chloroform) showed a single carbonyl absorption band at 1795 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.50; H, 5.45.

Attempted Aromatization of I.—The bisanhydride I (1.0 g.) was heated with 0.2 g. of sulfur in a sublimation tube at 220° for 30 min. Hydrogen sulfide was copiously evolved. The residue was sublimed at 100° and 0.75 mm. for 24 hr., and the sublimate was leached with carbon disulfide for 12 hr. Extraction of the residue with ether and concentration of the extracts gave a yellow solid. Its infrared spectrum (Nujol) showed anhydride bands at 1850 and 1785 cm.$^{-1}$, and the n.m.r. spectrum showed aromatic protons (3H) at τ 2.3 and unresolved multiplets from τ 6.3 to 7.3 (5H). The substance could not be obtained analytically pure.

Conversion of I to IIe.—A mixture of 2.5 g. of the bisanhydride I and 1.0 g. of sodium hydride (50% dispersion in mineral oil) in 30 ml. of toluene was refluxed under nitrogen for 24 hr. The toluene solution was filtered, washed with water, and concentrated under reduced pressure to yield 0.41 g. (20%) of dilactone IIe. Recrystallized from ethyl acetate, it melted at 150–151°, alone or admixed with an authentic sample, and its infrared spectrum was identical with that of the dilactone obtained above.

Preparation of Dimethyl Ester IV.—Following the procedure of Alder and Munz,[4] 0.6 g. of IIe was refluxed in 6 ml. of methanol containing 5 drops of concentrated sulfuric acid for 2 hr. Extraction of the cooled reaction mixture with ether and concentration of the extracts gave 0.47 g. (64%) of the ester. Recrystallized from aqueous methanol, it melted at 63–64° (lit.[4] m.p. 65°). The infrared spectrum (in chloroform, carbon tetrachloride, or carbon disulfide) showed a single, sharp band in the carbonyl region at 1745 cm.$^{-1}$.

Interconversion of Dilactone IIe and Diacid III. A.—A mixture of 0.20 g. of IIe, 0.1 g. of sodium carbonate, and 6 ml. of water was refluxed for 2 hr. The solution was filtered and acidified with concentrated hydrochloric acid. On cooling, 0.07 g. (32%) of crystalline diacid III precipitated; after recrystallization from acetonitrile, it melted at 177–179° (lit.[4] m.p. 177–179°). The infrared spectrum (Nujol) showed carbonyl bands at 1733 and 1700 cm.$^{-1}$.

B.—A solution of 70 mg. of diacid III in 2.5 ml. of acetic anhydride was refluxed for 2 hr., filtered, and concentrated at reduced pressure. The residue was recrystallized from ethyl acetate to afford 39 mg. (60%) of dilactone IIe, m.p. 150–151°. Identity was confirmed by comparison of infrared spectra and mixture melting point determination.

Acknowledgment.—We wish to express our gratitude to the Procter and Gamble Company for a fellowship to Hugh J. Barger, Jr.

The 2-Thia-1,2-dihydro- and -tetrahydrodicyclopentadienes[1]

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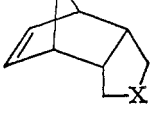
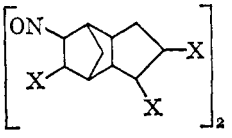
The preparation of methanesulfonate esters of six bicyclic 1,4-butanediols and the synthesis of *endo*- (IV), *exo*- (V), and *trans*-2-thia-1,2-dihydrodicyclopentadiene (VI) and the respective saturated sulfides (VII, VIII, and IX) are reported. The sulfonium salt (XVIII), which represents a new ring system, is also discussed.

It has been of particular interest in this laboratory to investigate the effect of hetero atoms at the 2-position of 1,2-dihydro-*endo*-dicyclopentadiene upon the steric course of reactions with acidic reagents. Compounds such as 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (I) and 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (II) have been prepared and their chemical reactivity has been investigated.[2-7] Haloamines (alkyl halides) of one of these compounds[2,5] (II) and several *vic*-

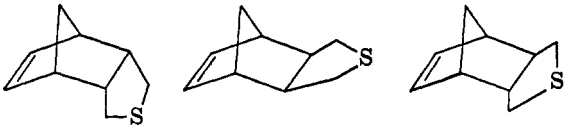


I, X=O
II, X=NH

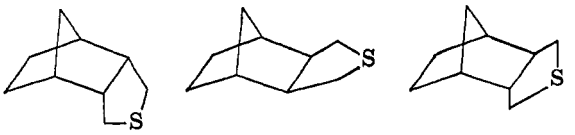


III

dihalo-1,2-dihydrodicyclopentadienenitroso halide dimers[8] (III) appear to contain an incipient mustard moiety which reacts like an alkylating agent with certain nucleophilic substances. In a search for additional compounds in which incipient mustard agents (evidenced by anchimeric and/or interannular effects) may be present, a variation of an established synthetic method has been successfully employed to prepare 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (IV), the first of a new sulfide type. Also, 2-thia-1,2-dihydro-*exo*-dicyclopentadiene (V) and the *trans* isomer (VI) have been synthesized, as well as the three saturated



IV V VI



VII VIII IX

sulfides, 2-thiatetrahydro-*endo*-dicyclopentadiene (VII), the *exo* isomer (VIII), and the *trans* isomer (IX).

It is of considerable interest that the progenitors of these sulfides, the methanesulfonate esters of the bicyclic 1,4-butanediols, are structurally related to the anticancer drug Myleran. These dimesylates of established stereochemistry provide an opportunity to study the stereochemical influences upon physiological activity in compounds related to Myleran.

(1) (a) Taken in part from a thesis 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 in part 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.

(2) P. Wilder, Jr., and C. F. Culberson, *J. Am. Chem. Soc.*, **81**, 2027 (1959).

(3) C. F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **25**, 1358 (1960).

(4) C. F. Culberson, J. H. Seward, and P. Wilder, Jr., *J. Am. Chem. Soc.*, **82**, 2541 (1960).

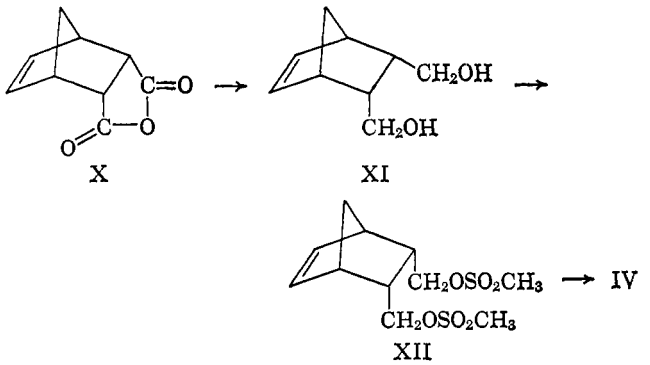
(5) C. F. Culberson and P. Wilder, Jr., *ibid.*, **82**, 4939 (1960).

(6) P. Wilder, Jr., and C. F. Culberson, *Chem. Ind.* (London), 1118 (1961).

(7) D. J. Cash, unpublished results, this laboratory.

(8) P. Wilder, Jr., and C. F. Culberson, *J. Org. Chem.*, **26**, 3556 (1961).

SCHEME I



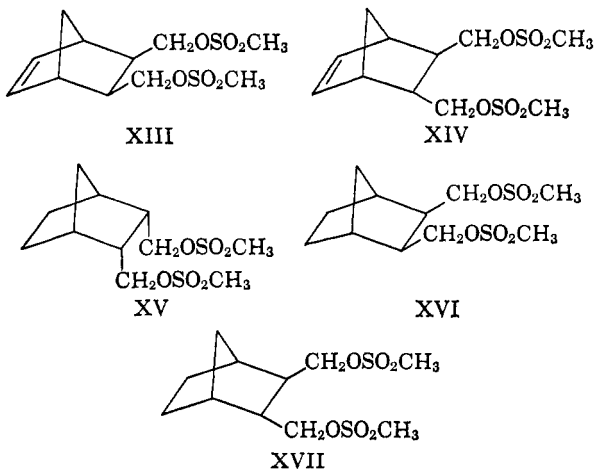
X XI XII

The synthesis of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene in Scheme I is typical of the preparation of the unsaturated sulfides. From the commercially available *endo-cis* adduct (X) of cyclopentadiene and maleic anhydride, *endo-cis*-5-norbornene-2,3-dimethanol (XI) was obtained by reduction with lithium aluminum hydride. On reaction of the diol with methanesulfonyl chloride, the methanesulfonate ester (XII) was obtained in good yield, and the sulfide was then prepared by a modification of the method of cyclization of Owen and Peto[9] using sodium sulfide. In several experiments it was found that the ditosylates would undergo cyclization under substantially the same conditions.

The dimesylate XIII for the preparation of 2-thia-1,2-dihydro-*exo*-dicyclopentadiene (V) was obtained from the *exo-cis*-dimethanol prepared in turn from the thermally rearranged *endo-cis*-anhydride.[10]

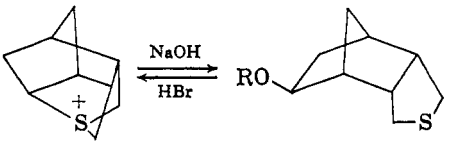
The *trans*-dimesylate XIV required for the preparation of *trans*-2-thia-1,2-dihydro-dicyclopentadiene (VI) was obtained from the lithium aluminum hydride reduction of the Diels–Alder adduct of cyclopentadiene and ethyl fumarate.

The saturated dimesylates, *endo-cis* (XV), *exo-cis* (XVI), and *trans* (XVII), were prepared either by catalytic hydrogenation of the corresponding unsaturated dimesylate or from the saturated dimethanol and methanesulfonyl chloride. The respective saturated sulfides VII, VIII, and IX were prepared by the route previously described.



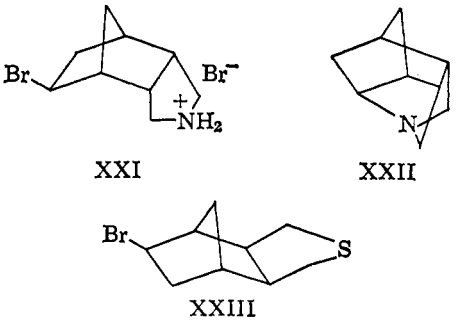
XIII XIV XV XVI XVII

That the 2-thia-*endo*-sulfide IV represents another example of an incipient mustard agent was evidenced by its reaction with HBr. With 48% HBr solution at steam-bath temperatures for several hours or with anhydrous HBr in dry ether or tetrahydrofuran at room temperature in only a few minutes, *endo*-sulfide IV afforded in good yield the sulfonium salt XVIII. By comparison, the secondary amine II readily forms an amine hydrobromide with HBr at room temperature, but only at elevated temperature does it give the bromoamine hydrobromide XX from which the cyclized tertiary amine XXI is obtained with alcoholic potash.[5] Soluble in water and alcohol, but insoluble in nonpolar solvents, the sulfonium salt readily formed a highly crystalline picrate in ethanol solution. With HCl solution the sulfide gave a hydroscopic sulfonium chloride which yielded the same picrate as that obtained from the sulfonium bromide XVIII or from the sulfide itself and picric acid. Also, it has been shown that the sulfonium salt undergoes displacement with aqueous sodium hydroxide to yield an alcohol, *exo*-9-hydroxy-2-thiatetrahydro-*endo*-dicyclopentadiene (XIX). The alcohol XIX was also obtained from the facile hydrolysis of the formate XX resulting from the reaction of *endo*-sulfide IV and excess formic acid. When treated overnight with HBr at steam-bath temperature, both XIX and XX afforded the sulfonium salt XVIII. Additional evidence for the structure of alcohol XIX was obtained from the pyrolysis of formate XX. The fact that the product of pyrolysis was sulfide IV, and not an *exo*-cyclic unsaturated sulfide, eliminated a possibility of attack by hydroxyl ion or formate ion at C-1 or C-3 of the salt XVIII.



XVIII XIX, R=H XX, R=HCO

Finally *exo*-sulfide V, unable to effect cyclization without a skeletal rearrangement, afforded in 48% aqueous HBr solution a covalent, organic-soluble compound, *exo*-9-bromo-2-thiatetrahydro-*exo*-dicyclopentadiene (XXIII), a reaction typical of 1,2-dihydro-*exo*-dicyclopentadienes, and no observable sulfonium bromide XVIII.



XXI XXII XXIII

Experimental[11]

***endo-cis*-5-Norbornene-2,3-dimethanol Dimethanesulfonate (XII).**—Into a 2-l. three-neck round-bottom flask, equipped with

(9) L. N. Owen and A. G. Peto, *J. Chem. Soc.*, 2383 (1955).
(10) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

(11) Melting points and boiling points are uncorrected. Analyses are by Galbraith Laboratories, Knoxville, Tenn., Triangle Chemical Laboratories, Chapel Hill, N. C., or Dr. Ing. A. Schoeller, Microanalytisches Laboratorium, West Germany. Gas chromatographic analyses were obtained with a Perkin-Elmer Model 154-C vapor fractometer using Ucon Polar and polypropylene glycol columns. Infrared analyses were obtained by the use of a Perkin-Elmer Model 137 recording spectrophotometer.

a thermometer and drying tube attached by means of a two-holed rubber stopper to one neck, a stirrer, and an addition funnel, was placed 138 ml. of dry pyridine (distilled over CaO). The flask was cooled in an ice–salt bath and 50 g. (0.44 mole) of methanesulfonyl chloride was added to the stirred pyridine at such a rate that the temperature of the mixture was maintained at 0°. Thirty grams (0.19 mole) of *endo-cis*-diol XI[4,12] in 124 ml. of dry pyridine was placed in the addition funnel and added dropwise to the stirred, chilled solution of mesyl chloride in pyridine. During addition the temperature was kept between 0 and 5°. When addition was complete, the mixture was stirred for 6 hr. at 0° and was left overnight in a refrigerator. Then, 300 ml. of 10% HCl diluted to 800 ml. with ice–water was added to the stirred mixture. The crystals, which precipitated readily, were removed by filtration and were stirred twice with water to remove excess pyridine. The product was recrystallized from absolute ethanol to constant melting point. The yield was 48.1 g. (80%), m.p. 99–100°.

Anal. Calcd. for $C_{11}H_{18}O_6S_2$: C, 42.58; H, 5.81. Found: C, 42.77; H, 5.72.

***exo-cis*-5-Norbornene-2,3-dimethanol Dimethanesulfonate (XIII).**—The *exo-cis*-dimesylate XIII was prepared from the corresponding diol[4,13] by the method described above. From 9.7 g. (0.063 mole) of diol, 14.6 g. (75%) of dimesylate XIII was obtained, m.p. 120°, from absolute methanol.

Anal. Calcd. for $C_{11}H_{18}O_6S_2$: C, 42.58; H, 5.81. Found: C, 42.49; H, 5.73.

***trans*-5-Norbornene-2,3-dimethanol Dimethanesulfonate (XIV).**—The *trans*-dimesylate was prepared from *trans*-5-norbornene-2,3-dimethanol[14,15] by the method employed above.

In one experiment 92.6 g. (0.60 mole) of the *trans*-dimethanol in 300 ml. of dry pyridine (distilled over CaO) was added dropwise to a solution of 154 g. (105 ml., sp. gr. 1.47) of methanesulfonyl chloride in 420 ml. of dry pyridine cooled to 0° in an ice–salt bath. The yield was 175 g. (94%), m.p. 68–70°, from absolute ethanol–ether.

Anal. Calcd. for $C_{11}H_{18}O_6S_2$: C, 42.58; H, 5.81. Found: C, 42.77; H, 5.95.

***endo-cis*-Norbornane-2,3-dimethanol Dimethanesulfonate (XV).**

A. By the Hydrogenation of *endo-cis*-5-Norbornene-2,3-dimethanol Dimethanesulfonate (XII).—The unsaturated dimesylate XII (2 g., 0.0065 mole) in ethyl acetate was hydrogenated in the presence of PtO_2 for at least 12 hr. The yield was 1.7 g. (84%) of a solid, m.p. 111–112°, from absolute methanol.

B. From *endo-cis*-5-Norbornene-2,3-dimethanol (XI).—*endo-cis*-Diol XI (28 g., 0.182 mole) in absolute ethanol was hydrogenated over PtO_2. A few grams of the crude product was recrystallized from ether, m.p. 65° (lit. 62°,[14] 65–66°[4]). The crude product was treated with methanesulfonyl chloride according to the procedure used to prepare the unsaturated *endo-cis*-dimesylate XII. The yield was 30.7 g. (54%), m.p. 112°, from absolute methanol. A mixture melting point with a sample made by the hydrogenation method above was not depressed.

Anal. Calcd. for $C_{11}H_{20}O_6S_2$: C, 42.31; H, 6.41. Found: C, 42.17; H, 6.48.

***exo-cis*-Norbornane-2,3-dimethanol Dimethanesulfonate (XVI).**—*exo-cis*-5-Norbornene-2,3-dimethanol (3 g., 0.0097 mole) was hydrogenated over PtO_2 for 12 hr. The yield was 1.8 g. (60%), m.p. 90–90.5°, from absolute methanol. On admixture with the starting material, the melting point was 87–102°.

Anal. Calcd. for $C_{11}H_{20}O_6S_2$: C, 42.31; H, 6.41. Found: C, 42.40; H, 6.53.

***trans*-Norbornane-2,3-dimethanol Dimethanesulfonate (XVII).**

A. By the Hydrogenation of *trans*-5-Norbornene-2,3-dimethanol Dimethanesulfonate (XIV).—Unsaturated dimesylate XIV (15 g., 0.0484 mole) in ethyl acetate was hydrogenated over PtO_2 for 12 hr. The yield was 11.4 g. (75%) of the saturated product, m.p. 85–86°, from absolute methanol.

B. From *trans*-Norbornane-2,3-dimethanol.—A solution of 5.3 g. (0.034 mole) of crude *trans* unsaturated diol in absolute ethanol was hydrogenated over PtO_2. The quantitative amount of hydrogen was readily absorbed. The crude saturated product was treated with methanesulfonyl chloride according to the method employed above to yield 6.1 g. (57% over-all) from absolute methanol, m.p. 85–86°. A mixture melting point with a sample of part A showed no depression.

Anal. Calcd. for $C_{11}H_{20}O_6S_2$: C, 42.31; H, 6.41. Found: C, 42.18; H, 6.36.

2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (IV).—A 1-l., one-neck round-bottom flask, with a delivery stopcock at the bottom and a three-way oblique-bore stopcock near the neck, was equipped with a reflux condenser and inclined in such a way as to permit a heating mantle to be placed between the flask and a magnetic stirring motor. An addition funnel was connected to one of the arms of the three-way stopcock by a 3-in. Tygon tubing. The flask was charged with 20 g. (0.065 mole) of *endo-cis*-dimesylate XII and 200 ml. of absolute methanol. Then, with stirring, the mixture was warmed until it was under reflux. Immediately, a solution of 50 g. of sodium sulfide nonahydrate in 120 ml. of water was added from the addition funnel over a period of 5 hr. The reaction mixture was refluxed with stirring for an additional 19 hr. during which time the sulfide being formed was routinely removed from the delivery stopcock. The reaction mixture was poured into ether. The ether layer was separated, washed with excess 10% NaOH, and dried over $MgSO_4$.

Additional sulfide was obtained from the reaction mixture by steam distillation. In order to separate the sulfide from water, enough solid NaCl was added to make a saturated solution to "salt out" the product. Finally, the product was dissolved in ether and was washed with 10% NaOH; the ether layer was dried over $MgSO_4$.

By combining both extracts, 7.6 g. (78%) of *endo-cis*-sulfide IV was recovered after one distillation. A vapor phase chromatographic analysis showed one major peak accounting for 98% of the material present, $n^{26}D$ 1.5546, b.p. 57° (0.45 mm.).

Anal. Calcd. for $C_9H_{12}S$: C, 71.05; H, 7.89. Found: C, 71.38; H, 7.93.

A methoidide was prepared by dissolving the sulfide in dry ether and adding a large excess of methyl iodide: m.p. 149–149.5° on recrystallization from absolute ethanol.

Anal. Calcd. for $C_{10}H_{15}IS$: C, 40.82; H, 5.11. Found: C, 40.78; H, 5.14.

A phenyl azide adduct was prepared by the addition of excess phenyl azide in ether to 0.36 g. of sulfide dissolved in anhydrous ether. After a few hours the phenyl azide adduct began to crystallize in long needles, m.p. 169–171° from ethanol.

Anal. Calcd. for $C_{15}H_{17}N_3S$: C, 66.42; H, 6.27. Found: C, 66.91; H, 6.17.

2-Thia-1,2-dihydro-*exo*-dicyclopentadiene (V).—The unsaturated *exo-cis* sulfide V was prepared by the method above yielding 7.4 g. (75%) of product from 20 g. (0.065 mole) of dimesylate. A vapor phase chromatographic analysis showed a purity of at least 99%, $n^{25}D$ 1.5553, b.p. 50° (0.45 mm.).

Anal. Calcd. for $C_9H_{12}S$: C, 71.05; H, 7.89. Found: C, 71.05; H, 8.01.

A mercuric chloride complex was prepared by the slow addition of a warm saturated solution of mercuric chloride in alcohol to 0.36 g. of sulfide in 8 ml. of absolute ethanol until no further precipitation occurred. The solid was removed by filtration, washed with alcohol, and recrystallized from absolute ethanol: m.p. 188–190°.

Anal. Calcd. for $C_9H_{12}Cl_2HgS$: C, 25.47; H, 2.87. Found: C, 25.26; H, 2.85.

A phenyl azide adduct was readily formed, m.p. 191–192° from ethanol.

Anal. Calcd. for $C_{15}H_{17}N_3S$: C, 66.42; H, 6.27. Found: C, 66.08; H, 6.06.

2-Thia-1,2-dihydro-*trans*-dicyclopentadiene (VI).—The *trans*-sulfide VI, prepared by the same method, yielded 5.4 g. (55%) from 20 g. of dimesylate XIV, $n^{24}D$ 1.5599, b.p. 55° (0.45 mm.).

Anal. Calcd. for $C_9H_{12}S$: C, 71.05; H, 7.89. Found: C, 71.13; H, H. 7.83.

A sulfone was prepared from a solution of 2 ml. of 30% H_2O_2 and 0.36 g. of sulfide dissolved in 2 ml. of glacial acetic acid. The reaction mixture was left overnight and excess acetic acid was evaporated on a steam bath until a solid was obtained which, on recrystallization from water, melted at 135.5–136°.

Anal. Calcd. for $C_9H_{12}O_2S$: C, 58.70; H, 6.53. Found: C, 58.25; H, 6.57.

2-Thiatetrahydro-*endo*-dicyclopentadiene (VII).—The saturated *endo* sulfide VII was prepared from the corresponding dimesylate XVII by the method employed for the unsaturated *endo*-sulfide IV.

From 28.0 g. (0.088 mole) of dimesylate in 300 ml. of absolute methanol and 75 g. of sodium sulfide nonahydrate in 180 ml. of water, 10.8 g. (78%) of a crude product was obtained. On dis-

(12) A. Winston, Ph.D. Thesis, Duke University, 1955.
(13) K. Alder and W. Roth, *Chem. Ber.*, **88**, 407 (1955).
(14) K. Alder and W. Roth, *ibid.*, **87**, 161 (1954).
(15) L. A. Feliu-Otero, M.A. Thesis, Duke University, 1962.

tillation a solid collected in the condenser, m.p. 50°, b.p. 70° (0.4 mm.). V.p.c. using a column of 15% Ucon Polar on Chromosorb W at 125° showed essentially a single peak.

Anal. Calcd. for $C_9H_{14}S$: C, 70.13; H, 9.09. Found: C, 70.18; H, 9.20.

The saturated *endo*-sulfide readily formed a methiodide, m.p. 162–164° from absolute ethanol.

Anal. Calcd. for $C_{10}H_{17}IS$: C, 40.54; H, 5.79. Found: C, 40.75; H, 6.02.

2-Thiatetrahydro-*exo*-dicyclopentadiene (VIII).—From 3.6 g. (0.0115 mole) of the saturated *exo*-dimesylate in 39 ml. of absolute methanol and 12 g. of sodium sulfide nonahydrate in 24 ml. of water, 1.2 g. (67%) of saturated *exo*-sulfide was obtained, b.p. 89° (1 mm.), $n^{27}D$ 1.5392. Only one peak was found on vapor phase chromatographic analysis.

Anal. Calcd. for $C_9H_{14}S$: C, 70.13; H, 9.09. Found: C, 70.83; H, 9.11.

The saturated *exo*-sulfide formed a methiodide, m.p. 167–170°.

Anal. Calcd. for $C_{10}H_{17}IS$: C, 40.54; H, 5.79. Found: C, 40.84; H, 5.57.

2-Thiatetrahydro-*trans*-dicyclopentadiene (IX).—In the method employed for preparation of the unsaturated *endo-cis*-sulfide IV, 22.7 g. (0.073 mole) of saturated *trans*-dimesylate in 220 ml. of absolute methanol was treated with 56 g. of sodium sulfide nonahydrate in 190 ml. of water. The yield was 9.0 g. (80%) of a colorless oil, isolated by vacuum distillation, b.p. 85–87° (0.5 mm.).

Anal. Calcd. for $C_9H_{14}S$: C, 70.13; H, 9.09. Found: C, 70.00; H, 8.62.

A sulfone was prepared by the method of Whitehead, Dean, and Fidler,[16] m.p. 86–87° from water.

Anal. Calcd. for $C_9H_{14}O_2S$: C, 58.06; H, 7.53. Found: C, 58.16; H, 7.55.

Cyclization of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (IV) with Hydrobromic Acid. A. With 48% Hydrobromic Acid.—A solution of 6.1 g. (0.040 mole) of pure unsaturated *endo*-sulfide in 6 ml. of absolute ethanol was stirred under reflux for 8 hr. on a steam bath with 13.7 ml. (0.12 mole) of 48% hydrobromic acid. The reaction mixture was dissolved in 10 ml. of absolute ethanol and the product was precipitated by the addition of excess dry ether. The sulfonium salt XVIII was removed by filtration and was recrystallized twice by solution in hot absolute ethanol and the addition of excess dry ether, after the alcoholic solution had come to room temperature. Finally, the salt was washed with ether and was dried in an oven at 60°. The yield was 6.0 g. (65%) of colorless crystals, which darkened on exposure to air, m.p. 245–247° dec.

B. With Anhydrous Gaseous Hydrobromic Acid in an Inert Solvent.—Into 2.0 g. (0.013 mole) of the unsaturated *endo*-sulfide in 150 ml. of anhydrous ether, was bubbled excess anhydrous gaseous hydrobromic acid, obtained by heating solid sodium bromide in polyphosphoric acid.

After several minutes, a white solid began to precipitate. When no further precipitation was observed, the reaction was halted. Excess acid was removed from the mixture by vigorous stirring at room temperature. Solid product was removed by filtration and was purified in the manner described above. The yield was 2.5 g. (81%), m.p. 245° dec. On admixture with a sample from procedure A, there was no depression of melting point.

Anal. Calcd. for $C_9H_{13}BrS$: C, 46.35; H, 5.58. Found: C, 46.73; H, 5.58.

The salt readily formed a picrate, m.p. 228–230° dec. from absolute ethanol.

Anal. Calcd. for $C_{15}H_{15}N_3O_7S$: C, 47.24; H, 3.94. Found: C, 47.00; H, 3.95.

Reaction of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (IV) and Picric Acid.—To 0.5 g. of sulfide IV was added 17 ml. of methanol saturated with picric acid and the reaction mixture was heated under reflux overnight. The product was isolated by the addition of dry ether, filtration, and recrystallization from absolute ethanol. A mixture melting point with the picrate above showed no depression. The infrared spectra of the two picrates were identical.

Cyclization of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (IV) with Concentrated Hydrochloric Acid.—To 4.1 g. (0.027 mole) of the unsaturated *endo*-sulfide in 5 ml. of *n*-hexane was added 5.4 g. (0.054 mole) of concentrated hydrochloric acid. The reaction mixture was stirred at room temperature for 2 days. The water layer was then separated, water was evaporated, and the sulfonium salt was precipitated from absolute ethanol by dry ether. The sulfonium chloride salt was highly hydroscopic.

For the purpose of identification, a picrate was prepared, m.p. 228–230°, which showed no depression with the picrate of the sulfonium bromide salt XVIII. Infrared spectra of the two picrates were identical.

The other layer, containing the *n*-hexane, was diluted with dry ether, washed with a solution of sodium carbonate, and dried over $MgSO_4$. After the solvents were removed under reduced pressure, a residue remained which was stirred and heated under reflux for 24 hr. with 0.75 g. of KOH in 3.5 ml. of absolute ethanol. The mixture was then poured into water and was extracted with ether. No unsaturated *exo*-sulfide V was found in the ether layer when retention times were compared in a vapor phase chromatographic analysis with a known sample.

Addition of Hydrobromic Acid to 2-Thia-1,2-dihydro-*exo*-dicyclopentadiene (V). Preparation of 9-*exo*-Bromo-2-thiatetrahydro-*exo*-dicyclopentadiene (XXII).—A mixture of 4.3 ml. (0.038 mole) of 48% hydrobromic acid and 2.3 g. (0.015 mole) of unsaturated *exo*-sulfide V was stirred at room temperature for 24 hr. A solution of Na_2CO_3 was added to neutralize excess acid, and the reaction mixture was extracted with ether. The ether layer was washed with water and was dried over $MgSO_4$. After the ether was evaporated at room temperature under vacuum, there remained a solid which was recrystallized twice from *n*-heptane in a Dry Ice–acetone bath, m.p. 53–55°.

Anal. Calcd. for $C_9H_{13}BrS$: C, 46.35; H, 5.58. Found: C, 46.46; H, 5.63.

No sulfonium bromide (XVIII) was observed in this reaction.

Preparation of 9-*exo*-Hydroxy-2-thiatetrahydro-*endo*-dicyclopentadiene (XIX).—To 2.8 g. (0.018 mole) of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (IV) in 3 ml. of anhydrous ether was added 2.9 g. (0.055 mole) of 88% formic acid. The reaction mixture was refluxed in a steam bath for 4 hr. Excess formic acid was removed by vacuum distillation, and the formate was distilled, giving a colorless liquid, b.p. 104–106° (0.7 mm.), $n^{25.5}D$ 1.5430.

To 1.7 g. (0.0086 mole) of the formate was added 0.721 g. (0.0128 mole) of potassium hydroxide dissolved in absolute alcohol, and the mixture was heated under reflux for 8 hr. The alcohol was removed by distillation, leaving a residue which was taken up in ether and dried over $MgSO_4$. After removal of ether, the solid residue was recrystallized from *n*-heptane in a Dry Ice–acetone bath giving 0.88 g. (60%) of a white solid, m.p. 131°.

Anal. Calcd. for $C_9H_{14}OS$: C, 63.53; H, 8.23. Found: C, 63.14; H, 8.08.

A methiodide was prepared, m.p. 151–153° from absolute ethanol.

Anal. Calcd. for $C_{10}H_{17}IOS$: C, 38.46; H, 5.45. Found: C, 38.46; H, 5.62.

Reaction of Sulfonium Salt XVIII with Aqueous Sodium Hydroxide.—A mixture of 9.5 g. (0.041 mole) of sulfonium bromide salt and 1.76 g. (0.044 mole) of NaOH in 60 ml. of water was stirred vigorously overnight at room temperature. The mixture was neutralized with 10% HCl and extracted with ether, and the ether layer was dried over $MgSO_4$. After ether was removed under vacuum, a solid residue remained which was recrystallized from *n*-heptane in a Dry Ice–acetone bath, m.p. 130°. A mixture melting point with XIX was not depressed. The infrared spectra of the alcohols were identical.

Pyrolysis of Formate XX.—The pyrolysis was carried out at atmospheric pressure in an apparatus designed for vacuum distillation. The formate, 1.14 g. (0.0060 mole), was heated with a small burner for about 1 min. The inner walls of the Vigreux column and the tip of the thermometer were covered with a colorless liquid. A cloudy vapor, probably formic acid, reached the condenser. At this moment vacuum was applied to flash over most of the liquid into a receiving flask and the cloudy vapor into a Dry Ice–acetone trap. V.p.c. of the product, using a Perkin-Elmer 154-0013A metal column of disodecyl phthalate at 170°, showed essentially a single peak at 16.3 min., which corresponded to the retention time of an authentic sample of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (IV).

(16) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).

Reaction of 9-*exo*-Hydroxy-2-thiatetrahydro-*endo*-dicyclopentadiene (XIX) with Hydrobromic Acid.—To 1 g. of XIX in absolute ethanol was added excess 48% hydrobromic acid. The mixture was held under reflux for 8 hr. on a steam bath and was stirred overnight. After excess HBr and the solvent were removed by evaporation, a solid residue remained which, after recrystallization, was identified as the sulfonium salt XVIII.

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The Preparation of 4-Pentenenitriles and 3,4-Pentadienenitriles from N-(2-Alkenyl)- and N-(2-Alkynyl)amides

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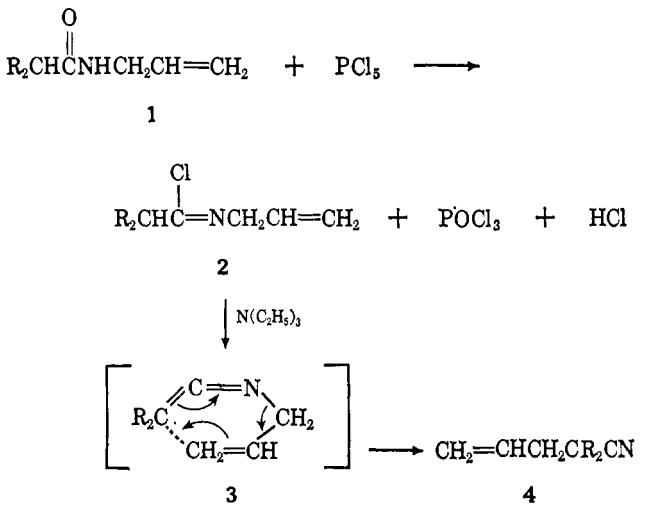
N-(2-Alkenyl)amides are converted to imino chlorides or imino chloride hydrochlorides with phosphorus(V) chloride or phosgene, respectively. These products, on treatment with a tertiary amine, give 4-pentenenitriles *via* a Claisen-type rearrangement. Since intermediates have not been isolated, it is not known whether the reaction proceeds through the formation of a discrete ketenimine or whether the process is a concerted one. The reaction appears to be intramolecular, however, since N-(2-butenyl)isobutyramide gives 2,2,3-trimethyl-4-pentenenitrile instead of 2,2-dimethyl-4-hexenenitrile. N-(2-Propynyl)butyramide gives 2-ethyl-3,4-pentadienenitrile. This reaction represents a new example of the Claisen-type rearrangement and provides a synthetic route to 4-pentenenitriles and 3,4-pentadienenitriles.

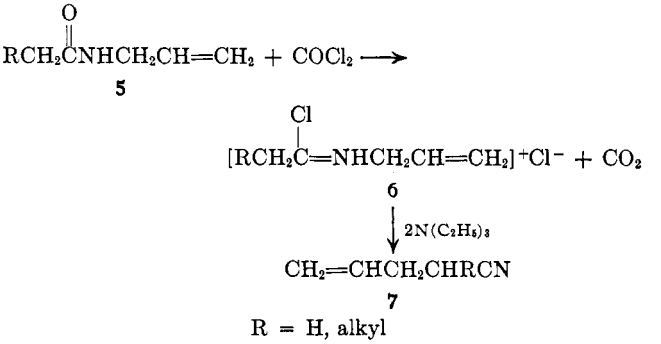
We should like to add an example to the already considerable list of systems which undergo Claisen-type rearrangements. It appeared of interest, despite expectations to the contrary, to determine whether N-(2-alkenyl)ketenimines, which had not been reported, would undergo such a rearrangement, leading to 4-pentenenitriles. Since the cumulative double-bond system is linear, one would not expect the ketenimines to lend themselves to six-membered, cyclic transition states.

Ketenimines themselves have been known for some time, but comparatively little work has been done with them. A classical route to ketenimines is analogous to the preparation of ketene from acid chlorides and a tertiary amine. An imino chloride is used in place of the acid chloride, and treatment with a base such as triethylamine leads, in most cases, to the formation of a ketenimine.[1] Imino chlorides, in turn, may be prepared from secondary amides by treatment with phosphorus(V) chloride or phosgene.

We found that when the amide possessed only one α-hydrogen atom, phosphorus(V) chloride was the preferred reagent. The mixture of amide **1** and phosphorus(V) chloride was heated in a solvent until hydrogen chloride evolution ceased. The phosphoryl chloride was removed by distillation under reduced pressure, and the imino chloride **2** was then distilled. Treatment of **2** with triethylamine in refluxing benzene gave the substituted 4-pentenenitriles **4**. The isolation of the ketenimine **3** was never accomplished.



When the starting amide **5** possessed more than one α-hydrogen atom, phosgene was found to be the preferred reagent. The reaction of **5** with phosgene was carried out in a solvent such as ether or tetrahydrofuran, and carbon dioxide was evolved. There resulted, presumably, the hydrochloride **6** of the imino chloride. Treatment of the crude salt with 2 moles of tertiary amine gave the nitrile **7**.



It is not known whether the formation of the unsaturated nitrile proceeds through the formation of a discrete ketenimine or whether the reaction is a concerted one. It appears to be intramolecular, however, since N-(2-butenyl)isobutyramide was converted, with inversion of the 2-butenyl group, to 2,2,3-trimethyl-4-pentenenitrile.

N-(2-Propynyl)butyramide (**8**) was converted, although in poor yield, to 2-ethyl-3,4-pentadienenitrile (**10**). This result is indeed striking, for, if the ketenimine intermediate **9** is involved, it contains two linear groups. Even if a concerted process is operative, the intermediate still contains the linear propynyl group.

Our crude nitriles sometimes contained small amounts of chlorine-containing impurities which were usually removed by washing with dilute acid. In one case we obtained evidence that the impurity was diethyl-

(1) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954).