol at -40 and $-78°$ gave 157 g (0.469 mol, 75%) of 3-cyclohexenylmethyl *p*-bromobenzenesulfonate (1), mp 33–35° (lit.[9] 34.5–35°).

3-Cyclohexenylmethyl Thioacetate (2).—To 400 ml of anhydrous methanol containing 3-cyclohexenylmethyl *p*-bromobenzenesulfonate (80 g, 0.242 mol) was added, with constant stirring at room temperature, 100 ml of anhydrous methanol containing 18.5 ml (0.262 mol) of thioacetic acid and 14.5 g (0.258 mol) of potassium hydroxide. Preparation of the potassium thioacetate solution required a methanolic solution of potassium hydroxide to be added to a cooled methanolic solution of thioacetic acid.

After 24 hr of stirring at room temperature, the reaction was filtered to remove precipitated potassium *p*-bromobenzenesulfonate. Methanol was removed from the filtrate under reduced pressure. To the remaining yellow oil was added 100 ml of water and 200 ml of methylene chloride. The methylene chloride layer was then washed with 100 ml of saturated sodium hydrogen carbonate and finally two 100-ml portions of water. The methylene chloride was then dried over anhydrous magnesium sulfate and evaporated at reduced pressure to give 38.5 g (0.266 mol, 94%) of a clear yellow liquid, bp 62–63° (0.8 mm), n^{25}_{D} 1.5118.

Anal. Calcd for $C_9H_{14}OS$: C, 63.58; H, 8.30. Found: C, 63.57; H, 8.36.

3,4-Dibromocyclohexeneylmethyl Thioacetate (3).—To 40 g (0.235 mol) of 3-cyclohexenylmethyl thioacetate and 200 ml of carbon tetrachloride cooled in an ice bath, in subdued light, was added 38.5 g (0.240 mol) of bromine in small increments, with stirring, over a period of 0.5 hr. After addition, the reaction was kept at 0° for 1 hr. The reaction was then washed with 50 ml of saturated sodium hydrogen sulfite. The carbon tetrachloride solution was dried over anhydrous magnesium sulfate and concentrated at reduced pressure. A 75-g (90%) yield of crude product was obtained, bp 150–155° (0.07 mm), n^{25}_{D} 1.5693. A sample for analysis was obtained by molecular distillation at reduced pressure.

Anal. Calcd for $C_9H_{14}Br_2OS$: C, 32.75; H, 4.28. Found: C, 33.08; H, 4.34.

***endo*-4-Bromo-6-thiabicyclo[3.2.1]octane (5).**—Thirty-five g (0.106 mol) of 3,4-dibromocyclohexylmethyl thioacetate was added to a refluxing solution of 600 ml of methanol containing 15 g (0.268 mol) of potassium hydroxide in a 2-l. flask under nitrogen. After refluxing for 24 hr, an additional 37 g (0.112 mol) of 3,4-dibromocyclohexylmethyl thioacetate in 200 ml of methanol and 100 ml of methylene chloride solution and 17.5 g (0.312 mol) of potassium hydroxide in 100 ml of methanol were added to the refluxing solution. After refluxing for another 24 hr, an additional 15 g (0.265 mol) of potassium hydroxide was added. Twenty hr after the final addition of potassium hydroxide (total reaction time 68 hr), the solvent was removed under reduced pressure. To the crude product was then added 400 ml of methylene chloride. The methylene chloride solution was extracted with two 150-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give a yellow oil. Passing this yellow oil through a column containing 500 g of Woelm's Neutral Alumina with 1% benzene–99% hexane solution gave 2 g of an unknown unsaturated compound. Continued elution with a 10% benzene–90% hexane solution gave 29 g (0.140 mol, 62%) of 5 as a clear liquid, bp 82° (0.09 mm), n^{25}_{D} 1.5762.

Anal. Calcd for $C_7H_{11}BrS$: C, 40.65; H, 5.35. Found: C, 41.02; H, 5.56.

6-Thiabicyclo[3.2.1]octane (6).—*endo*-4-Bromo-6-thiabicyclo[3.2.1]octane (5) (1 mmol, 0.207 g), 0.510 g (1.5 mmol) of triphenyltin hydride, and 5 mg of azobisisobutronitrile were added to a small sublimation apparatus fitted with a drying tube. The reaction mixture was heated at 80° for 24 hr. The cold finger was removed from the sublimator and yielded 20 mg of crystalline compound. The ir[4] of this compound proved to be identical with that of 6-thiabicyclo[3.2.1]octane prepared by Birch and colleagues.[5]

6-Thiabicyclo[3.2.1]oct-3-ene (4).—To 50 ml of ethylene glycol were added 4.14 g (20 mmol) of *endo*-4-bromo-6-thiabicyclo[3.2.1]octane and 8.95 g (160 mmol) of potassium hydroxide. This solution was heated to 180° and kept between 180 and 190° for 18 hr. After 18 hr the reaction was cooled and 400 ml of water was added. The aqueous solution was extracted with three 100-ml portions of pentane. The pentane extracts were combined and solvent was removed at reduced pressure. About 40 ml of water was added to the residual oil and the aqueous mixture was extracted with 40 ml of pentane. The pentane extract was dried over anhydrous magnesium sulfate. Removal of solvent at reduced pressure gave 1.6 g of a clear yellow oil containing 6-thiabicyclo[3.2.1]oct-3-ene. The material was purified by preparative gas phase chromatography on an SE-30 column. Pure 4 had bp 197–200°, n^{20}_{D} 1.5601.

Anal. Calcd for $C_7H_{10}S$: C, 66.62; H, 7.99. Found: C, 66.67; H, 8.05.

Dipole Moment of *endo*-4-Bromo-6-thiacyclo[3.2.1]octane.—The Dipolemeter DM 01 manufactured by Wissenschaftlich-Technische Werkstatten was used for the measurements. The dipole moments were measured in benzene solution at 25 ± 0.01°. The moments were calculated essentially by the method of Halverstadt and Kumler[10] utilizing an IBM 707 computer programmed as described by Allinger.[11] The dipole moment data are $\alpha = 17.491$, $\beta = 0.986$, $\epsilon_1 = 2.2724$, $P_2 = 297.7$, $d = 0.87329$, and $M_{\mathrm{D}} = 45.9360$ giving a dipole moment of 3.510 ± 0.019 D.

The model compounds used for calculation of the predicted dipole moments were cyclohexyl bromide (2.24 D),[12] thiane (1.71 D),[13] thiolane (1.90 D),[13] and cyclohexylmethyl sulfide (1.66 D).[14]

Registry No.—2, 27345-73-9; 3, 27345-75-1; 4, 27345-74-0; 5, 27345-76-2.

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[8] We thank Professor N. A. LeBel for providing nmr spectra of these model compounds.

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[10] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

[11] N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

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[13] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 3521 (1959).

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Condensation–Cyclization Reactions of Electron Deficient Aromatics. II. Stable Bicyclic Immonium Zwitterions from Enamines and *sym*-Trinitrobenzene[1]

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Received August 24, 1970

It has been known for quite some time that Meisenheimer complexes[2] like 1 are formed from *sym*-trinitro-

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[1] Previous paper: M. J. Strauss, T. C. Jensen, H. Schran, and K. O'Conner, *J. Org. Chem.*, **35**, 383 (1970).

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