EXPERIMENTAL

trans-2-*o*-Tolylcyclohexanol (I) is a known compound (10).

trans-2-*o*-Tolyl-*trans*-5-hydroxycyclohexanol-3,3,-6,6-d_4 (II) and *trans*-2-*o*-tolyl-*cis*-4-hydroxycyclohexanol-3,3,6,6-d_4 (III) were prepared by the method previously reported for the corresponding nondeuterated compounds (11) except that butadiene-1,1,4,4-d_4 (12) was used in the Diels-Alder condensation step.

cis-4-*tert*-Butylcyclohexanol-3(axial)4,4-d_3 (IV) and the corresponding *trans* isomer (V) have been reported in a previous communication (13). Detailed synthesis of these 2 compounds will be reported in a subsequent publication.

4-*tert*-Butyl-*trans*-1,4-cyclohexanediol-3,3,4,5-d_4 (VI) and the corresponding *cis*-diol (VII) have been reported previously (9).

The NMR spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as internal reference.

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Elucidation of the Configuration of an Intermediate in the Synthesis of *cis*-β-Acetoxystyrene II

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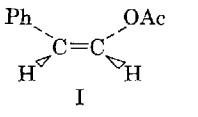
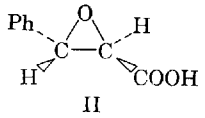
The configuration of *erythro*-α-hydroxy-β-toluene-*p*-sulfonyloxypropionic acid (III) was proved through conversion to the known methyl *erythro*-β-phenyl-α,β-ditoluene-*p*-sulfonyloxypropionate (VIII). Compound III represents the key intermediate in the conversion of *trans*-β-phenylglycidic acid (II) to *cis*-β-acetoxystyrene (I) and elucidation of the *erythro* configuration for III substantiates the original proposal that decarboxylative elimination of the probable acetate derivative (IV) occurred *trans*.

RECENTLY, the authors reported (1) a stereoselective synthesis for *cis*-β-acetoxystyrene (I) from *trans*-β-phenylglycidic acid (II). The key intermediate in the synthesis involved formation of the α-hydroxy-β-tosyloxy compound (III) through reaction of *trans*-β-phenylglycidic acid with *p*-toluenesulfonic acid in dry ether.

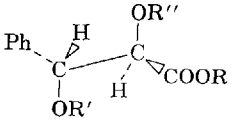
Assignment of the *erythro* configuration to compound III was originally based on the stereoselective formation of *cis*-β-acetoxystyrene (I) which was proposed to have formed by *trans* decarboxylative elimination of the corresponding α-acetoxy derivative (IV). Since the α-acetoxy derivative (IV) was not isolated when compound III was treated with acetic anhydride in pyridine (1)[1] and since some openings of benzylic epoxides with various Bronsted acids in nonpolar medium have been shown to occur with retention of configuration (2) independent evidence for the configuration of the β-tosyloxy-α-



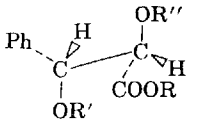
I



II



III, R = R'' = H, R' = Ts
IV, R = H, R' = Ts, R'' = Ac
V, R = R' = R'' = H
VII, R = CH_3, R' = Ts, R'' = H
VIII, R = CH_3, R' = R'' = Ts
IX, R = CH_3, R' = R'' = H



VII, R = R' = R'' = H
X, R = CH_3, R' = R'' = Ts
XI, R = CH_3, R = R'' = H

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[1] *cis*-β-Acetoxystyrene was formed directly from compound III. Formation of the enol acetate was rationalized on the basis of the instability of the α-carboxy-β-tosyloxy system.

hydroxy acid (III) was desirable. Such evidence would confirm our original proposal that the decarboxylative elimination did indeed occur *trans*.

Our earlier attempts (1) to prepare stable derivatives of compound III which could subsequently be compared to derivatives of the known *erythro* (V) and *threo* (VI) diols (3) were unsuccessful. This was probably due to the instability of the α-carboxy-β-tosyloxy system which readily decomposed under relatively mild conditions. In order to obtain stable derivatives, intermediate III was converted to its methyl ester (VII) through treatment with ethereal diazomethane. Subsequent reaction of compound VII with *p*-toluenesulfonyl chloride in pyridine afforded the ditosyl derivative (VIII) which was identical in all properties to the ditosylated methyl ester which we prepared according to the method of Linstead and co-workers (4) from the known *erythro* diol methyl ester (IX).

Admixture of VIII and the ditosylated methyl ester (X) prepared from the known *threo* diol methyl ester (XI) gave a depression in melting point while admixture with the known *erythro* diol methyl ester gave no such depression. In addition, the infrared spectra of the *erythro* and *threo* ditosylated methyl esters (VIII and X) differed in the region between 8 and 16 μ. The *erythro* ditosylates prepared by either method had additional peaks at 9.70, 10.92, and 11.89 μ, while the *threo* ditosylate exhibited peaks at 10.96 and 12.01 μ. These data prove that the α-hydroxy-β-tosyloxy intermediate has the *erythro* configuration and that decarboxylative elimination of the probable acetate intermediate occurred *trans*.

EXPERIMENTAL[2]

Erythro - α,β - dihydroxy - β - phenylpropionic Acid (V).—A suspension of 28 Gm. (0.15 mole) sodium *trans*-β-phenylglycidate in 420 ml. of 10% sodium hydroxide was heated at reflux for 1.5 hr. After cooling to room temperature, the mixture was acidified with hydrochloric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure affording a yellow oil. The oil crystallized affording 7.2 Gm. (32.8%) of white crystalline solid. Recrystallization from acetone–ether–skellysolve B yielded 6 Gm. (28%) of product, m.p. 121–121.5°. [Reported m.p. 122° (3).]

Threo - α,β - dihydroxy - β - phenylpropionic Acid (VI).—Utilization of the above procedure with sodium *cis*-β-phenylglycidate (5) afforded the *threo* dihydroxy acid in 67% yield. Recrystallization from ether yielded a white crystalline compound, m.p. 140–141°. [Reported m.p. 141–142° (3).]

Methyl Erythro - α - hydroxy - β - phenyl - β-toluene - p - sulfonyloxypropionate (VII) from Erythro - α - hydroxy - β - phenyl - β - toluene - p-sulfonyloxypropionic Acid (III).—A suspension of 5 Gm. (0.016 mole) of *erythro*-α-hydroxy-β-phenyl-β-toluene-*p*-sulfonyloxypropionic acid in 200 ml. of anhydrous ether was cooled to 0°. To this suspension was added an ethereal solution of diazomethane (6) until evolution of nitrogen ceased and the solution acquired a pale yellow color. Excess diazomethane was destroyed by dropwise addition of glacial acetic acid. Removal of the solvent under reduced pressure afforded 3.5 Gm. (67%) of oil which could not be crystallized in our hands but which was converted directly to the *erythro* ditosylate (VIII).

Methyl Erythro - β - phenyl - α,β - ditoluene - p-sulfonyloxypropionate (VIII) from Methyl Erythro-α-hydroxy-β-phenyl-β-toluene - p - sulfonyloxypropionate (VII).—Methyl *erythro*-α-hydroxy-β-toluene-*p*-sulfonyloxypropionate (1.75 Gm., 0.005 mole) was dissolved in 5 ml. of pyridine and the solution was cooled to 0°. To this solution was added 1.5 Gm. (0.005 mole) of *p*-toluenesulfonyl chloride with vigorous stirring. The mixture was shaken and allowed to stand for 30 min. at 25°, poured onto 50 Gm. of ice, and extracted with two 100-ml. portions of ether. The ether layer was washed with two 100-ml. portions of 5% hydrochloric acid and with 100 ml. of water. The ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. A white, solid residue remained weighing 1.5 Gm. (59%). Recrystallization from methanol yielded white needles, m.p. 129–131°. Mixed melting point with an authentic sample of *erythro* ditosylate prepared from the known *erythro* diol was 129–131°. Mixed melting point with the known *threo* ditosylate 110–112°.

Anal.—Calcd. for $C_{24}H_{24}O_8S_2$: C, 57.1; H, 4.8; S, 12.4. Found: C, 56.9; H, 4.5; S, 12.5

[2] All melting points are corrected and were taken with a Thomas-Hoover melting point apparatus. Infrared spectra were taken with a Beckman IR-5A spectrophotometer. Elemental analyses were run by Clark Microanalytical Laboratory, Urbana, Ill., and Crobaugh Laboratories, Charleston, W. Va.

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