EXPERIMENTAL

Materials. Sebacyl chloride, mercaptans, and benzene thiols with the exception of *n*-nonyl and *n*-decyl mercaptans were obtained from Eastman. *n*-Nonyl and *n*-decyl mercaptans were obtained from Matheson Company and Aldrich Chemical Company respectively.

All melting points are uncorrected. The properties, yields, and analyses of the dithiol esters of sebacic acid are summarized in Table I.

Methyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, benzyl, phenyl, p-tolyl, and β-naphthyl dithiosebacates. To 11.95 g. (0.05 mole) of sebacyl chloride in a 250-ml. round-bottomed flask fitted with a reflux condenser and immersed in an ice-bath was added 0.11 mole of the appropriate mercaptan or thiophenol and the mixture was allowed to stand overnight. The resulting solid then was heated for six hours on a steam-bath. The dithiol sebacates were all crystallized from acetone-alcohol except the β-naphthyl derivative which was crystallized from acetone.

Ethyl, n-propyl, isopropyl, n-butyl, and isobutyl dithiolsebacates. To 11.95 g. (0.05 mole) of sebacyl chloride in a 250-ml. round-bottomed flask fitted with a reflux condenser and immersed in an ice-bath was added 0.11 mole of the appropriate mercaptan and the mixture was allowed to stand overnight. The product then was heated on a steam-bath for six hours, dissolved in ether, and washed first with two 50-ml. portions of 10% sodium bicarbonate solution and then with two 50-ml. portions of water. After drying the ethereal solution over sodium sulfate, the solvent was removed by distillation and the resulting liquid was distilled under diminished pressure.

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The Chlorohydrins Derived from *trans*-Benzalacetophenone Oxide

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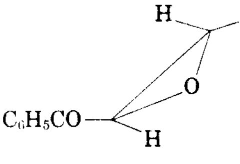
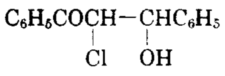
The reaction of *trans*-benzalacetophenone oxide (I) with hydrogen chloride in ethanol has been reported to yield a chlorohydrin, m.p. 105–107°, formulated as II.[1] The same reactants in ether solution were found to yield a chlorohydrin, m.p. 71–72°, formulated as IIIa or IIIb; the latter product was also formed by treatment of the oxide I with stannic chloride in benzene.[2,3] The recent discovery that certain α,β-epoxy ketones react with hydrogen chloride to yield chlorohydrins with retention of configuration[4] raised the question as to whether the two chlorohydrins derived from the oxide I were structural isomers (*i.e.* II and III) or diastereoisomers (*i.e.* IIIa and IIIb).

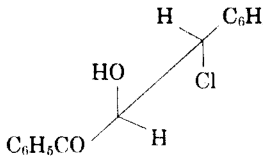


I

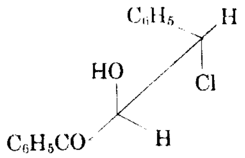


$$\underset{\text{Cl}}{C_6H_5COCH}-\underset{\text{OH}}{CHC_6H_5}$$

II



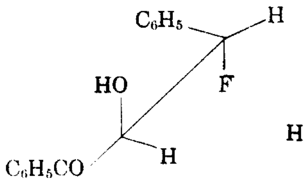
IIIa



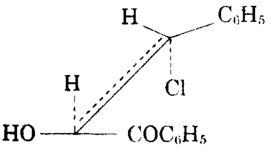
IIIb

$C_6H_5COCOCH_2C_6H_5$

IV



V



VI

Dehydrochlorination of each of the isomeric chlorohydrins with a boiling solution of sodium acetate in ethanol yielded the diketone IV, isolated as its quinoxaline. The possibility that the diketone IV could have been formed from the oxide I which, in turn, might have been formed from the chlorohydrin II was excluded since the oxide I was stable under the conditions of the dehydrochlorination. The two isomeric chlorohydrins must therefore have structures IIIa and IIIb.

The higher-melting chlorohydrin was observed to yield the diketone IV much more slowly than the lower-melting isomer. This observation suggests that the chlorohydrin melting at 106–107° has the *erythro* configuration IIIa since the transition state VI for the concerted dehydrochlorination of this isomer requires the sterically unfavorable eclipsing of the phenyl and benzoyl groups.[5] The isolation of the *trans* oxide I as a second component of the dehydrochlorination reaction mixture as well as the conversion of the higher-melting isomer to I by treatment with cold, alcoholic sodium methoxide confirmed the assignment of configuration IIIa to the higher-melting chlorohydrin.

Consequently, the stereoisomeric chlorohydrin, m.p. 71–72°, has the *threo* configuration IIIb resulting from opening of the oxide ring of I with retention of configuration. The reaction of IIIb with either alcoholic sodium acetate or cold, alcoholic

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(1) O. Widman, *Ber.*, **49**, 477 (1916).

(2) H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954).

(3) 2,3 - Epoxy - 1 - (4 - methoxyphenyl) - 3 - phenyl - 1-propanone was reported by H. Jorlander [*Ber.*, **49**, 2782 (1916)] to yield two different chlorohydrins, formulated as analogs of II and III, when treated with hydrogen chloride in either ethanol or acetic acid.

(4) H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **78**, 1726 (1956).

(5) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956).

sodium methoxide produced the diketone; neither the oxide I or the stereoisomeric *cis*-benzalacetophenone oxide[6] could be isolated from either of the reaction mixtures. It will be noted that the conversion of the *threo* chlorohydrin IIIb to *cis*-benzalacetophenone oxide would require the phenyl and benzoyl groups to be eclipsed; the dehydrochlorination of IIIb to yield the diketone IV involves the energetically favorable staggered orientation of the benzoyl and phenyl groups.

The fluorohydrin which was formed by the reaction of the oxide I with boron trifluoride in ether[7] was found to undergo the same reactions as the chlorohydrin IIIb. The fluorohydrin, m.p. 113–114°, has therefore, been assigned the *threo* configuration V.

EXPERIMENTAL

Preparation of the chlorohydrins. A solution of 1.0 g. (0.0045 mole) of *trans*-benzalacetophenone oxide in 25 ml. of anhydrous ether, cooled in an ice-bath, was saturated with hydrogen chloride. The mixture was allowed to stand in an ice-bath for 75 minutes, and then was washed with cold water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual yellow oil crystallized from ether-petroleum ether mixture. Recrystallization from hexane afforded the *threo* chlorohydrin IIIb as white prisms, m.p. 70–72°, yield 0.51 g. (43%). An additional recrystallization sharpened the melting point of the product to 71–72°. The infrared spectrum[8] of the product has bands at 3510 cm.$^{-1}$ (O—H), 1695 cm.$^{-1}$ (conjugated C=O) and 1115 cm.$^{-1}$ (C—O of a secondary alcohol).

The *erythro* chlorohydrin IIIa was prepared according to the procedure of Widman,[1] a reaction time of 75 minutes being employed. The product crystallized from hexane as white prisms, m.p. 105–107° (lit.[1] 106–107°), yield 44%. The infrared spectrum[8] of the product resembles closely the spectrum of the *threo* isomer in all regions of the spectrum; diagnostic bands are found at 3510 cm.$^{-1}$ (O—H), 1690 cm.$^{-1}$ (conjugated C=O) and 1115 cm.$^{-1}$ (C—O of a secondary alcohol).

Reactions with alcoholic sodium acetate. Solutions of 0.5 mmole of the compounds tested at 82 mg. (1.0 mmole) of sodium acetate in 10 ml. of 95% ethanol were refluxed for the appropriate times, diluted with water, and cooled. After any *trans*-benzalacetophenone oxide (identified by a mixture melting point with an authentic sample) present had been removed the solutions were treated with 100 mg. (0.55 mmole) of *o*-phenylenediamine dihydrochloride, boiled for 30 minutes, and cooled. Any 2-benzyl-3-phenylquinoxaline (identified by a mixture melting point with an authentic sample)[1] present was collected on a filter and recrystallized from aqueous ethanol if necessary. The results are summarized in Table I.

Reactions with alcoholic sodium methoxide. Cold solutions of the compounds to be tested in 10 ml. of absolute ethanol were treated with one equivalent of sodium methoxide as described by Wasserman and Aubrey.[4] A 0.5-mmole sample of the *erythro* chlorohydrin IIIa (m.p. 105–107°) produced *trans*-benzalacetophenone oxide (72% yield), the reaction time being of 20 minutes. Samples (1.0 mmole) of the *threo* chlorohydrin IIIb (m.p. 71–72°) and the *threo* fluorohydrin V were allowed to react for periods of both 20 minutes and 60 minutes. In no case could either of the benzalacetophenone oxides be isolated. After a 60 minute reaction period the fluorohydrin V produced 2-benzyl-3-phenylquinoxaline (28% yield) accompanied by the unchanged fluorohydrin (18% recovery). The analogous reaction with the chlorohydrin IIIb produced 2-benzyl-3-phenylquinoxaline (27%).

TABLE I

REACTIONS OF THE HALOHYDRINS WITH ALCOHOLIC SODIUM ACETATE

Compound	Reaction time, Min.	Yield of oxide I, %	Yield of the quinoxaline of IV, %
IIIa	35	—	10
	180	32	26
IIIb	35	—	61
V	35	—	54
I	35	91	—
	180	92	—

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[6] The preparation of this compound has been described by H. H. Wasserman and N. E. Aubrey [*J. Am. Chem. Soc.*, **77**, 590 (1955)].

[7] H. O. House, *J. Am. Chem. Soc.*, **78**, 2298 (1956).

[8] Determined in carbon tetrachloride solution with a Baird double beam infrared recording spectrophotometer, model B, equipped with a sodium chloride prism.

Some *m*-Biphenylyl-Substituted Silicon Compounds

HENRY GILMAN AND GLEN LICHTENWALTER

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In connection with the investigation of monomeric organosilicon compounds having special thermal properties, a number of *m*-biphenylyl-substituted silicon compounds has been prepared. A similar group of *p*-biphenylyl-substituted compounds has recently been synthesized[1] by condensing chlorosilanes and *p*-chlorobiphenyl with sodium in ether by a method similar to that used by Schumb and co-workers[2] in the preparation of tetraphenylsilane.

In our preparation of the *m*-biphenylyl-substituted compounds, chlorosilanes were reacted with *m*-biphenylyllithium which was prepared from the interaction of *m*-bromobiphenyl with lithium wire in ether. The preparation of *m*-biphenylyllithium was patterned after the preparation of *o*-biphenylyllithium.[3]

The totally aromatic compounds listed in Table II were all crystalline solids with the exception of phenyl-tri-*m*-biphenylylsilane which formed a supercooled liquid. Attempts to crystallize this glass-like material from common solvents were unsuccessful, although an apparently amorphous powder with

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[1] L. Spialter, D. C. Priest, and C. W. Harris, *J. Am. Chem. Soc.*, **77**, 6227 (1955).

[2] W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938).

[3] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955).