Tritylation of 1-Ethoxy-2-methoxybenzene.—A mixture of this compound (7 g), and triphenylmethanol (12 g), dissolved in glacial acetic acid (200 ml) and concentrated sulfuric acid (9 ml), was heated at 50° for 3 days. The solution was poured into water and the solid, on recrystallization from nitromethane (7 g, 38.6%), had mp 147–149°. The product mixed with triphenylmethanol showed depression of melting point, while on admixture with either 3-ethoxy-4-methoxytetraphenylmethane (X) or 4-ethoxy-3-methoxytetraphenylmethane (XI) the melting point was raised. The infrared spectra of the last two compounds showed that the tritylation product of 1-ethoxy-2-methoxybenzene consisted of a mixture of both.

3-Ethoxy-4-methoxytetraphenylmethane (X).—This was prepared from 3-ethoxy-4-hydroxytetraphenylmethane (III) by etherification with methyl iodide according to the general method described above. The solid (85%), after sublimation under vacuum, had mp 192°.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.29; H, 6.60. Found: C, 84.89; H, 6.77.

4-Ethoxy-3-methoxytetraphenylmethane (XI).—This was prepared from 4-hydroxy-3-methoxytetraphenylmethane (II) by etherification with ethyl iodide according to the general method described above. The solid (78%), after sublimation under vacuum, had mp 159–160°.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.29; H, 6.60. Found: C, 85.33; H, 6.43.

Product Analysis.—On leaving the most concentrated reaction mixtures used for the kinetic measurements in the water baths for 1 or 2 days, precipitates were recovered which consisted of the pure tritylated derivatives with the trityl group in the position *para* relative to the hydroxy group. The mother liquors yielded only triphenylmethanol and the unreacted substrate. In the case of *o*-isopropoxyphenol, compound $C_{41}H_{32}$ was also recovered after longer stays as described.

Reaction Kinetics.—The dilatometric and radiometric[22] methods followed here were previously described.[1] In this study an average molar contraction for the reaction of 18.69 ± 2.30 ml mole^{-1} was found.

(22) We thank Dr. M. A. Tamers and Mr. A. Carsten for the counting of our radioactive samples.

Protection of the Hydroxyl Group with Vinyl Thioethers

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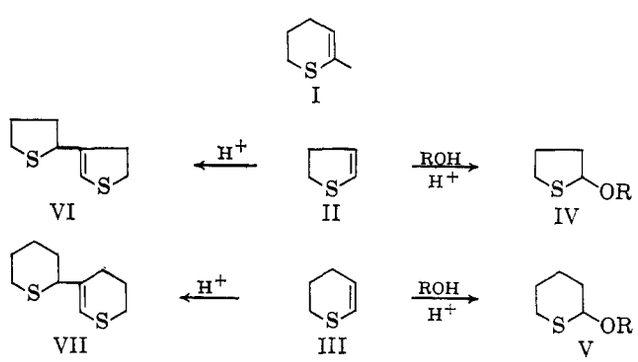
The cyclic vinyl thioethers, 2,3-dihydrothiophene (II) and 2,3-dihydro-4H-thiopyran (III), react with alcohols, under acid catalysis, by addition to the double bond. The preparation of adducts with cholestanol, cyclopentanol, and 5′-O-acetylthymidine is described. The protective grouping can be removed readily by reaction with silver ion at neutral pH. Implications of the technique for the synthesis of ribonucleotides are discussed.

The intensive efforts which have been devoted to the chemical formation of 3′–5′-interribonucleotide linkages[1] have served to remove a major obstacle from the synthesis of ribonucleic acid chains. An element of prime importance in such a synthesis is the availability of a blocking agent for the 2′-hydroxyl function which can survive a variety of manipulations at other centers and yet be removable under relatively mild conditions. Both these requirements have been met, in previous work, by use of either the tetrahydropyranyl ether[2] or the acetate ester.[3] In the former case, unblocking has sometimes required acid conditions more vigorous than desirable for the total survival of the remaining species; in the latter case, alkaline hydrolysis of the acetate liberates the 2′-hydroxyl which may interact with the neighboring phospho diester function.[1] In either case, the use of acid or alkaline conditions limits the extent to which protective groups may be used for other purposes in other regions of the molecule.

Several years ago, the use of dihydropyran for the protection of sulfhydryl functions in peptide synthesis was explored in this laboratory.[4] It was shown that the adduct obtained with this reagent could survive a variety of chemical treatments and that the blocking group could be ultimately removed by addition of silver or mercuric ions at neutral pH and at low temperatures. It seemed reasonable to suppose that the same reaction, by interchange of the respective hetero atoms, could be applied to the synthesis of ribonucleotides by protection of an hydroxyl function with a sulfur analog of dihydropyran.

The most readily available reagent for this purpose, 2,3-dihydro-6-methyl-4H-thiopyran (I),[5] failed to form a stable adduct with simple alcohols, most likely because of a facile acid-catalyzed reversibility at the tertiary reaction center.



The simpler vinyl thioethers, 2,3-dihydrothiophene (II)[6] and 2,3-dihydro-4H-thiopyran (III),[7,8] behaved as expected, forming the adducts IV and V, respectively. These vinyl thioethers differ from their oxygen analogs by their ease of polymerization in the presence of traces of acid, occasionally with explosive rapidity. Since the addition of an hydroxyl function to the olefinic bond itself requires acid catalysis, it became necessary

(1) For an extensive bibliography, see D. Söll and H. G. Khorana, *J. Am. Chem. Soc.*, **87**, 350, 360 (1965).

(2) M. Smith, D. H. Rammler, I. H. Goldberg, and H. G. Khorana, *ibid.*, **84**, 430 (1962); D. H. Rammler and H. G. Khorana, *ibid.*, **84**, 3112 (1962).

(3) D. H. Rammler, Y. Lapidot, and H. G. Khorana, *ibid.*, **85**, 1989 (1963).

(4) G. F. Holland and L. A. Cohen, *ibid.*, **80**, 3765 (1958).

(5) L. Bateman and R. W. Glazebrook, *J. Chem. Soc.*, 2834 (1958).

(6) G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961); *Tetrahedron*, **18**, 15, 903 (1962).

(7) For an alternative method of preparation, *cf.* W. E. Parham, L. Christensen, S. H. Gruen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

(8) Alternatively, 3,4-dihydro-2H-thiopyran.

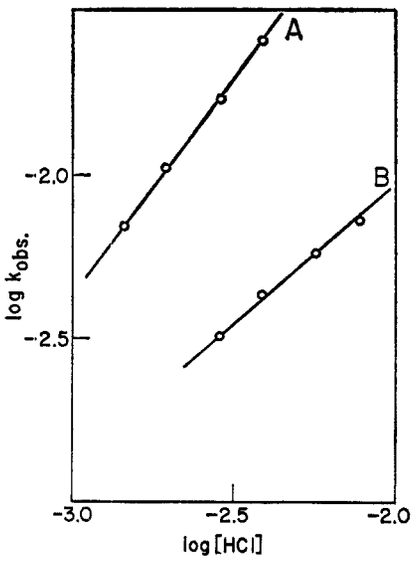


Figure 1.—Dependence of rate of reaction of cyclopentanol with vinyl thioethers on acid concentration: A, 2,3-dihydrothiophene (II); B, 2,3-dihydro-4H-thiopyran (III).

to search for reaction conditions which would encourage addition with a minimum of polymerization of the reagent.

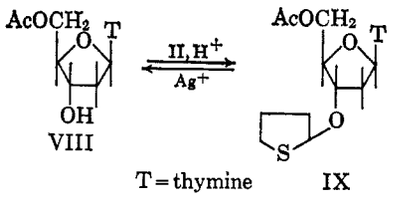
Exploratory runs with cholestanol as the alcohol revealed that addition could be effected by using small amounts of acid (trifluoroacetic or hydrochloric) in an inert diluent and relatively long reaction times. Following their purification by chromatography on Florisil, adducts of cholestanol with both II and III were obtained in crystalline form and in yields of 75 and 35%, respectively. The original alcohol was regenerated rapidly and cleanly by decomposition of the adducts with aqueous silver nitrate.

For more detailed studies, cyclopentanol was chosen as a simple analog of the ribofuranoside ring system. The rate of disappearance of the reagent was followed (up to 50–90% conversion) by the decrease in spectral absorption at 242 mμ in the case of II and at 226 mμ in the case of III. The reactions with both vinyl thioethers obey the pseudo-first-order rate law and, in each case, the rates (log k) show a linear dependence on the concentration of acid (−log[HCl]) present (Figure 1).[9] Within the range of acid concentrations used in these experiments, polymerization of the reagent was limited largely to the formation of the dimers, VI and VII, respectively.[6,10] As in the principal addition reaction, II was found to be more reactive toward dimer formation than its six-membered homolog, III. In each case studied, no difficulty was encountered in isolating the adduct free of dimer contamination. Although dimer formation consumes a portion of the reagent and may obscure ultraviolet spectral assay, no experimental conditions could be found to suppress the side reaction entirely. Because of its over-all greater reactivity, dihydrothiophene was chosen for initial studies in the nucleic acid field.

(9) The rate data obtained was insufficient to permit any inferences regarding mechanism.

(10) Reasoning by electronic principles, we have assigned head-to-tail structures to these dimers: C. Bergland and S.-O. Lawesson [*Arkiv Kemi*, **20**, 225 (1963)] conclude, from desulfurization experiments, that the dimer of II has a head-to-head structure, although their published nmr spectrum seems to agree more closely with structure VI.

The 5′-hydroxyl function of thymidine was protected by selective acetylation[11] and the resulting 5′-O-acetylthymidine (VIII) was allowed to react with dihydrothiophene in chloroform. Following chromatographic purification on Florisil, the adduct IX was obtained in 57% yield. Following treatment of the adduct with an aqueous solution of silver nitrate, 5′-O-acetylthymidine (VIII) was found (by tlc) to be the only nucleoside derivative present in the reaction mixture.



These studies illustrate the application of cyclic vinyl thioethers as protective agents for hydroxyl functions in general and, particularly, for those cases in which exposure either to acid or alkaline conditions must be avoided in a subsequent step. The possibilities for selective unblocking of functional groups in a polyfunctional compound are self-evident.

Experimental Section[12]

2,3-Dihydro-6-methyl-4H-thiopyran (I) was prepared, in improved yield, by a variation of the published procedure.[5] A mixture of 98 g (1.0 mole) of redistilled hex-5-en-2-one (Chemicals Procurement Laboratories), 38–40° (23 mm), and 76 g (1.0 mole) of redistilled thiolacetic acid was heated on a steam bath under nitrogen for 0.5 hr, followed by irradiation (General Electric Photospot lamp, RSP2) for an additional 3–5 hr. An infrared spectrum of the crude product showed the complete absence of olefinic absorption at 6.1 μ. Traces of volatile material were removed by maintaining the product at 40° under a pressure of 0.5 mm for several hours.

To a solution of 71 g of potassium hydroxide in 700 ml of 50% methanol was added 87 g of the above material. The mixture was heated at reflux under nitrogen for 4 hr; the methanol was removed by distillation. The residual solution was acidified with hydrochloric acid and extracted with three 150-ml portions of ether. The combined extracts were washed with water, dried over magnesium sulfate, and concentrated to a pale yellow oil.

To a solution of 52.7 g (0.4 mole) of the crude mercapto ketone in 150 ml of benzene was added 5.0 g of *p*-toluenesulfonic acid and cyclodehydration effected by azeotropic distillation. When the separation of water had terminated (90% of theory), the solvent was removed under reduced pressure. The residue was fractionally distilled to yield 25 g (55%) of the vinyl thioether (I): bp 67–68° (30 mm); λ_{max} 228 and 247 mμ (ε 4000 and 2330, respectively, in acetonitrile).

Attempted Addition of Alcohols to I.—Solutions of I in ethanol containing catalytic amounts of hydrochloric or trifluoroacetic acid were maintained at 25° and at reflux for varying periods of time. No significant change was observed in the ultraviolet spectrum nor could an adduct be detected by thin layer chromatography. Experiments with cyclopentanol in acetonitrile were equally negative.

2,3-Dihydrothiophene (II) was prepared by pyrolysis of 2-benzoyloxytetrahydrothiophene[6] and fractionation of the distillate. The fraction boiling at 37° (40 mm) was found, by gas chromatographic analysis, to be free of contaminants: λ_{max} 242 mμ (ε 5400, acetonitrile); $\lambda_{max}^{CCl_4}$ 3.24, 6.32, 10.0, and 10.95 μ.

(11) P. T. Gilham and H. G. Khorana, *J. Am. Chem. Soc.*, **80**, 6212 (1958).

(12) Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer in acetonitrile and ethanol; infrared spectra were measured on a Perkin-Elmer Model 21 double-beam spectrophotometer. Microanalyses were performed by the Analytical Service Laboratory of this institute. Florisil was used as purchased from the Floridin Co., Tallahassee, Fla.

By storage over a layer of activated alumina at 0°, the material could be kept for months without alteration.

2,3-Dihydro-4H-thiopyran (III).[7]—Tetrahydrothiopyran was allowed to react with *t*-butyl perbenzoate, following the procedure used for tetrahydrothiophene.[6] Pyrolysis of the crude ester and fractionation of the distillate gave, in 50% yield, a fraction boiling at 41–42° (10 mm), which was found, by gas chromatographic analysis, to be free of contaminants: λ_{max} 226 and 249 mμ (ε 5850 and 2950, respectively in acetonitrile); $\lambda_{max}^{CCl_4}$ 3.28, 6.22, 10.55, and 11.70 μ.

Dimer of 2,3-Dihydro-4H-thiopyran (VII).—To a solution of 3.1 g of 2,3-dihydro-4H-thiopyran (III) in 10 ml of acetonitrile was added 0.1 ml of trifluoroacetic acid, and the mixture was allowed to stand at room temperature for 10 days. Following addition of 0.2 ml of saturated sodium carbonate solution, the mixture was dried over sodium sulfate, filtered, and vacuum-distilled to give 1.92 g of oil. A solution of the oil in petroleum ether (60–70°) was adsorbed onto a column of 50 g of Florisil (200–300 mesh) and the column eluted with the same solvent in 20-ml portions. Fractions 7–47 gave 1.14 g of the dimer, VII, as a colorless oil: λ_{max} 222 and 243 mμ (ε 6960 and 6080, respectively, in acetonitrile); $\lambda_{max}^{CHCl_3}$ 6.21, 10.61, 11.12, and 11.96 μ.

Anal. Calcd for $C_{10}H_{16}S_2$: C, 59.94; H, 8.05; S, 32.01; mol wt, 200.4. Found: C, 60.18; H, 8.25; S, 32.40; mol wt (cryoscopic in benzene), 199.

Dimer of 2,3-Dihydrothiophene (VI).[6,10]—Attempted synthesis of the dimer of II under the conditions described above for the dimerization of III led to a violent reaction and polymerization. However, by use of one-tenth the quantity of trifluoroacetic acid, the reaction could be controlled and the dimer isolated by chromatography on Florosil, as above: λ_{max} 247 mμ (ε 6920, acetonitrile); $\lambda_{max}^{CCl_4}$ 6.23, 9.56, and 10.32 μ.

Anal. Calcd for $C_8H_{12}S_2$: C, 55.76; H, 7.03; S, 37.22; mol wt, 172.3. Found: C, 56.24; H, 7.27; S, 36.77; mol wt (cryoscopic in benzene), 178.

Cholestanol Adduct of III.—To a solution of 2.0 g of cholestanol in 25 ml of chloroform (purified by passage through a silica gel column) was added 3 ml of 2,3-dihydro-4H-thiopyran (III) and 0.5 ml of trifluoroacetic acid. The mixture was heated at reflux for 6 days with exclusion of air. The solution was cooled, diluted with 50 ml of chloroform, extracted with 5% aqueous potassium carbonate, and washed with water and the chloroform layer was dried over sodium sulfate. Following filtration and removal of the solvent at reduced pressure, the oily residue was dissolved in petroleum ether (bp 60–70°) and adsorbed onto 100 g of Florisil (60–100 mesh). Elution was performed as follows, collecting 125-ml fractions: 1–13, petroleum ether (60–70°); 14–20, petroleum ether–benzene (10:1.5); 21–26, benzene–ethanol (1:1). Fractions 2 and 3 gave 0.44 g of III, identified by its infrared spectrum in solution. Fractions 5–16 yielded 0.81 g (35%) of the adduct as colorless crystals; further elution led to the recovery of 1.25 g of cholestanol. Following recrystallization from acetone–methanol, the adduct melted at 144–146°; its infrared spectrum showed the absence of olefinic absorption.

Anal. Calcd for $C_{32}H_{56}OS$: C, 78.62; H, 11.55; S, 6.56. Found: C, 78.40; H, 11.32; S, 6.76.

Cholestanol Adduct of II.—Following the procedure described above, the cholestanol adduct of dihydrothiophene was obtained, after purification on a Florisil column, in 75% yield, mp 114–115°.

Anal. Calcd for $C_{31}H_{54}OS$: C, 78.41; H, 11.46; S, 6.75. Found: C, 78.43; H, 11.16; S, 7.02.

Regeneration of Cholestanol from Its Adducts.—To a solution of 100 mg of the cholestanol adduct of 2,3-dihydro-4H-thiopyran in 50 ml of acetone was added a solution of 0.35 g of silver nitrate in 1 ml of water. The reaction mixture was boiled for several minutes and filtered to remove the precipitate of silver δ-mercaptovaleraldehyde. The solution was diluted with water and the acetone was removed by evaporation, cholestanol separating as colorless crystals. Following recrystallization from acetone–methanol, 85% of cholestanol was recovered: mp 142–143°. The product was identified by mixture melting point and by comparison of its infrared spectrum with that of an authentic sample.

Similar treatment of the cholestanol adduct of 2,3-dihydrothiophene led to the recovery of cholestanol in 90% yield.

Cyclopentanol Adduct of 2,3-Dihydrothiophene.—A mixture of 5.5 g of cyclopentanol, 5.5 g of 2,3-dihydrothiophene, and 1 ml of acid reagent (prepared by addition of 0.03 ml of concentrated hydrochloric acid to 5 ml of acetonitrile) was diluted to a volume of 10 ml with acetonitrile and stored at room temperature for seven days. Following addition of 0.5 ml of saturated sodium carbonate solution, the mixture was dried over sodium sulfate and filtered, and the solvent was removed under reduced pressure. The residual oil (8.9 g) was dissolved in petroleum ether (bp 60–70°) and adsorbed onto a column of 110 g of Florisil (100–200 mesh). The column was eluted with the same solvent, fractions of 125 ml being collected. Fraction 3 was rechromatographed on 100 g of Florisil (200–300 mesh); the column was eluted with petroleum ether, 20-ml fractions being collected by means of an automatic fraction collector. Fractions 24–57, which showed no significant ultraviolet absorption, were pooled and the solvent was evaporated to give 1.13 g of the adduct, a colorless oil which showed no olefinic character, either in its infrared or nmr spectrum.

Anal. Calcd for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61; mol wt, 172.3. Found: C, 62.46; H, 9.50; S, 18.61; mol wt, 183.

Kinetic Studies.—A stock solution of acid was prepared by adding 0.04 ml of concentrated hydrochloric acid to 5 ml of acetonitrile. A mixture of 1.08 g (0.0125 mole) of cyclopentanol, 1.08 g (0.0125 mole) of 2,3-dihydrothiophene, and an appropriate amount of acid stock solution was diluted to 10 ml with acetonitrile and stored at 25°. Aliquots were withdrawn with a 10-μl syringe and injected into 10 ml of acetonitrile. The optical density at 242 mμ was determined at varying time intervals, using a Cary Model 14 spectrophotometer. At each acid concentration used, the first-order rate law was followed for at least 50% conversion. Rate constants were determined graphically and are recorded in Figure 1 *vs.* concentration of acid.

The same procedure was used for the higher homolog; in this case, 1.25 g (0.0125 mole) of 2,3-dihydro-4H-thiopyran was mixed with 1.08 g of cyclopentanol, hydrochloric acid and acetonitrile being added as described above. The progress of the reaction was followed by disappearance of the chromophore at 226 mμ.

5′-O-Acetylthymidine (VIII).—To a solution of 5.0 g of thymidine in 20 ml of dry pyridine was added 2.5 ml of acetic anhydride. The reaction mixture was stored at room temperature for 3 days. After removal of the solvent *in vacuo*, the remaining gum was dissolved in a small volume of dichloromethane and adsorbed onto a column of 80 g of Florisil (60–100 mesh), and the column was eluted as follows: 1–9, 125-ml fractions of chloroform; 10–15, 125-ml fractions of chloroform–ethanol (10:1); 16–17, 125-ml fractions of ethanol. Fractions 2–9 yielded 2.7 g of 3′,5′-di-*O*-acetylthymidine as colorless crystals, mp 127–128° (lit.[11] mp 126–127°); fractions 11–15 gave 2.8 g of the crude monoacetyl compound. Crystallization from dichloromethane–ethanol afforded 2.0 g of 5′-O-acetylthymidine as colorless crystals, mp 144–146°. Rechromatography of VIII on Florisil (200–300 mesh) using the solvent system ethanol–acetonitrile–dichloromethane (2:3:5) provided a product with mp 150–151° (lit.[11] mp 150°).

Dihydrothiophene Adduct of 5′-O-Acetylthymidine (IX).—To a solution of 0.5 g of 5′-O-acetylthymidine (VIII) in 12 ml of chloroform was added 2 ml of 2,3-dihydrothiophene and 0.4 ml of acid stock solution (prepared by dilution of 0.04 ml of concentrated hydrochloric acid with 5 ml of acetonitrile). The reaction mixture was stored at room temperature for 4 days and transferred directly to a column of 75 g of Florisil (60–100 mesh), and the column was eluted as follows: 1–5, 250-ml fractions of dichloromethane; 6–15, 125-ml fractions of acetonitrile–dichloromethane (1:1). Fractions 1–4 contained the dimer of 2,3-dihydrothiophene, which was not investigated further. Fractions 7–12 gave 0.43 g of the crude adduct which was dissolved in dichloromethane and adsorbed onto 65 g of Florisil (200–300 mesh). By means of an automatic fraction collector, a total of 50 5-ml fractions were collected, using acetonitrile–dichloromethane (1:1). Fractions 19–44 gave 0.37 g (57%) of the adduct as a colorless gum. Crystallization could not be effected despite repeated chromatography. The material was found homogeneous by thin layer chromatography on Florisil (200–300 mesh) containing 15% calcium sulfate binder: R_f 0.80 (dichloromethane–acetonitrile 1:1); 0.55 (chloroform–acetonitrile 7:3). 5′-O-Acetylthymidine migrates with R_f values of 0.20 and 0.10, respectively, using these solvent systems. For analysis, the material was dried at room temperature *in vacuo* for several days.

Anal. Calcd for $C_{16}H_{22}O_6N_2S$: C, 51.88; H, 5.99; N, 7.56; S, 8.66. Found: C, 51.98; H, 6.19; N, 7.72; S, 8.99.

Regeneration of 5′-O-Acetylthymidine from Its Adduct.—To a solution of 0.1 g of the adduct IX in 5 ml of acetonitrile was added 5 ml of 0.1 *N* silver nitrate. The mixture was stored at room temperature for 2 hr and filtered, and the solvent was removed under reduced pressure. Thin layer chromatography, using the system described above, indicated the complete decomposition of the adduct; the presence of 5′-O-acetylthymidine (R_f 0.75) was demonstrated by use of the solvent system ethanol–acetonitrile–dichloromethane (2:3:5); the same solvent system indicated the absence of thymidine (R_f 0.50) in the reaction mixture.

Stereochemical Studies. IV. Asymmetric Selection *via* Elimination. Formation of Optically Active Olefins During Pyrolyses of Optically Active Esters

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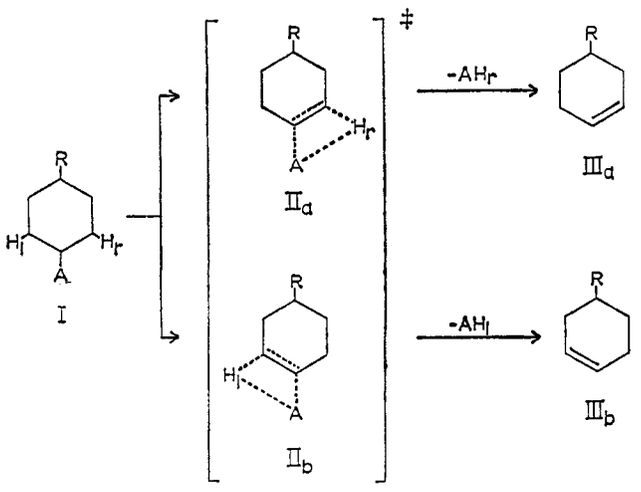
Careful pyrolysis of each of the four possible stereoisomeric 4-methylcyclohexyl hydratropates [*trans*-(−)-(*R*), *trans*-(+)-(*S*), *cis*-(−)-(*R*), and *cis*-(+)-(*S*)] has, in each case, resulted in the formation of optically active 4-methylcyclohexene. The significance of these results are discussed in terms of a possible topological description of the transition state for the pyrolytic *cis* elimination of esters.

While many examples of addition processes involving asymmetric selection[1] have been recorded,[2] asymmetric selection *via* elimination has not received anything like similar attention.

Our interest in asymmetric elimination lay in the realization that such processes could provide a useful tool for configurational correlation and, perhaps more intriguing, that an asymmetric elimination process might be an extremely sensitive probe for information useful in detailing transition state topology.

We envisioned a general model system which, in principal, would allow asymmetric selection during elimination. The system could contain any even-membered ring with substituents (R and A) symmetrically disposed so that neither ring atom bearing a substituent would be asymmetric. The 1,4-disubstituted cyclohexane system (I) meets these requirements (Scheme I).

SCHEME I



Let the relative steric arrangement of R and A be known (*cis* or *trans*), and let A contain an asymmetric atom possessing only one of its two possible configurations. System I would then be optically active by virtue of A.

In addition, the group A must be one which is known to undergo *cis* elimination (ester, amine oxide, sulfoxide, or phosphine oxide). The two transition states for the *cis* elimination of AH from I may then be represented by IIa and IIb. Under the requirements and restrictions set down for I, these transition states must bear a diastereoisomeric relationship to one another, and therefore differ in energy. Consequently, one transition state represents a lower energy pathway for elimination than the other, and the enantiomeric olefin resulting from the lower energy pathway would be expected to predominate, providing optical activity in the product olefin.

We have submitted this concept to experimental test in the case of esters[3] and sulfoxides,[4] are in the process of examining amine oxides,[5] and wish now to report our results on the ester study in detail.

Discussion

At the outset of this work we recognized that the alkaloid hyoscyamine IX possesses all the structural requirements deemed necessary to give rise to an asymmetric elimination process, *i.e.*, production of tropidine, optically active owing to enrichment of one enantiomer (Xa or Xb) (Scheme II) during the elimination of tropic acid.

We, therefore, submitted hyoscyamine to careful pyrolysis under a variety of conditions, but in no case were we able to detect any optical activity present in

(1) Rather than pursue the confusing practice of classification under one of the various and vaguely defined terms used heretofore (asymmetric destruction, induction, synthesis, transformation, etc.), the term asymmetric selection is suggested to mean any chemical reaction that gives rise to partial or absolute enrichment of one enantiomer over the other in the product.

(2) For a partial account of a number of examples, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) A preliminary account was reported earlier by S. I. Goldberg and F.-L. Lam [*Tetrahedron Letters*, 1893 (1964)] and presented before the Division of Organic Chemistry, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 48S.

(4) S. I. Goldberg and M. S. Sahli, *Tetrahedron Letters*, 4441 (1965). The observation of stereospecificity in the pyrolysis of steroidal sulfoxides by D. M. Jones and M. A. Sand [*Proc. Chem. Soc.*, 81 (1964)] is probably another example of the general concept.

(5) G. Berti and G. Bellucci [*Tetrahedron Letters*, 3853 (1964)] have reported in preliminary fashion the presence of asymmetric selection during pyrolysis of optically active N-methyl-N-(4-methylcyclohexyl)-N-phenylamine oxide.