minations were weighed with an accuracy of 1 p.p.h.; the isomeric composition of the mixture was calculated from the weight and isomeric composition of the sample as determined by analysis and the weight of pure *cis* or *trans* 3,5-dinitrobenzoate used and this calculated composition was compared with the composition determined from the melting point of the mixture. The calculated compositions agreed with the observed compositions within 1% which is well within experimental error. For example 8.83 mg. of 3,5-dinitrobenzoate containing 23.5% of the *trans* isomer by analysis was mixed with 1.00 mg. of pure *trans* 3,5-dinitrobenzoate to give a mixture calculated to contain 31% of the *trans* isomer. This mixture melted at 73.4° corresponding to 31% *trans*. The temperature reported is that at which the last solid disappeared.

Reduction of 2-methylcyclopentanone. A 2.0-g. sample (0.020 mole) of 2-methylcyclopentanone was reduced except where otherwise noted. All products were dried over potassium carbonate and distilled at *ca.* 35 mm. (b.p. <80°) to avoid the possibility of acid-catalyzed or thermal isomerization. Yields are included for comparison only and are not representative of those obtainable on a preparative scale.

A. Sodium borohydride. A large excess (eight fold) of solid sodium borohydride was added to a solution of the ketone in 25% aqueous methanol according to the procedure of Cram and Greene[7] for the reduction of L-(−)-3-cyclohexyl-2-butanone. From 1.28 g. (0.013 mole) of 2-methylcyclopentanone a 67% yield of 2-methylcyclopentanol was obtained which contained 73% of the *trans* isomer.

Reduction was also carried out by adding the ketone to a small (35%) excess of sodium borohydride in water. In this way a 75% yield of 2-methylcyclopentanol containing 74% of the *trans* isomer was obtained.

B. Sodium and alcohol. 2-Methylcyclopentanone was reduced with sodium and alcohol according to the procedure described by Dauben, Tweit, and Mannerskantz[9] for the reduction of *trans*-1-decalone except that the reaction mixture was cooled in an ice-salt bath during addition of the sodium and then was stirred overnight while cooling continually. A 56% yield of 2-methylcyclopentanol which contained 86% of the *trans* isomer was obtained. The product of a duplicate experiment contained 88% of the *trans* isomer. The low yield was probably due to base-catalyzed condensation of the original ketone; that it was not caused by selective destruction of one stereoisomer of the product was shown by subjecting mixtures of *cis*- and *trans*-2-methylcyclopentanol of known isomeric composition to the reaction conditions. The compositions were not changed.

C. Sodium and moist ether. Reduction with sodium and moist ether was carried out essentially according to the procedure of Vogel[10] for the preparation of methyl *n*-butyl carbinol. An 82% yield of 2-methylcyclopentanol containing 90% of the *trans* isomer was obtained. The product of a duplicate experiment contained 91% of the *trans* isomer.

D. Aluminum isopropoxide. The modified procedure of Macbeth and Mills[11] for ketones which condense readily was used for the reduction of 2-methylcyclopentanone with aluminum isopropoxide. When the reaction mixture was worked up as soon as reduction was complete, a 39% yield of 2-methylcyclopentanol which contained 24% *trans*-2-methylcyclopentanol was obtained from 3.0 g. (0.031 mole) of 2-methylcyclopentanone. A duplicate experiment gave identical results. In this case the low recovery of material was due to loss at some time in the isolation of the product, probably by evaporation during distillation of the relatively large amounts of isopropyl alcohol. This loss did not involve any fractionation of stereoisomers. When a 2.0-g. sample of 2-methylcyclopentanol of known isomeric composition was subjected to the isolation procedure, a 43% recovery of material of unchanged isomeric composition was obtained.

When the reaction mixture was refluxed for ten hours after reduction was complete the product contained 37% *trans*-2-methylcyclopentanol.

E. Catalytic hydrogenation. 2-Methylcyclopentanone (1.5 g., 0.015 mole) was hydrogenated without solvent at room temperature and 60 p.s.i. gage pressure with 0.08 g. of Adams platinum oxide catalyst in a Parr Series 3190 catalytic hydrogenation apparatus. Since the theoretical amount of hydrogen was too small to make an observable difference in pressure, shaking was continued for five days to insure complete reduction. After removal of the catalyst by filtration the product was distilled and a 70% yield of 2-methylcyclopentanol containing 71% *trans*-2-methylcyclopentanol was obtained. The product of a duplicate experiment contained 72% of the *trans* isomer.

Hydrogenation of 3.0 g. (0.031 mole) of 2-methylcyclopentanone in purified[12] glacial acetic acid for a period of three weeks did not result in complete reduction. The catalyst was removed by filtration and the reaction mixture was added to 570 ml. of 2.5 *N* sodium hydroxide. After refluxing for one hour to saponify any 2-methylcyclopentyl acetate formed, the alcohol was removed by azeotropic distillation with water. The distillate was saturated with potassium carbonate and extracted with ether. The almost negligible amount of 3,5-dinitrobenzoate derivative which was obtained from the product melted at 101.5–104.0° indicating that condensation had occurred.

Equilibration of cis- and trans-2-methylcyclopentanol. A solution of 3.0 g. (0.031 mole) of 2-methylcyclopentanol and 1 microdrop of 2-methylcyclopentanone[13] in 15 ml. of dry[14] isopropyl alcohol was refluxed with 44 ml. of 0.75 *M* aluminum isopropoxide in dry isopropyl alcohol. About 50% of the material was recovered regardless of time. Data are summarized in Fig. 1.

Attempted equilibration with sodium apparently led to condensation. Starting from the *trans* side the melting point of the 3,5-dinitrobenzoate derivative first decreased and then increased; individual results were not reproducible.

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[9] Dauben, Tweit and Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

[10] Vogel, *A Text-book of Practical Organic Chemistry*, 2nd ed., Longmans, Green and Co., London, 1951, p. 256.

[11] Macbeth and Mills, *J. Chem. Soc.*, 2646 (1949).

[12] Bruce and Ralls, *Org. Syntheses*, Coll. Vol. II, 191 (1943).

[13] The presence of a carbonyl compound is a necessary condition for effecting equilibration [Doering and Aschner, *J. Am. Chem. Soc.*, **71**, 838 (1949)].

[14] Isopropyl alcohol was dried by refluxing with and distilling from calcium oxide.

Dithiol Sebacic Esters

Richard Sasin, Gerald S. Weiss, Arthur E. Wilfond, and George S. Sasin

Received June 8, 1956

This paper describes the synthesis and the properties of some dithiol sebacates. A literature search revealed that previous to this study only cyclohexyl and 2-methyl cyclohexyl dithiol sebacates were prepared.[1] These compounds were formed by the addition of dithiol sebacic acid to the appropriate olefin.

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[1] Cunnen, *Journal of Applied Chemistry* (*London*), 2, 353 (1952).

TABLE I

DITHIOL ESTERS OF SEBACIC ACIDS

Ester	Formula	Yield, %	M.P., °C.	B.P., 1 mm., °C.	n_D^{20}	d_4^{20}	Analyses Sulfur Calc'd	Analyses Sulfur Found
Methyl	$C_{12}H_{22}O_2S_2$	78	59				24.4	24.2
Ethyl	$C_{14}H_{26}O_2S_2$	70	14[a]	169–170	1.4962	1.011	22.1	22.0
n-Propyl	$C_{16}H_{30}O_2S_2$	88	17[a]	195–197	1.4980	1.000	20.2	20.4
Isopropyl	$C_{16}H_{30}O_2S_2$	85	7[a]	176–178	1.4934	0.988	20.2	20.2
n-Butyl	$C_{18}H_{34}O_2S_2$	80	13[a]	199–200	1.4941	0.985	18.5	18.4
Isobutyl	$C_{18}H_{34}O_2S_2$	75	7[a]	198–200	1.4920	0.980	18.5	18.2
n-Amyl	$C_{20}H_{38}O_2S_2$	75	34				17.1	16.8
n-Hexyl	$C_{22}H_{42}O_2S_2$	64	30				15.9	16.0
n-Heptyl	$C_{24}H_{36}O_2S_2$	83	47				14.9	14.7
n-Octyl	$C_{26}H_{50}O_2S_2$	81	45				14.0	13.7
n-Nonyl	$C_{28}H_{54}O_2S_2$	88	57				13.1	12.9
n-Decyl	$C_{30}H_{58}O_2S_2$	83	56				12.5	12.7
Benzyl	$C_{24}H_{30}O_2S_2$	74	75				15.5	15.2
Phenyl	$C_{22}H_{26}O_2S_2$	81	61				16.6	16.7
p-Tolyl	$C_{24}H_{30}O_2S_2$	81	70				15.5	15.5
β-Naphthyl	$C_{30}H_{30}O_2S_2$	90	105				13.2	12.9

[a] Solidification point.

Interest in lubricating oil additives and plasticizers prompted us to prepare a series of dithiol sebacic esters with mercaptans ranging in chain length from one to ten carbon atoms as well as some aromatic dithiol esters. The dithiol esters were formed in good yield by the action of mercaptans or benzene thiols on sebacyl chloride. The properties, yields obtained and analyses are summarized in Table I.

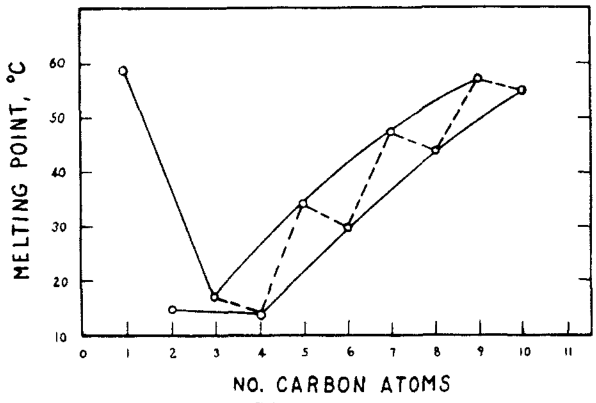

Figure 1.

Figure 1 shows a plot of the melting points of *n*-dithiol esters and the number of carbon atoms in the thiol group. The *n*-dithiol esters show an alternation of the melting points. The esters prepared from the mercaptans containing an odd number of carbon atoms form a smooth curve from *n*-propyl to *n*-nonyl and the esters prepared from the mercaptans containing an even number of carbon atoms form a smooth curve from *n*-butyl to *n*-decyl. All of the dithiol esters with the exception of ethyl through butyl are white crystalline solids and should be useful in the identification of individual mercaptans and benzene thiols.

A plot of the reciprocal of melting points expressed in degrees Kelvin $\left(\frac{1}{T}\right)$ and the reciprocal of the number of repeating units $\left(\frac{1}{n}\right)$ of the normal sebacic dithiol esters gives a straight line with the esters prepared from the mercaptans containing an even number of carbon atoms and another straight line with the esters prepared from the mercaptans containing an odd number of carbon atoms. By extrapolation, (Figure 2) the convergence temperature for the dithiol esters of odd-numbered mercaptans was found to be 145° and for the dithiol esters of even-numbered mercaptans 154°.[2,3] The melting point data obtained from methyl and ethyl dithiol sebacic esters, due to the polarity of the functional groups, does not fit the curve.

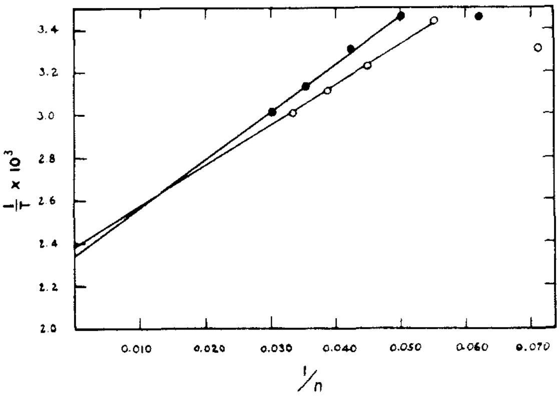

Figure 2.

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(2) Huggins, *J. Phys. Chem.*, **43**, 1083 (1939).

(3) Brande and Nochod, *Determination of Organic Structures by Physical Methods*, Academic Press, Inc., New York, 1955, page 6.

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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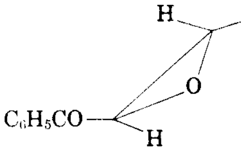
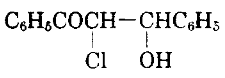
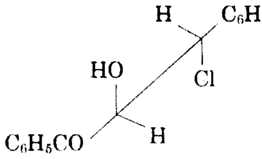
The reaction of *trans*-benzalacetophenone oxide (I) with hydrogen chloride in ethanol has been reported to yield a chlorohydrin, m.p. 105–107°, formulated as II.[1] The same reactants in ether solution were found to yield a chlorohydrin, m.p. 71–72°, formulated as IIIa or IIIb; the latter product was 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).

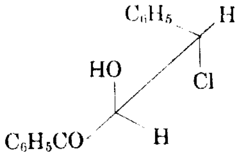

I



$$C_6H_5CO\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}C_6H_5$$

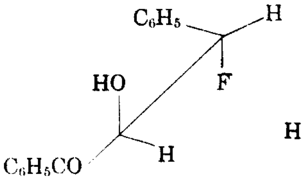
II

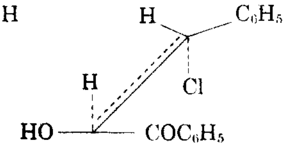

IIIa


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).