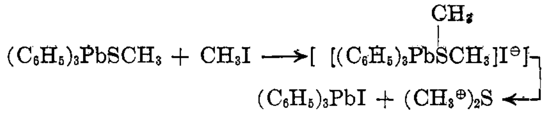
compounds show, besides the usual absorptions associated with aromatic compounds and the respective group attached to the sulfur, the band at 1052 cm.$^{-1}$, typical for organolead compounds.[9]

Methyl iodide reacted quantitatively at room temperature with thiomethyl triphenyllead to yield triphenyllead iodide and dimethyl sulfide, probably through an unstable sulfonium salt intermediate:



$$(C_6H_5)_3PbSCH_3 + CH_3I \longrightarrow [\ [(C_6H_5)_3Pb\overset{CH_3}{\overset{|}{S}}CH_3]I^{\ominus}] \rightarrow (C_6H_5)_3PbI + (CH_3{}^{\oplus})_2S$$

This reaction did not take place with triphenyllead thiolacetate; apparently the acetyl group decreases the electron density at the sulfur atom so that formation of a sulfonium intermediate becomes impossible.

Mineral acids cleaved the lead–sulfur bond preferentially; however, cleavage of lead–phenyl bonds was always detected. For example, mixtures of triphenyllead chloride, diphenyllead dichloride, and lead chloride were obtained from the reaction of thioalkyl triphenyllead compounds and hydrochloric acid.

Throughout the course of this work, thin-layer chromatography was found to be valuable for separation of the organolead compounds. Dithizone spray reagent reacted to form yellow spots with the monosubstituted lead compounds, red spots from the disubstituted products, and gave no reaction with tetraphenyllead.[10]

Experimental

A typical example for the preparation of the triphenyllead sulfur compounds described by route 1 is given.

The lead mercaptides[11] were prepared from the thiol and lead acetate in aqueous alcohol and after washing with water were dried in a vacuum desiccator.

Triphenyllead chloride, 4.86 g. (10 mmoles), and lead (II) *n*-propyl mercaptide, 1.79 g. (5 mmoles), in 100 ml. benzene were refluxed with stirring for 3 hr. During this time the yellow mercaptide was converted into white lead chloride which was filtered off at the end of the reaction period. The filtrate was evaporated and the residue recrystallized from ethanol, yield 4.84 g. (95%), m.p. 57–58°.

Preparation of Thiobutyl Triphenyllead from Triphenyllead Hydroxide and 1-Butanethiol (Route 2).—Triphenyllead hydroxide,[12] 0.91 g. (2 mmoles), and 1-butanethiol, 0.18 g. (12 mmoles), were mixed in 50 ml. of ethyl ether and shaken for 24 hr. Filtration and evaporation yielded a colorless oil. The oil was purified by chromatography on neutral alumina, eluting with benzene; yield: 0.68 g. (65%).

Synthesis of Thiomethyl Triphenyllead by Route 1.—Triphenyllead chloride, 4.86 g. (10 mmoles), was added to a stirred suspension of sodium sulfide pentahydrate, 8.40 g. (50 mmoles), in 100 ml. of ethyl alcohol during a period of 1 hr. while the reaction temperature was kept below 30°. The excess sodium sulfide and sodium chloride were filtered off and the alcohol removed from the filtrate under vacuum. The white residue was extracted with benzene and the benzene evaporated. To the remaining solid was added methyl iodide, 1.41 g. (10 mmoles), in 50 ml. of benzene. After filtering and evaporation of the benzene, recrystallization from ethanol and *n*-hexane gave bistriphenyllead sulfide, 1.14 g. (25%), m.p. 139–141° (identified by mixed melting point with an authentic sample[3]).

The combined mother liquor was concentrated and yielded thiomethyl triphenyllead, 3.47 g. (68%), m.p. 103–106°, recrystallized from *n*-hexane).

Reaction of Thiomethyl Triphenyllead with Methyl Iodide.—Thiomethyl triphenyllead, 1.12 g. (2.3 mmoles), was dissolved in excess methyl iodide (30 ml.). After a few minutes the solution became cloudy and a precipitation occurred slowly over a period of 6 hr. The excess methyl iodide was removed under vacuum and the residue shown to be 1.30 g. of pure triphenyllead iodide,[13] m.p. 140–141°. Mixed melting point with an authentic sample gave no depression.

Reactions of Tetraphenyllead with Thiolacetic Acid (Route 3). Diphenyllead Bisthiolacetate.—Tetraphenyllead, 2.58 g. (5 mmoles), dissolved in 20 ml. of thiolacetic acid was refluxed for 5 min. The excess of thiolacetic acid was removed under vacuum and the residue recrystallized from ethanol. The yield was 1.55 g. (60%) and the m.p. was 94–95°.

Anal. Calcd. for $C_{16}H_{16}O_2S_2Pb$: C, 37.56; H, 3.15; Pb, 40.50; S, 12.54. Found: C, 37.73; H, 3.36; Pb, 40.50; S, 12.46.

Diphenyllead bisthiolacetate was also prepared by the reaction of diphenyllead dichloride with lead thiolacetate—analogous to route 4—in boiling toluene; yield 81%.

The reaction of tetraphenyllead with 1 mole of thiolacetic acid in boiling benzene (2 hr.) yielded 70% tetraphenyllead, 12% triphenyllead thiolacetate, and 6% diphenyllead bisthiolacetate.

Thin-layer Chromatography.—Thin-layer chromatography of the organolead compounds was carried out on silica gel G (25 μ), using benzene as a solvent in most cases. Potassium permanganate solution or a solution of dithizone in chloroform[10] was used as a spray.

Acknowledgment.—The authors are grateful to C. DiPietro of these laboratories for the microanalyses.

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The Stereochemistry of an Ivalin Degradation Product[1]

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The hydroxyketolactone II obtained by ozonolysis of dihydroivalin (I)[2] exhibited a positive Cotton effect (molecular amplitude about 1750°) which seemed surprising in view of the relatively strong negative Cotton effect displayed by 4-keto steroids (molecular amplitude −9400°) and *trans*-10-methyl-1-decalone.

The hydroxyl group, being equatorial and in the upper left quadrant, should, according to the octant rule,[3] make a positive contribution to the total dispersion picture. However, no reference compounds of incontrovertible stereochemistry had been scrutinized for the purpose of assessing the effect of hydroxyl groups in a situation of this type, and the observed inversion of the Cotton effect seemed, *a priori*, greater than might have been expected. It should also be noted that inspection of models failed to reveal any reasons for distortions due to steric or electrostatic interactions which might result in conformational changes.

To explain the observed rotatory dispersion curve, we considered the possibility that epimerization at C-5 might have taken place during the work-up. This

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(1) Supported in part by grants from the National Science Foundation (NSF-G-14396) and the Eli Lilly Company, Inc.

(2) W. Herz and G. Högenauer, *J. Org. Chem.*, **27**, 905 (1962).

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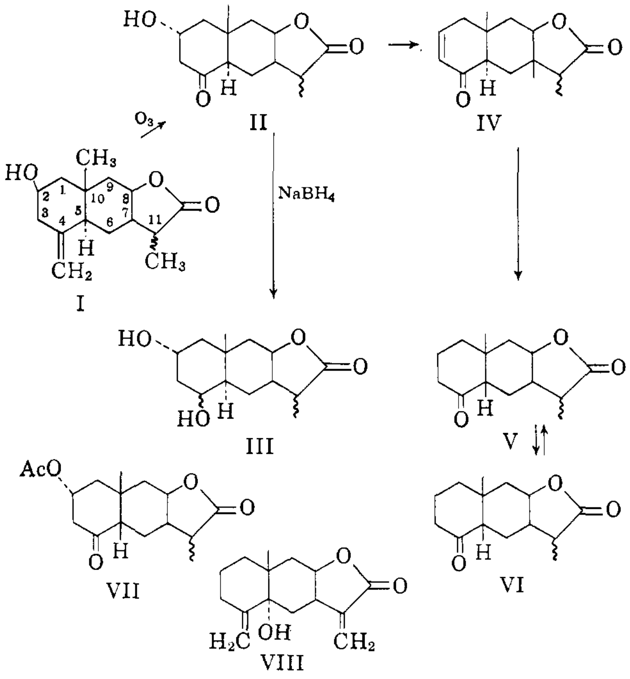
would have resulted in a substance with a *cis* A-B-ring fusion, and, indeed, the curve of II was very similar to that of *cis*-10-methyl-1-decalone. We now report that this is not the case and that the hydroxyketolactone is accurately represented by II.



Sodium borohydride reduction of II gave a diol (III) which could be obtained more directly by sodium borohydride reduction of the ozonide derived from I. It is quite unlikely that the second route involves epimerization at C-5 since under similar circumstances the very labile 3-keto-A-nor-5-α-steroids are not converted to the more stable 5-β-isomers.[4] We conclude that the formation of II from I is not accompanied by inversion at C-5; and II must therefore have the same configuration at C-5 as I, *i.e.*, *trans.*

Since hydride reduction of 4-cholestanone is reported to give mainly 4-β-cholestanol,[5] the reduction of II might be expected to result in the formation of an axial C-4 hydroxyl group. However, the diol III was isolated in less than 50% yield so that no conclusion is possible about the stereochemistry of III at C-4.

Additional evidence for retention of configuration at C-5 was provided by the following reaction sequence. Dehydration of II, as described previously,[2] furnished the α,β-unsaturated ketone IV which was catalytically reduced to V, m.p. 201°. The optical rotatory dispersion curve of this substance was comparable to that of *trans*-10-methyl-1-decalone of appropriate absolute configuration (negative Cotton effect).[6] Hence, if II were a *cis* rather than a *trans* isomer, its conversion to V would have had to be attended by another epimerization at C-5, which again seemed extremely unlikely.

In the meantime, V has also been obtained[7] by degradation of telekin (VIII). The properties reported by Benešova, Herout, and Klyne[7] compared well with the properties of the material isolated by us. and a comparison of the rotatory dispersion curves kindly carried out by Professor Klyne established their identity.

Epimerization of V with potassium carbonate in tetralin yielded an equilibrium mixture containing 55% of V and 45% of a new substance,[8] which on the basis of the rotatory dispersion curve (positive Cotton effect) is the *cis* isomer VI.[9] Although the m.p. of VI was unsharp, it behaved as a pure substance on thin-layer chromatography and could be readily differentiated from V.

The composition of the equilibrium mixture did not differ significantly from the equilibrium mixture of the *cis*- and *trans*-10-methyl-1-decalones.[10] Hence substitution by a *cis*-lactone group at C-7 and C-8 appears to exert little effect on the relative stabilities of the 10-methyl-1-decalones.

The abnormally large effect of the 2-α-hydroxy group on the optical rotatory dispersion curve of II still remains to be explained. The acetate VII exhibits what appears to be a very weak positive Cotton effect of small amplitude (*a* about +7).[11] This could be due to the normal positive octant effect of acetate (Δa OAc = +32). The larger Δa for the hydroxyl group may perhaps arise through hydrogen bonding.

Experimental[12]

Ozonolysis of Dihydroivalin.—(a) A solution of 0.5 g. of I in 50 ml. of ethyl acetate was ozonized at −70°. Excess ozone was removed by a stream of oxygen. The solution was allowed to come to room temperature (separation of a solid) and transferred to a hydrogenating bottle. The solid was dissolved in methanol and added to the ethyl acetate solution which was reduced at 20 lb., catalyst 0.1 g. of 5% palladium-charcoal. After filtration and removal of solvent, there was obtained 0.3 g. of II, m.p. 178–180° on recrystallization from acetone–petroleum ether.

(b) A solution of 0.2 g. of I in 15 ml. of methylene chloride and 5 ml. of methanol was ozonized at −70°. The solution was allowed to come to room temperature and mixed with 0.2 g. of sodium borohydride in 10 ml. of methanol. After a half-hour, another 0.1 g. of sodium borohydride was added and left for 4 hr. Then 2 ml. of acetic acid was added, the solvent was evaporated *in vacuo*, the residue was mixed with water and thoroughly extracted with chloroform. The dried chloroform extracts were concentrated, and the residue recrystallized from benzene containing a small amount of ethanol; yield 0.05 g. of the diol III, m.p. 203–205°.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72; O, 25.17. Found: C, 65.69; H, 8.64; O, 25.39.

III was also obtained in 0.05 g. yield by sodium borohydride reduction of 0.15 g. of II in methanol, m.p. and m.m.p. 103–205°. The two samples had identical infrared spectra and mobility on a thin-layer chromatogram (acetone on silica gel).

Reduction of IV.—A solution of 0.35 g. of IV in 50 ml. of ethanol was reduced at atmospheric pressure with 50 mg. of 10% palladium–charcoal. Removal of solvent and recrystallization from alcohol furnished 0.26 g. of V, m.p. 201–202°, optical rotatory dispersion curve in methanol, $(\phi)_{305}$ −1180°, $(\phi)_{270}$ +1420°, *a* − 25, infrared bands at 1770 and 1715 cm.$^{-1}$, reported m.p. for the material from isotelekin[7] 202–203°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 71.16; H, 8.53; O, 20.31. Found: C, 70.98; H, 8.36; O, 20.52.

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(8) The percentage values are based on crystalline product isolated from the mixture, total recovery 70% of starting material.

(9) Compare with the curve of *cis*-10-methyl-1-decalone.[6]

(10) F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

(11) For terminology, see W. Klyne, "Advances in Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, p. 239.

(12) Melting points are uncorrected. Analyses are by Dr. F. Pascher, Bonn, Germany. Infrared spectra were run on a Perkin–Elmer Infracord spectrophotometer in chloroform solution.

This substance was unaffected on refluxing with potassium carbonate in toluene. Sodium methoxide in refluxing methanol yielded starting material and three transformation products (thin-layer chromatogram); the mixture could not be separated by column chromatography.

A solution of 0.1 g. of V in 10 ml. of tetralin was refluxed with 100 mg. of freshly heated anhydrous potassium carbonate for 4 hr., allowed to stand at room temperature, and filtered. The potassium carbonate was washed with benzene, and the combined organic solvents evaporated *in vacuo*. The residue gave two spots on thin-layer chromatography (silica gel–anhydrous ether), one of which corresponded to starting material.

The crude product was dissolved in benzene and chromatographed over acid-washed alumina. Benzene eluted nothing. Benzene–anhydrous ether (2:1, 25-ml. fractions) eluted an oil in the first 50 ml. (fraction A) and a solid in the subsequent 75 ml. (fraction B). Fraction B on crystallization from ethyl acetate–petroleum ether yielded 0.04 g. of starting material, m.p. and m.m.p. 200°.

Fraction A on crystallization from ether–petroleum ether gave an epimer, wt. 0.03, which was homogeneous in thin-layer chromatography but had m.p. 97–107°. The m.p. did not improve even after four crystallizations. The infrared spectrum exhibited bands at 1770 and 1715 $cm.^{-1}$ and differed significantly from that of V in the fingerprint region. Optical rotatory dispersion curve in methanol, $(\phi)_{310}$ 2000°, $(\phi)_{270}$ −1100°, a + 31.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53; O, 20.31. Found: C, 71.35; H, 8.58; O, 20.18.

The optical rotatory dispersion curve of VII[2] in methanol exhibited $(\phi)_{305}$ +800°, $(\phi)_{282.5}$ +110°, a + 7°. However, the weak intensities make it doubtful whether these values represent true peaks and troughs.

Acknowledgment.—We wish to express our thanks to Professor W. Klyne for the optical rotatory dispersion curves.

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cis- and *trans*-Stilbene Sulfides

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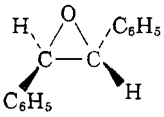
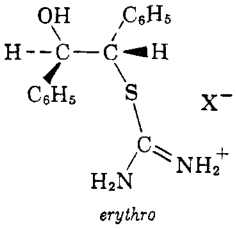
The preparation and reactions of a wide variety of stilbene oxides have been reported in the literature.[1] However, the sulfur analogues have not been previously described. Culvenor, Davies, and Health[2] attempted to convert stilbene oxide, presumably the *trans* isomer, to an episulfide by the use of thiourea. The only products isolated were stilbene, urea, and sulfur. This observation led them to conclude that stilbene episulfide was too unstable to exist. That both styrene sulfide[3] and tetraphenylethylene sulfide[4] have been reported suggested that the intermediate diphenyl and triphenylethylene sulfides should also be capable of existence.

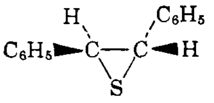
Bordwell[5] reported the preparation of a variety of episulfides by treatment of epoxides with thiourea and acid to afford thiuronium salts, which when treated with alkali yielded episulfides. Application of Bordwell's procedure has afforded both *cis*- and *trans*-stilbene sulfides from the corresponding *cis*- and *trans*-stilbene oxides. The analytically pure thiuronium sulfates [*erythro*-*S*-(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate (IIa) from *trans*-stilbene oxide (I) and *threo*-*S*-(1,2-diphenyl-2-hydroxyethyl)thiuronium sulfate (V) from *cis*-stilbene oxide (IV)] were obtained in high yield without purification. When treated with base, the thiuronium salts afforded the expected sulfides (III from II and VI from V) in nearly quantitative yield. When stored at room temperature, unprotected from light, *cis*-stilbene sulfide (VI), m.p. 77–78°, is stable, but *trans*-stilbene sulfide (III), m.p. 53–54°, slowly deteriorates to what appears to be a polymer. When protected from light and stored at 5°, *trans*-stilbene sulfide is quite stable.

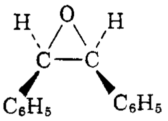

I. (*d*, *l* pair)

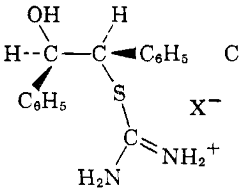

erythro

IIa. $X^- = 1/2\ SO_4^{-2}$

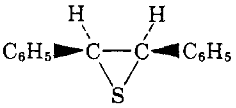
b. X^- = *d*-camphorsulfonate


III. (*d*, *l* pair)


IV. (*meso*)


threo

V. $X^- = 1/2\ SO_4^{-2}$


VI. (*meso*)

The fact that *trans*-stilbene oxide (I) afforded a lower melting sulfide than that derived from *cis*-stilbene oxide (IV) suggested that the reaction may not have proceeded through the generally accepted two-inversion path for conversion of simpler oxides to episulfides by thiourea[6] or thiocyanate,[7] but that perhaps the *trans* oxide had yielded the *cis* sulfide. The greater stability of the *cis* sulfide was also consistent with this possibility.

Evidence bearing on this question was obtained from ultraviolet and n.m.r. spectra, and stereochemical studies. The ultraviolet absorption maxima of *trans*-stilbene oxide (I) appear at longer wave lengths than those of *cis*-stilbene oxide (IV).[8] It has been shown that the red shifts in *trans*-stilbene oxide arise from conjugation of the three-membered ring with the two phenyl groups.[8] In the *trans* oxide the phenyl groups may assume that geometry which gives the most favorable orbital overlap. In the *cis* isomer, however, the steric hindrance of the two eclipsed phenyl groups is so great that its ultraviolet spectrum is almost identical to that of bibenzyl. The geometries of the sulfides cannot be much different from the oxides, so that, if the sulfur-containing three-membered ring is also

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[1] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, chap. 1, pp. 1–60.

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