ployed as reaction medium. After reaction with a halide, the resin could be regenerated by the same procedure; some mechanical deterioration of the resin occurred on stirring limiting its use to three nitrile preparations. One milliliter of wet resin was taken as one milliequivalent of cyanide ion.

General Procedure for the Preparation of Nitriles.—The general procedure is illustrated by the preparation of phenylacetonitrile (run 1, Table I). A mixture of 8.6 g. of benzyl bromide (0.05 mole) in 100 ml. of 95% ethanol and 50 ml. of Amberlite IRA-400 (cyanide form) (0.05 equiv.) was stirred for 1.5 hr. in a 300-ml. erlenmeyer flask. The temperature of the reaction mixture was maintained at 65° by means of a heating tape wound around the flask; continual stirring was provided by a magnetic stirrer. The extent of reaction could be followed conveniently by testing the supernatant liquid with silver nitrate solution. The resin was removed by filtration and washed with five 10-ml. portions of ethanol; the combined filtrates were concentrated under reduced pressure and then distilled to give 3.1 g. of phenylacetonitrile (53%), b.p. 110–111°/15 mm., $n^{27}D$ 1.5201 (lit. b.p. 107°/12 mm.,[19] $n^{25}D$ 1.5211[20]). The infrared spectrum of the compound was identical with that of an authentic sample.

The other nitriles prepared in this study had the following physical constants: *p*-tolylaceto-, b.p. 239–241° (lit.,[21] b.p. 242–243°); *p*-bromophenylaceto-, m.p. 47–48° (lit.,[22] m.p. 46–47°); *m*-chlorophenylaceto-, b.p. 153–155°/26 mm. (lit.,[23] b.p. 134–136°/10 mm.); *o*-phenylenediaceto-, m.p. 59–60° (lit.,[24] m.p. 60°); allyl cyanide, b.p. 116–118° (lit.,[25] b.p. 114–116°). All of the above compounds showed the expected infrared spectra and in all cases exhibited nitrile stretching bands.

All of the starting halides were commercial products and were redistilled or recrystallized prior to use.

1,2,3-Tris(*p*-nitrophenyl)-2-cyanopropane (IV or V).—The addition of 50 ml. of Amberlite IRA-400 (cyanide form) to a solution of 10.8 g. of *p*-nitrobenzyl bromide (0.05 mole) in 100 ml. of ethanol gave a bright red solution immediately; the resin turned black. The mixture was stirred at 70° for 1 hr., filtered, and the resin was washed with ethanol and ether. The resin was then washed with several portions of acetone; concentration of the acetone washings gave 1.6 g. (36%) of tan needles, m.p. 202–204°, which were recrystallized from aqueous acetone to give colorless crystals of IV, m.p. 204–204.5°.

Anal. Calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.34, 61.18; H, 3.77, 3.71; N, 13.52, 13.69.

The infrared spectrum (Nujol mull) of this material showed typical *p*-nitrophenyl (857.6, 1603, 1613) and nitro (1348, 1538 cm.$^{-1}$) absorptions; a maximum at 267 mμ (log ε = 4.48) was observed in the ultraviolet (95% ethanol). The n.m.r. spectrum in deuteroacetone showed peaks at τ = 1.85, 2.00, 2.15, 2.28, 2.50, 2.65, and 6.24. Additional quantities of IV could be isolated from the original ethanol solution and washings by dilution with water.

The tris compound (IV) was hydrolyzed by heating with sulfuric acid and sodium chloride at 190° for 1 hr.; after cooling the solution was poured over ice to give a colorless precipitate. Recrystallization of the precipitate from aqueous acetone gave colorless crystals, m.p. 231.5–234°. The product was insoluble in chloroform, acetonitrile, carbon tetrachloride, water, and 10% sodium hydroxide. The infrared spectrum (Nujol mull) showed typical strong carboxyl (1310, 1690) and nitro (1350, 1515 cm.$^{-1}$) absorptions.

(19) R. Anschütz and W. Berns, *Ber.*, **20**, 1390 (1887).
(20) P. Walden, *Z. Physik. Chem.* (Leipzig), **59**, 385 (1907).
(21) B. Radziszewski and P. Wispak, *Ber.*, **18**, 1280 (1885).
(22) W. Wislicenus and H. Elvert, *ibid.*, **41**, 4121 (1908).
(23) N. Campbell and J. E. McKail, *J. Chem. Soc.*, 1251 (1948).
(24) C. W. Moore and J. F. Thorpe, *ibid.*, 175 (1908).
(25) P. Bruylants, *Bull. soc. chim. Belg.*, **31**, 175 (1922).

On the Palladium-catalyzed Hydrogenolysis of the Epoxysuccinic Acids[1]

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The hydrogenolysis of *cis*-epoxysuccinic acid and *trans*-epoxysuccinic acid in aqueous solution with palladium-on-charcoal catalyst leads to the formation of malic acid, succinic acid, and diglycolic acid. Hydrogenolysis of the epoxides to malic acid proceeds in a *trans* fashion, *threo*-3-deuterio-DL-malic acid and *erythro*-3-deuterio-DL-malic acid resulting from *cis*-epoxysuccinic acid and *trans*-epoxysuccinic acid, respectively. Mixed *erythro*- and *threo*-2,3-dideuteriosuccinic acids result from *cis*-epoxysuccinic acid and *threo*-2,3-dideuteriosuccinic acid results from *trans*-epoxysuccinic acid. Malic acid is not an intermediate for the formation of succinic acid.

The hydrogenolysis of the epoxysuccinic acids has been under investigation in this laboratory and it has been noted[2] in a preliminary fashion that the hydrogenolysis of *cis*-epoxysuccinic acid in 9:1 dioxane–deuterium oxide with deuterium yields *threo*-DL-3-deuteriomalic acid, opening of the epoxide ring with inversion having taken place. In this paper further results on the identity and steric configuration of the products obtained by hydrogenolysis of the epoxysuccinic acids are reported. Interest in these hydrogenolyses stems from the fact that the products (with deuterium), *threo*-DL-3-deuteriomalic acid, mixed *erythro*- and *threo*-2,3-dideuteriosuccinic acids and diglycolic acid from *cis*-epoxysuccinic acid and *erythro*-DL-3-deuteriomalic acid, *threo*-2,3-dideuteriosuccinic acid and diglycolic acid from *trans*-DL-epoxysuccinic acid are pertinent to mechanisms of hydrogenolysis of epoxides.[3,4] Of further interest, these hydrogenolyses provide a convenient synthetic route to *threo*- and *erythro*-3-deuterio-DL-malic acids and the *threo*- and *erythro*-3-deuterio-DL-chlorosuccinic acids which may be obtained from the malic acids. These four acids provide convenient substrates for studying the stereochemistry of enzymatic and non-enzymatic dehydrations,[2] dehydrochlorinations,[5] and dehydrogenations.[5]

(1) Abstracted in part from the Ph.D. thesis of Thomas P. Fondy, August, 1961.
(2) O. Gawron, A. J. Glaid, III, and T. P. Fondy, *J. Am. Chem. Soc.*, **83**, 3634 (1961).
(3) F. J. McQuillin and W. O. Ord, *J. Chem. Soc.*, 3169 (1959).
(4) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

Experimental

General Procedure for Hydrogenolysis.—Hydrogenolyses were carried out at room temperature in the usual Paar apparatus. For small scale (1–2 mmoles) exploratory experiments, the tank was replaced by a small section of appropriately threaded pipe and small glass bottles were used as the reaction vessels. With these modifications, the dead air space was approximately 50 ml. Small scale hydrogenations at atmospheric pressure were carried out in a three-necked, 100-ml. flask equipped with a pressure-equalizing dropping funnel and a magnetic stirrer and connected to a gas buret containing dibutyl phthalate. For hydrogenations with deuterium, Volk Radiochemical Co. 99.7% deuterium gas (500 p.s.i.) was used and as required 99.9% deuterium oxide from Bio-Rad Laboratories. The catalyst used for all runs was

(5) O. Gawron, A. J. Glaid, J. Francisco, and T. P. Fondy, unpublished work.

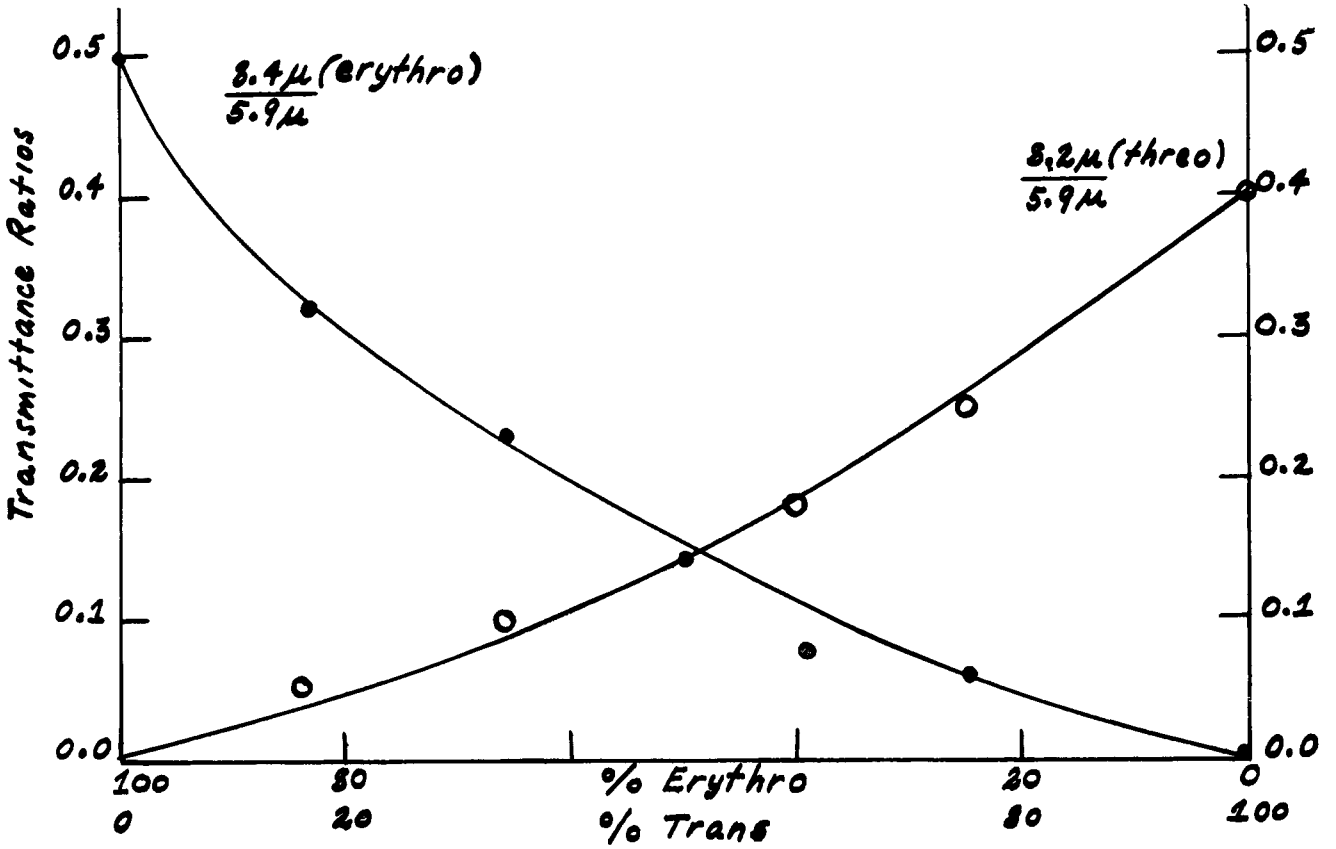

Fig. 1.—Variation in transmittance at 8.4 μ for *erythro*-1,2,3,4-tetradeuteriosuccinic acid and at 8.2 μ for *threo*-1,2,3,4-tetradeuteriosuccinic acid in synthetic mixtures of the two acids. The transmittances are reported relative to the transmittance at 5.9 μ, this absorption band being common to both acids.

palladium (10% on charcoal) obtained from the Matheson Company.

Spectral Standards and Infrared Differentiation of *erythro*- and *threo*-2,3-Dideuteriosuccinic Acids.—*erythro*- and *threo*-2,3-Dideuteriosuccinic acids were prepared by hydrogenation with deuterium of maleic and fumaric acids, respectively, according to the procedure of Childs and Bloch.[6] The dideuterio acids were then converted to the corresponding 1,2,3,4-tetradeuterio acids by solution in deuterium oxide followed by lyophillization. Infrared spectra of Nujol mulls of the resulting *erythro*-1,2,3,4-tetradeuteriosuccinic acid and *threo*-1,2,3,4-tetradeuteriosuccinic acid were obtained with a Perkin–Elmer Model 137 instrument. The spectra showed only minor variation from the corresponding spectra[6] for *erythro*-2,3-dideuteriosuccinic acid and *threo*-2,3-dideuteriosuccinic acid. For differentiation purposes the sharp peaks at 7.9 μ and 8.4 μ for *erythro*-1,2,3,4-tetradeuteriosuccinic acid and at 7.8 μ and 8.2 μ for *threo*-1,2,3,4-tetradeuterio succinic acid were used. For approximate estimation of relative amounts of each of the two acids the transmittances at 8.2 μ for the *threo* acid and at 8.4 μ for the *erythro* acid were utilized. The transmittance at each of these absorption bands was measured relative to the transmittance at 5.9 μ, an absorption band common to both acids and calibration curves obtained in this way for synthetic mixtures of the two acids are given in Fig. 1.

Hydrogenolysis (with Deuterium) of *cis*-Epoxysuccinic Acid.—The acid protons of *cis*-epoxysuccinic acid,[7,8] chromatographically pure, were exchanged by solution in 99.9% deuterium oxide and lyophillization. Four and one-tenth grams (30.6 mmoles) of the exchanged acid was dissolved in 50 ml. of deuterium oxide and after addition of 1 g. of catalyst, hydrogenolysis with deuterium at an initial pressure of 50 p.s.i. was begun. Deuterium uptake ceased after 8 hr. and an additional 600 mg. of catalyst was added and hydrogenolysis was continued for 12 hr. The total uptake was 122 p.s.i., corresponding to approximately 50 mmoles deuterium uptake.

Isolation and Identification of Products: Succinic Acid.—The reaction mixture was filtered and the catalyst was thoroughly washed with 15 ml. of boiling deuterium oxide. The filtrate and wash were combined and refrigerated at 4° for 24 hr. Filtration at the end of this period yielded 300 mg. of relatively pure 1:1 mixed *erythro*- and *threo*-1,2,3,4-tetradeuteriosuccinic acids, the characterization and isomer ratio being determined by the spectral method described above.

Anal. Calcd. for $C_4H_2D_4O_4$: D, 66.7%. Found: D, 67.0%.

***threo*-3-Deuterio-DL-malic Acid.**—The above filtrate was taken to dryness (rotatory evaporator, water aspirator, 40°) and the residue was subjected to chromatography[5] with a 3.5-cm. column containing 30 g. of celite[9] mixed with 15 ml. of 0.5 *N* hydrochloric acid as the stationary phase, 12.3:1 chloroform–ethanol as the eluent and 10.0 ml. fractions being collected. Fractions 146 to 305 were pooled, solvent was removed *in vacuo*, and the residue was recrystallized from ether–petroleum ether to yield 450 mg. of 3-deuterio-DL-malic acid melting 122–124°.[10]

Anal.[12] Calcd. for $C_4H_5DO_5$: C, 16.6 atom %. Found: D, 16.5 atom %.

For determination of stereochemistry, the 3-deuterio-DL-malic acid was lyophillized twice from deuterium oxide and n.m.r. spectra were obtained as previously outlined.[2] The compound showed a coupling constant of 4.3 ± 0.2 c.p.s. for the two nonequivalent protons, characteristic of authentic[2,13] *threo*-3-deuterio-DL-malic acid, albeit evidence from solid state n.m.r. studies[14] indicates the presence of some —CH_2— groups and presumably, therefore, some —CDOH— groups.

Diglycolic Acid.—Fractions 23 to 105 from the chromatographic separation of *threo*-DL-3-deuteriomalic acid were pooled and the solvent was removed *in vacuo*. The residue was taken

(6) C. R. Childs, Jr., and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961).
(7) E. Weitz, H. Schobbert, and H. Seibert, *Ber.*, **68B**, 1163 (1935).
(8) O. Gawron, A. J. Glaid, III, A. LoMonte, and S. Gary, *J. Am. Chem. Soc.*, **80**, 5856 (1958).
(9) Johns-Manville, #535.
(10) DL-Malic acid, m.p. 127–128.5,° can be obtained by repeated recrystallization from acetone–carbon tetrachloride.[11] To conserve material, recrystallization from acetone–carbon tetrachloride was not attempted.
(11) R. Descamps, *Bull. soc. chim. Belg.*, **48**, 201 (1939); **49**, 91 (1940).
(12) After solution in water and lyophillization to remove residual deuterium from the carboxyl groups.
(13) O. Gawron and T. P. Fondy, *J. Am. Chem. Soc.*, **81**, 6323 (1959).
(14) H. S. Gutowsky, personal communication.

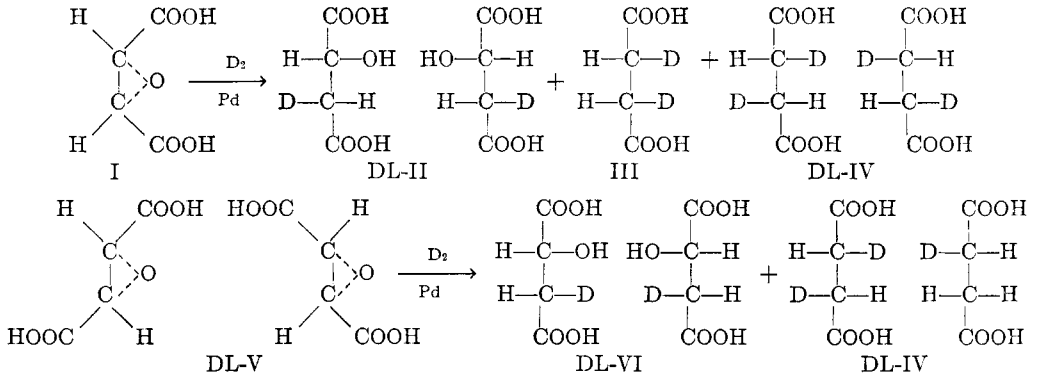

Fig. 2.—Stereochemistry of the malic acids and succinic acids obtained by hydrogenolysis, with deuterium, of *cis*-epoxysuccinic acid and *trans*-epoxysuccinic acid.

up in ether and 500 mg. of a mixture of succinic acid and diglycolic acid was precipitated by the addition of petroleum ether. The mixed acids were resolved by column chromatography (eluent, 1:1 ether–benzene; stationary phase, 25 g. Celite, 12.5 ml. 0.5 *N* hydrochloric acid in a 3.5-cm.-diameter column, 10-ml. fractions collected). Fractions 64 to 94 were pooled and after partial removal of solvent *in vacuo* 57 mg. of diglycolic acid crystallized from solution. The acid was identified by its melting point, 140.5–141.5°, mixed melting point, 141–142°, with authentic diglycolic acid and by column chromatography (eluent, 18:2:1 chloroform-*n*-butyl alcohol–ethanol; stationary phase, 5.0 g. of Celite 2.5 ml. of 0.5 *N* hydrochloric acid in 1.0 cm. diameter column; 3-ml. fractions collected) with admixed authentic diglycolic acid, a single peak with a maximum at fraction 21 being obtained.

Product Ratios.—Seven grams of *cis*-epoxysuccinic acid was subjected to palladium-catalyzed hydrogenolysis with deuterium as described above. After deuterium uptake ceased (20% oxide unchanged, as determined by column chromatography), the reaction mixture was filtered free of catalyst, the catalyst was washed with hot water, and the combined filtrate and wash was taken to dryness *in vacuo*. A 20-mg. aliquot of the residue subjected to analytical chromatography (eluent, 18:2:1 chloroform-n-butyl alcohol–ethanol; stationary phase, 5.0 g. of Celite, 2.5 ml. of 0.5 *N* hydrochloric acid in a 1.0 cm. diameter column; 3.0-ml. fractions collected) yielded molar ratios of 1:2:5 for succinic acid:diglycolic acid:malic acid.

Hydrogenolysis (with Deuterium) of *trans*-DL-Epoxysuccinic Acid.—Five grams of *trans*-DL-epoxysuccinic acid[15] previously lyophillized from deuterium oxide was dissolved in 60 ml. of deuterium oxide and after the addition of 3.5 g. of catalyst, hydrogenolysis with deuterium at an initial pressure of 58 p.s.i. was carried out. After cessation of deuterium uptake, product isolation was carried out in the manner described above for the hydrogenolysis of the *cis*-epoxysuccinic acid. Nine hundred milligrams of 2,3-dideuteriosuccinic acid and 160 mg. of 3-deuterio-DL-malic acid were obtained. Diglycolic acid was not isolated, but its presence was determined by column chromatography. The succinic acid was converted to the 1,2,3,4-tetradeuteriosuccinic acid by recrystallization from deuterium oxide and identified as the *threo*-derivative by comparison of its infrared spectrum with that of the authentic *threo*-1,2,3,4-tetradeuterio succinic acid. The malic acid was lyophyllized from deuterium oxide and its n.m.r. spectrum was obtained as previously described.[2,13] Its spectrum and coupling constant, 7.6 ± 0.2 c.p.s., were the same as for authentic *erythro*-3-deuterio-DL-malic acid.[2,16] In a separate experiment utilizing 2.00 g. of the *trans* oxide dissolved in 30 ml. of water, 1.00 g. of catalyst and hydrogen at an initial pressure of 55 p.s.i., 1.73 g. of mixed products was obtained after filtration, washing of catalyst, and evaporation to dryness *in vacuo*.[17] Analytical chromatography (18:2:1 chloroform-*n*-butyl alcohol–ethanol; 5 g. of Celite, 2.5 ml. of 0.5 *N* hydrochloric acid, 1-cm. column) of 20.0 mg. of the mixture demonstrated 14.6 mole per cent diglycolic acid, 27.4 mole per cent malic acid, and 58.0 mole per cent succinic acid plus unchanged *trans* oxide.[18]

(15) R. Kuhn and F. Ebel, *Ber.*, **58**, 919 (1925).

(16) R. A. Alberty and P. Bender, *J. Am. Chem. Soc.*, **81**, 542 (1959).

(17) Acetic acid could not be detected in the distillate.

(18) Mixtures of succinic acid with *trans*-DL-epoxysuccinic acid could not be resolved by this eluent combination nor by others that were tried.

Results and Discussion

The products that were obtained on hydrogenolysis of both *cis*-epoxysuccinic acid and *trans*-DL-epoxysuccinic acid in aqueous solution are, without regard to their stereochemistry, malic acid, succinic acid, and diglycolic acid. The formation of these products can be rationalized without regard to mechanism by assuming that each bond of the epoxy ring is susceptible to hydrogenolysis. That a single carbon–oxygen bond of an epoxy ring may be hydrogenolyzed with hydrogen and catalyst or with a hydride ion bearing reagent is, of course, well established[4] and the formation of malic acid is thus expected. Apparent simultaneous hydrogenolysis of both carbon–oxygen bonds of the epoxy ring accounts for the formation of succinic acid, the epoxy ring in this instance being analogous to episulfides and sulfides.[19] Finally, hydrogenolysis of the carbon–carbon bond of the epoxy ring, presumably because α-epoxides are structurally analogous to cyclopropanes,[4] accounts for the formation of diglycolic acid. In keeping with the above interpretation of the reaction, malic acid in aqueous solution was recovered intact after shaking with the catalyst both in the presence and absence of hydrogen and the epoxides in aqueous solution were recovered in good yield (80%) after shaking with catalyst. In particular, maleic acid and fumaric acid were not found on shaking the epoxides with catalyst. However, the finding that some deuterium is present on the methine carbon of the monodeuterio-DL-malic acid obtained from the hydrogenolysis of the *cis*-epoxide suggests that a limited amount of malic acid may have arisen by a different pathway than direct opening of the epoxide ring. Such a pathway could conceivably be initial rearrangement[4] of the epoxide to the ketone, oxaloacetic acid, and subsequent reduction of the ketone to 2-deuterio-DL-malic acid.

Fig. 2 presents the stereochemical configuration of the reactants and products with the exception of the diglycolic acids, the latter not having been investigated. It is to be noted that *cis*-epoxysuccinic acid (I) yields *threo*-3-deuterio-DL-malic acid (II) and that *trans*-DL-epoxysuccinic acid (V) yields *erythro*-3-deuterio-DL-malic acid (VI) and that in each case, ring opening has occurred with inversion. This opening with inversions of the epoxide ring to give malic acid is not inconsistent with the interpretation that a hydride ion causes hydrogenolysis. A similar interpretation has been given for

(19) R. Mozingo, D. E. Wolfe, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 103 (1943).

the hydrogenolysis of unsaturated cyclopropanes.[20] Of further interest, acid inhibits while alkali accelerates hydrogen uptake of the substrates under study. Thus hydrogenolysis at 50 p.s.i. of *trans*-epoxysuccinic acid in 0.5 *N* hydrochloric acid results in negligible hydrogen uptake. The usual effect of acid is to catalyze epoxide hydrogenolysis[3] and this effect plus other results has led to the view[3] that hydrogenolysis takes place *via* acid catalyzed ring opening to give a carbonium ion which then accepts hydrogen. It is clear that this mechanism cannot be operative in the formation of malic acid from the epoxysuccinic acids. Of further interest, the product ratio is changed on going from an aqueous solution of *trans*-epoxysuccinic acid to neutral, pH 7.0, solution.[21] At pH 7.0, malic acid is the main product, while in aqueous solution, pH 2, diglycolic acid and succinic acid are found in quantity. It would seem that with these substrates product composition is affected by acidity,[22] hydrogenolysis of both carbon–oxygen bonds, and of the carbon–carbon bond being increased in the acid solution.

From Fig. 2 it is to be seen that *threo*-2,3-dideuteriosuccinic acid[23] (IV) results from the hydrogenolysis of *trans*-epoxysuccinic acid (V), the deuterium atoms having added in a *cis* fashion and, presumably, displacing by backside attack the oxygen atom of the epoxide. This latter point, of course, cannot be established conclusively from the present data. *cis*-Epoxysuccinic acid (I), on the other hand, yielded a 1:1 mixture of *erythro*-2,3-dideuteriosuccinic acid (III) and *threo*-2,3-dideuterioscuccinic acid (IV). The mixture of stereoisomers of dideuteriosuccinic acid obtained from epoxysuccinic acid cannot be attributed to racemization of the product, *erythro*-2,3-dideuteriosuccinic acid, expected on the basis of *cis*-hydrogen addition, since the same mixture was found on incomplete hydrogenolysis[24] and also racemization of *erythro*-2,3-dideuteriosuccinic acid did not occur in a control experiment. Another possible explanation for the mixture of stereoisomers, the racemization of *cis*-epoxysuccinic acid to *trans*-epoxysuccinic acid prior to hydrogenolysis is ruled out by the steric purity of the *threo*-3-deuterio-DL-malic acid obtained from the *cis*-epoxysuccinic acid. It would thus seem that with *cis*-epoxysuccinic acid hydrogenolysis occurs by both *cis* and *trans* addition of deuterium or, more likely, that some half-hydrogenated state[25] may exist in two configurations which yield, on completion of hydrogenation by *cis* addition, both isomers of 2,3-dideuteriosuccinic acid.

Acknowledgment.—This research was supported, in part, by research grant GM 06245 from the Division of General Medical Sciences, Public Health Service.

(20) E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5389 (1959).

(21) The approximate pK_1 and pK_2 values of *cis*-epoxysuccinic acid and *trans*-epoxysuccinic acid are 2.2, 3.7, and 2.2, 3.2, respectively (unpublished work of O. Gawron and T. P. Fondy).

(22) In a preliminary experiment, hydrogenolysis at 50 p.s.i. of *trans*-epoxysuccinic acid in glacial acetic acid resulted in 40% hydrogen uptake after 48 hr. Analytical chromatography did not demonstrate any malic or diglycolic acids and presumably, succinic acid was formed. Tartaric acid was not apparent.

(23) However, the possibility that several percent of the *erythro* isomer is present can not be excluded by the spectrophotometric technique.

(24) Two grams of *cis*-epoxysuccinic acid in 30 ml. of deuterium oxide was hydrogenolyzed for one hour with 0.26 g. of catalyst at an initial deuterium pressure of 40 p.s.i. to yield 83 mg. (4.5%) of succinic acid.

(25) I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

Stepwise Reduction of *gem*-Dihalocyclopropanes with Tri-*n*-butyltin Hydride[1]

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The reduction of substituted *gem*-dibromocyclopropanes to monobromocyclopropanes can be effected in good yield with tri-*n*-butyltin hydride at temperatures below 40°. This radical reaction gives a mixture of isomers in most of the cases where one has the possibility of forming *cis* and *trans* isomers. A tentative assignment of structure of some of the isomer pairs (*e.g.*, *cis*- and *trans*-7-bromobicyclo[4.1.0]heptane) is made on the basis of n.m.r. data. Preferential reduction of 7-bromo-7-chlorobicyclo[4.1.0]heptane to the chlorocyclopropane is easily accomplished under these conditions. Reduction of 7,7-dichlorobicyclo[4.1.0]heptane with tri-*n*-butyltin hydride requires temperatures of *ca.* 140°. The partial reduction of bromoform, tribromofluoromethane, carbon tetrachloride, and chloroform by tri-*n*-butyltin hydride is reported.

Our recent work[3] on the preparation of cyclopropyltin compounds *via* cyclopropylmagnesium bromide made a study of substituted cyclopropyltin compounds of interest to us. Such a study required the corresponding cyclopropyl bromides, and this paper reports the preparation of such bromides by the reduction of the readily accessible *gem*-dibromocyclopropanes[4,5] with tri-*n*-butyltin hydride.

The reduction of organic halides to the corresponding hydrocarbons by organotin hydrides,

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H$$

was discovered by van der Kerk, *et al.*[6] Several examples of this reaction have been described since then.[7-9] Kuivila[9] has reported the stepwise reduction

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(2) (a) Alfred P. Sloan Research Fellow; (b) Fellow of the M.I.T. School for Advanced Study, 1961–1962; (c) on leave from the Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan.

(3) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(4) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

(5) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(6) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

(7) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **25**, 2203 (1960).

(8) (a) E. J. Kupchik and R. E. Connolly, *ibid.*, **26**, 4747 (1961); (b) E. J. Kupchik and R. J. Kiesel, *Chem. Ind.* (London), 1654 (1962).

(9) H. G. Kuivila, Organic Chemistry Colloquium, Harvard University, February 28, 1961; H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962).