3-Cyclohexylpropionic Acid (from Cyclohexyllithium and Ether).—To 6.3 g (0.90 g-atom) of lithium shot of high (0.8%) sodium content in 10 ml of diethyl ether was added 53.6 g (0.41 mole) of cyclohexyl chloride in 200 ml of ether. After reaction had begun, the system was cooled to and kept at −24°. After addition was complete, the mixture was stirred at room temperature for 48 hr. It was then poured onto Dry Ice, hydrolyzed, and neutralized with acid. Extraction with ether in the usual manner and separation by solubility in 10% aqueous sodium carbonate gave 12 g of nonacidic material (not investigated further) and 4.3 g of a liquid acid. Whereas cyclohexanecarboxylic acid is a solid, mp 30°,[7] 3-cyclohexylpropionic acid melts at 16°.[7] The infrared spectrum of the product agreed with that of authentic 3-cyclohexylpropionic acid prepared directly from the appropriate lithium compound and carbon dioxide. The liquid acid was converted, *via* thionyl chloride and ammonia, to the amide, mp 117–119°, after recrystallization from ether–ethanol (lit.[8] mp 120°; cyclohexanecarboxamide mp 185–186°[9]).

3-Cyclohexylpropionic Acid (from Cyclohexyllithium and Ethylene).—To 6.2 g (0.89 g-atom) of lithium shot of high (0.8%) sodium content in 10 ml of freshly purified tetrahydrofuran was added, over a 2-hr period, 47.4 g (0.40 mole) of cyclohexyl chloride in 190 ml of tetrahydrofuran. After reaction had begun at room temperature, the rest of the addition was conducted at −70° (Dry Ice bath). After overnight stirring at −25°, the dark gray mixture was saturated with ethylene bubbled in continuously for 16 hr. It was then poured onto pulverized dry ice and hydrolyzed and the solvent evaporated. By the usual ether extractive procedure there was isolated 3.7 g of a liquid acidic fraction. Its infrared absorption spectrum agreed with that of authentic 3-cyclohexanepropionic acid, and its amide derivative melted at 117°.

2-Cyclohexylethyltricyclohexylsilane (from Cyclohexyllithium in Ether).—To 2.1 g (0.30 g-atom) of lithium wire of high (0.8%) sodium content in 100 ml of anhydrous diethyl ether was gradually added, over a 4-hr period, 16.2 g (0.14 mole) of cyclohexyl chloride in 150 ml of ether. After initiation of the endothermic reaction at room temperature, the rest of the addition occurred at −30°. Then, to the mixture warmed to room temperature, 10 g (0.034 mole) of tricyclohexylfluorosilane was added. The reaction system was stirred for 30 hr, hydrolyzed, neutralized, and extracted with ether. After drying, evaporation, and recrystallization from pentane–ethanol, there was obtained 5.9 g (48%) of 2-cyclohexylethyltricyclohexylsilane, mp 103–104°.

Anal. Calcd for $C_{26}H_{48}Si$: C, 80.34; H, 12.45; Si, 7.21; mol wt, 388.7. Found: C, 80.02; H, 12.29; Si, 7.78; mol wt (vapor osmometric), 386.

The identity of the product was confirmed by comparison with an authentic sample, described below, *via* mixture melting point, infrared absorption spectrum, and vapor phase chromatographic retention time on a DC-550 silicone-coated capillary column in a Barber-Colman Model 61-C chromatograph.

2-Cyclohexylethyltricyclohexylsilane (from 2-Cyclohexylethyl Bromide).—To a mixture of 3.0 g (0.01 mole) of tricyclohexylfluorosilane and 0.76 g (0.11 g-atom) of lithium wire of high (0.8%) sodium content in 3 ml of anhydrous diethyl ether was gradually added 9.56 g (0.05 mole) of 2-cyclohexylethyl bromide[10] in 15 ml of ether. After the first few drops of halide had initiated reaction, as evidenced by cloudiness and activity at the metal surface, the system was cooled to −25° and maintained at that temperature during the rest of the addition for a total of 3 hr. After further stirring at room temperature for 37 hr, the reaction mixture was hydrolyzed with excess water and neutralized with 3 *N* hydrochloric acid. The ether phase and ether washings of the water phase were collected, dried, and evaporated. The residue was recrystallized from pentane–ethanol mixture to give 2.3 g (59%) of 2-cyclohexylethyltricyclohexylsilane, mp 102–103°.

Anal. Calcd for $C_{26}H_{48}Si$: C, 80.34; H, 12.45; Si, 7.21; mol wt, 388.7. Found: C, 80.27; H, 12.24; Si, 7.23; mol wt (vapor osmometric), 382.

exo,cis-2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol *via* an Interannular Interaction[1]

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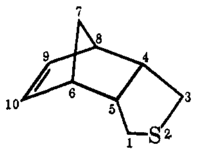
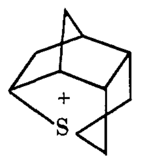
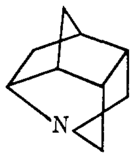
In a recent paper[3] the preparation of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (I) was described along with its facile cyclization to the sulfonium salt II, similar to the previously reported tertiary amine[4] III. Now we wish to report an example of a remarkable interannular interaction in which the bromosulfonium salt IV in a mildly alkaline solution specifically gives *exo,cis*-2-thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol (V).



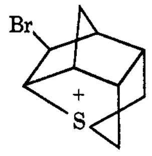
I



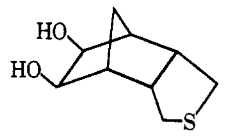
II



III

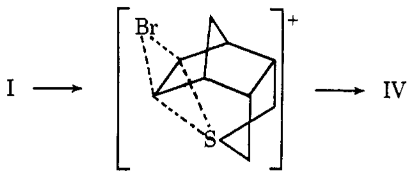


IV



V

Bromination of sulfide I in chloroform under mild conditions afforded the bromosulfonium salt (IV) in excellent yield. It is significant that no material having the *exo*-ring skeleton was observed among the reaction products. Most certainly reaction occurs through the bromonium intermediate VI which collapses to give the product IV.



VI

In lithium carbonate solution the salt IV was transformed smoothly into *cis*-glycol V. The structure of V was assigned on the basis of (1) a doublet at 3626 and 3689 cm^{-1} in the infrared corresponding to a $\Delta\nu$ of 63 cm^{-1} characteristic of strongly bonded *cis* glycols,[5]

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[7] G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 2385 (1926).

[8] N. Zelinsky, *Ber.*, **41**, 2676 (1908).

[9] W. Markownikoff, *ibid.*, **25**, 3355 (1892).

[10] Prepared by the method of G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 1089 (1926).

[1] (a) Taken from a dissertation submitted by L. A. Feliu-Otero to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, 1965. (b) The support of this research by Research Grant CA-4298 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, and, in part, by funds from an American Cancer Society Institutional Grant to Duke University is gratefully acknowledged.

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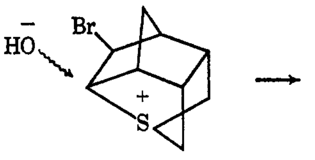
[3] P. Wilder, Jr., and L. A. Feliu-Otero, *J. Org. Chem.*, **30**, 2560 (1965).

[4] P. Wilder, Jr., and C. F. Culberson, *J. Am. Chem. Soc.*, **81**, 2027 (1959); C. F. Culberson and P. Wilder, Jr., *ibid.*, **82**, 4939 (1960).

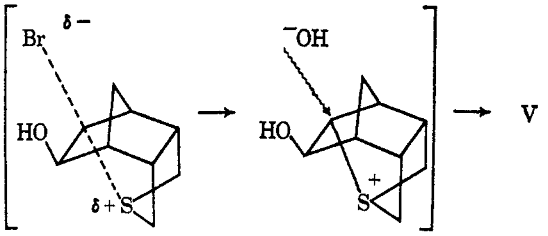
[5] L. P. Kuhn, *ibid.*, **74**, 2492 (1952).

(2) a positive periodic acid test, and (3) an independent synthesis from I with permanganate oxidation. The glycol was characterized by oxidation to its sulfone.

In the transformation IV → V, the initiating step is undoubtedly the nucleophilic attack of hydroxyl ion from the less encumbered (*exo*) side of the sulfonium ion. Formation of the specifically *cis* glycol (V), rather than *trans*, suggests a sulfonium ion (VII) which suffers a second displacement by hydroxyl from the *exo* side and not an epoxide intermediate derived from an incipient *cis* bromohydrin or the hydroxy sulfonium ion (VII). The intermediacy of VII would also preserve the *endo* stereochemistry of the molecule.



IV



VII

Finally, no product indicative of nucleophilic displacement at other methylenes adjacent to sulfur (C_1 and C_3) was observed.

Experimental Section[6]

2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (I) was prepared by the method previously described.[3]

Reaction of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene and Bromine. Preparation of Bromosulfonium Bromide (IV).—To 1.52 g (0.010 mole) of unsaturated *endo*-sulfide in 6 ml of dry chloroform cooled in an ice bath was added dropwise with stirring 1.76 g (0.011 mole) of bromine in 4 ml of dry chloroform. When addition was complete, dry ether was added and the precipitate was separated by vacuum filtration. After solution of the solid in hot absolute methanol and then precipitation with ether, there was obtained 2.59 g (83%) of the colorless salt, mp 117–118°.

Anal. Calcd for $C_9H_{12}Br_2S$: C, 34.62; H, 3.85. Found: C, 34.62; H, 3.84.

Reaction of Bromosulfonium Bromide (IV) with Lithium Carbonate. Preparation of *exo,cis*-2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol (V).—A mixture of 2 g (0.006 mole) of IV, 1.15 g (0.016 mole) of lithium carbonate, 5 ml of absolute methanol, and 11 ml of water was refluxed for 2 days according to the method of Roberts.[7] The reaction mixture was then extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The solvents were removed under vacuum and the residue was recrystallized from absolute methanol-heptane, mp 102–106°. This substance gave a positive test for a *cis*-vicinal diol.[8]

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.06; H, 7.53. Found: C, 58.33; H, 7.74.

A sulfone was prepared, mp 180–181°, from absolute methanol-heptane after being chilled in a Dry Ice-acetone bath. This material also gave a positive test for a *cis*-vicinal diol.

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.54; H, 6.42. Found: C, 49.31; H, 6.26.

Reaction of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (I) with Potassium Permanganate.—A procedure similar to the method of Kwart and Vosburgh[9] was employed. A solution of 4.21 g (0.027 mole) of potassium permanganate in 7 ml of water and 70 ml of reagent grade acetone was added slowly with stirring to a solution of 2.7 g (0.018 mole) of *endo*-sulfide I in 4 ml of reagent grade acetone previously cooled to −20° in a Dry Ice-acetone bath. When addition was complete, the reaction was allowed to come gradually to 0°. Manganese dioxide was removed by filtration. The resulting solution was saturated with Dry Ice, and potassium carbonate was separated by filtration. The solution was treated with Norit and solvent was removed by slow evaporation at room temperature. An oily residue was obtained. Treatment with boiling acetone dissolved the glycol which was precipitated by the addition of heptane and chilling in a Dry Ice-acetone bath, mp 102–106°, mmp with V 102–106°.

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[6] Melting points are uncorrected.

[7] J. D. Roberts, E. R. Trumball, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

[8] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 145.

[9] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

9-*t*-Butylanthracene[1]

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The Grignard reaction of anthrone is often used for the preparation of 9-alkylanthracenes.[2,3] Russell found, however, that *t*-butylmagnesium chloride and anthrone yield isobutylene and the magnesium salt of anthrone rather than 9-*t*-butylanthracene.[2] A reexamination of this reaction employing excess *t*-butylmagnesium chloride[4] revealed that 9-*t*-butyl-9-hydroxy-9,10-dihydroanthracene (I) is formed in 28% yield. The spectroscopic properties of I (Experimental part) support this structure. Alcohol I is stable at its melting point and is not dehydrated by mild reagents, *e.g.*, cupric sulfate in refluxing xylene. The compound is degraded to anthracene in acid-catalyzed elimination reactions. However, I is readily converted to 9-*t*-butylanthracene (II) by phosphorus pentoxide in carbon tetrachloride.[5] Hydrocarbon II forms an adduct with maleic anhydride and is oxidized to anthraquinone. These findings and the definitive spectroscopic properties (Experimental Section) establish the structure.

Compounds I and II react with trifluoroacetic acid at −10° to yield 9-*t*-butyl-9-trifluoroacetoxy-9,10-dihydroanthracene (III). This structural assignment is based on the similar spectroscopic properties of I and III and the fact that III is hydrolyzed to I under basic conditions. Ester III is not stable. It slowly decomposes to anthracene during storage at ambient temperature. The decomposition is rapid in the presence of acids.

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[1] This work was supported by a grant (G25190) from the National Science Foundation.

[2] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

[3] R. LaLonde and R. Calas, *Bull. Soc. Chim. France*, 766 (1959).

[4] Excess Grignard reagent is necessary. For a discussion of the problem see E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 288–291.

[5] K. G. Flynn and G. Bergson, *Acta Chem. Scand.*, **18**, 2002 (1964).