

Noteworthy exceptions to this generalization appear in the results of earlier investigations by Howard who reported the formation of secondary alcohols containing the trichloromethyl group along with an alkyl group in those cases where the alkyl group is ethyl, *n*-propyl,² isopropyl or *n*-butyl.³ The yields reported are not high and no mention is made of other reaction products. Gilman and Abbott¹ have studied the reaction of chloral with ethylmagnesium halides; they were unsuccessful in synthesizing the secondary alcohol, but obtained a considerable amount of trichloroethanol.

The research projects here reported were undertaken to investigate further the reaction of chloral with alkylmagnesium halides. The results are in accordance with the generalization of Gilman and Abbott.

Experimental

Chloral and *n*-Amylmagnesium Bromide.—The Grignard reagent was prepared in the usual manner by the slow addition of a 0.25-mole portion of *n*-amyl bromide dissolved in a like volume of anhydrous ether to 0.25 g. atom of magnesium turnings in 200 ml. of anhydrous ether. In those cases where the procedure of normal addition was followed 0.25 mole of freshly distilled chloral dissolved in a like volume of anhydrous ether was dropped slowly into the prepared Grignard reagent. The reaction flask was immersed in an ice-water-bath and the rate of addition was controlled so that no refluxing of the ether was evident. Following the addition of the chloral the mixture was warmed to room temperature and refluxed for one-half hour. In the inverse addition the Grignard reagent was removed and added slowly to 0.25 mole of chloral dissolved in 100 ml. of anhydrous ether. During addition of the reagent the reaction mixture was cooled as in the normal addition. In both types of addition a considerable amount of solid separated during the course of the reaction. The product was hydrolyzed by pouring into an ice-water mixture and then cleared by the addition of 10% aqueous acetic acid. The ether layer was removed and washed in turn with sodium bicarbonate solution, sodium bisulfite solution and water, then dried over anhydrous sodium sulfate.

The ether and the pentene-1 which was formed in the reaction were removed by distillation. The major portion of the ether and hydrocarbon was distilled off by using a hot water-bath; following this the residue was heated in an oil-bath to a bath temperature of 110°, and the distillate collected with the main portion. In order to facilitate the determination of the amount of pentene-1 present it was converted into 1,2-dibromopentane; this was accomplished by treating the ether solution with a slight excess of bromine in subdued light. Following this the ether was removed by distillation and the residual oil was washed in turn with sodium bicarbonate solution and water. After a period of drying over anhydrous calcium chloride the product was distilled under diminished pressure to obtain the 1,2-dibromopentane; boiling point 72–74° at 15 mm.

The oily residue from the removal of ether and pentene-1 was subjected to fractional distillation under diminished

pressure. The fraction which distilled at 95–99° at 125 mm. was shown to be trichloroethanol through the preparation of the *m*-nitrobenzoate, melting point 75°, and the α -naphthyl urethan, melting point 119–120°. The results are summarized in Table I.

Chloral and *n*-Hexylmagnesium Bromide.—The procedure employed was similar to that for chloral and *n*-amylmagnesium bromide. Twenty-five hundredths mole portions of *n*-hexyl bromide and chloral, and 0.25 g. atom of magnesium were used. In the separation of the ether and hexene-1 from the reaction mixture the distilling flask was heated in an oil-bath to a bath temperature of 130°. The 1,2-dibromohexane distilled at 87–89° at 15 mm. Results are given in Table II.

TABLE II

Experiment no. Products isolated	Normal addition, g.		Inverse addition, g.
	1	2	
CCl ₃ CH ₂ OH	21	22.5	26
C ₆ H ₁₂ Br ₂ (1,2)	28	27	33.5
Tarry residue	4.2	4.5	2.0

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Optical Crystallographic Properties of DDT

BY ERNEST L. GOODEN

The prominence in insecticide research of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane, commonly called DDT, has prompted an investigation of the principal optical crystallographic properties of this compound. The results obtained to date are reported here.

The sample used was the para-para' isomer (m. p. 108°)¹ purified by successive recrystallizations of technical DDT from ethanol.

Careful consideration was given to the changeability of the refractive index matching liquids. The liquids used for α and β were aqueous solutions of mercuric potassium iodide. Because these solutions are sensitive to changes in humidity, each use of a given liquid was accompanied by a measurement of its refractive index (*n_D*) on the same day. Determination of γ , which is beyond the range of aqueous mercuric potassium iodide, was done with solutions of sulfur in methylene iodide, and the indices of these were checked within a day or two of their use. Since DDT is noticeably soluble in methylene iodide, allowance was made, in the following way, for the alteration of index of the matching liquid surrounding the crystals: A solution of sulfur in methylene iodide known to produce a nearly perfect match for DDT crystals in the γ -indicating position was transferred to a glass-stoppered hollow prism, and the refractive index measured on a spectrometer, with sodium light, both before and after the addition of DDT to practical saturation. The DDT was found to lower the index of

TABLE I

Experiment no. Products isolated	Normal addition, g.		Inverse addition, g.
	1	2	
CCl ₃ CH ₂ OH	19	20	23
C ₆ H ₁₀ Br ₂ (1, 2)	24	23	27
Tarry residue	5.5	5.0	5.0

(2) Howard, THIS JOURNAL, 48, 774 (1926).

(3) Howard, *ibid.*, 49, 1068 (1927).

(1) The pure material and melting point datum were supplied by Stanley A. Hall, of this Bureau.

the solution by 0.011, and this amount was subtracted from the first estimate of γ as obtained on the basis of the indices of the uncontaminated liquids.

White-light illumination, controlled by a doorbell switch to avoid prolonged heating of the slide, was supplemented in the more critical observations by sodium light.

The characteristics found are as follows: Habit (from ethanol): needles or long prisms, more or less flattened, with elongation parallel to Y (vibration direction for β). Refractive indices (sodium light): α , 1.618; β , 1.626; γ , 1.755. Optical character positive, shown decisively both by refractive indices and by the selenite plate. Sign of elongation variable, depending on the position at which the rolling needle comes to rest, since the lengthwise apparent index is β and the other may be either above or below. Optic axial angle calculated from refractive indices, 30° ; agrees with Bertrand lens measurements within normal observational error. Extinction, in general, parallel to crystal length; thorough study of extinction angles complicated by marked tendency to twinning. Crystal system probably orthorhombic; which is in agreement with X-ray diffraction evidence reported by others.²

(2) G. L. Clark and F. W. Cagle, Jr., *Science*, **101**, 465-466 (1945).
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The Reduction of Diethylstilbestrol Compounds¹

BY WILLARD HOEHN AND HERBERT E. UNGNADE

The hydrogenation of diethylstilbestrol and its dimethyl ether in the presence of Raney nickel or other catalysts leads to the low-melting racemic dihydro compounds.² The phenolic rings are not affected unless the reaction is carried out under drastic conditions of temperature and pressure. Even then, the hydrogen uptake is slow.³

In view of the work of Docken and Spielman,² the perhydro compound of diethylstilbestrol is presumably derived from *racemic* dihydrostilbestrol which is first formed, during the reduction, and thus different from the perhydrohexestrol of Lane and Wallis⁴ which was obtained by hydrogenation of the *meso*-dihydro isomer.

The results of the present investigation show that it is possible to perhydrogenate diethylstilbestrol in good yield in a relatively short time if rigorous conditions are used. A perhydro compound has been separated from the reaction mixture and characterized by its dibenzoate and by conversion to the corresponding diketone. The mixture also contains some octahydro compounds.

(1) This paper was presented before the Organic Division of the 105th Meeting of the American Chemical Society held in Detroit, Michigan, April 11-16, 1943.

(2) Docken and Spielman, *This Journal*, **62**, 2163 (1940).

(3) Major, Christman and Folkers, U. S. Patent 2,350,361 (1944).

(4) Lane and Wallis, *This Journal*, **66**, 994 (1943).

If the hydrogenation is interrupted before the required amount of hydrogen is absorbed, the product consists of a mixture of perhydro compound and a larger amount of octahydro compounds. The mixture remaining after removal of the perhydro compound is difficult to separate. Fractional crystallization has given two solids whose composition corresponds to octahydro compounds.

When one or both hydroxyl groups in diethylstilbestrol are methylated, the hydrogenation over nickel catalyst stops after absorption of one mole of hydrogen under the same conditions under which diethylstilbestrol is perhydrogenated. The dimethyl ether gives the racemic dihydro compound which has been identified by demethylation to *racemic*-dihydrodiethylstilbestrol. The monomethyl ether, on the other hand, gives a dihydro compound which can be demethylated to *meso*-hexestrol.

Experimental⁵

3,4-Di-(4-hydroxycyclohexyl)-hexane (I).—*trans*-Diethylstilbestrol (50 g.) was dissolved in 100 cc. of methanol and reduced with hydrogen in the presence of 10 g. of Raney nickel under an average pressure of 265 atm. The temperature was maintained at 210° for seven and one half hours. After cooling, the methanol solution was filtered and the solvent removed by distillation. Ether and petroleum ether (1:1) (1000 cc.) were added to the residue, and the solid which precipitated was filtered and washed with three 25-cc. portions of ether. Crystallization of the solid from ethyl acetate yielded 16 g. of 3,4-di-(4-hydroxycyclohexyl)-hexane (I) melting at $188-188.5^\circ$.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 76.50; H, 12.13; mol. wt., 468. Found: C, 76.14; H, 12.11⁶; mol. wt., 490.

The dibenzoate of this compound melted at $137-138^\circ$.

Oxidation of the dihydric alcohol (I) in acetic acid by means of chromic acid resulted in a 95% yield of 3,4-di-(4-oxocyclohexyl)-hexane melting at $65-67^\circ$. Recrystallization from petroleum ether (b. p. 69°) raised the melting point to 75° .⁷

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.57; H, 10.86. Found: C, 78.08; H, 11.09.⁸

The disemicarbazone of the diketone melted at $180-182^\circ$.

3-(4-Hydroxyphenyl)-4-(4-hydroxycyclohexyl)-hexane (II).—The filtrate from the preparation of the perhydro compound (I) was extracted with three 50-cc. portions of 2 N sodium hydroxide solution. The solvent layer was washed with water. The combined alkaline extracts and washings were acidified with dilute hydrochloric acid and extracted with ether. The extract was dried over sodium sulfate and distilled to remove the solvent. The residue was dissolved in three times its weight of benzene. The material which separated was filtered, recrystallized from benzene and dried. It melted at $60-61^\circ$. Recrystallization from cyclohexane raised the melting point to $92-94^\circ$ (II).

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.52; H, 9.64.⁸

Benzoylation of this compound (II) with benzoyl chloride in the presence of pyridine yielded a dibenzoate which melted at $113-114^\circ$. *Anal.* Calcd. for $C_{22}H_{36}O_4$: mol. wt., 484. Found: mol. wt., 478.

(5) All melting points are uncorrected. Molecular weights were determined by the Rast method.

(6) Semimicro analysis by E. Milberger, University of Missouri.

(7) Later work by Ungnade and Ludutsky (*J. Org. Chem.*, in press) indicates that the diketone exists in polymorphic forms.

(8) Microanalysis by Arlington Laboratories.