amide, 17709-95-4; *N*-methylthiophenylacetamide, 77130-13-3; *N*-methylthioacetanilide, 5310-07-6; *N*-benzyl-2-piperidone, 4783-65-7; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-dimethylphenylacetamide, 18925-69-4; *N*-methylphenylacetamide, 6830-82-6; *N*-methylacetanilide, 579-10-2; P_4S_{10}, 12066-62-5.

Stereospecific Synthesis of Optically Active Succinic-d_2 Acid

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Succinic-*d* acid has played a central role in the determination of configuration of molecules whose chirality is due to the presence of deuterium. It is readily available, easily purified, and has a high specific rotation in the ultraviolet region of the spectrum.[1]

(2*R*,3*R*)-(−)-Succinic-d_2 acid has previously been prepared by transformation of (4*R*)-4,5-dihydroxy-2-oxovaleric acid to 2-oxoglutaraldehydic acid by *Pseudomonas saccharophila* in D_2O.[2] Degradation afforded (−)-succinic-d_2 acid containing nearly two deuteriums and having nearly twice the rotation of (−)-succinic-*d* acid. To date, chemical synthesis of succinic-d_2 acid has been reported only as the racemate.[3]

During the course of some other investigations, a synthesis of optically active succinic-d_2 acid became necessary, both as an important intermediate, and as a means of estimating the optical purity of some related systems. We report here a stereospecific chemical synthesis of both enantiomers of succinic-d_2 acid from 2,3-dideuterio-2,3-dibromobutane-1,4-diol.

Results

The synthetic sequence which was employed is summarized in Schemes I and II. The synthesis and resolution of 2,3-dideuterio-2,3-dibromobutane-1,4-diol (Scheme I) was achieved by a slight modification of the procedures of Feit[4] and is described in the Experimental Section. Reduction of (2*R*,3*R*)-(+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol ($[\alpha]^{20}_D$ +39.4° (*c* 2.9, methanol), mp 112–114 °C; lit.[4] for (2*R*,3*R*)-(+)-2,3-dibromobutane-1,4-diol) $[\alpha]^{20}_D$ +40.0° (*c* 2, methanol), mp 114.5 °C) with lithium aluminum hydride in THF followed by hydrolysis afforded a mixture which was not isolated but oxidized directly with potassium permanganate to (2*S*,3*S*)-(+)-2,3-dideuteriosuccinic acid. Mass analysis of succinic-d_2 anhydride derived from this acid by refluxing with acetic anhydride indicated that 1% undeuterated and 14% monodeuterated succinic acid was present. Proof that the lithium aluminum hydride reduction occurred stereospecifically was demonstrated by conversion to *trans*-1,2-dideuteriocyclobutane (Scheme II). No cis isomer could be detected by infrared spectroscopy[5] Inversion of configuration during hydride reduction was demonstrated by the fact that (2*R*,3*R*)-(+)-2,3-dibromodideuteriobutane-1,4-diol (absolute configuration related to L-threitol by Feit) gave (2*S*,3*S*)-(+)-dideuteriosuccinic acid. The absolute configuration of (2*R*,3*R*)-(−)-2,3-dideuteriosuccinic acid has been related to (*R*)-(−)-succinic-*d* acid by nonenzymatic methods by Portsmouth, Stoolmiller, and Abeles.[2]

† NSFURP student, summer 1979.

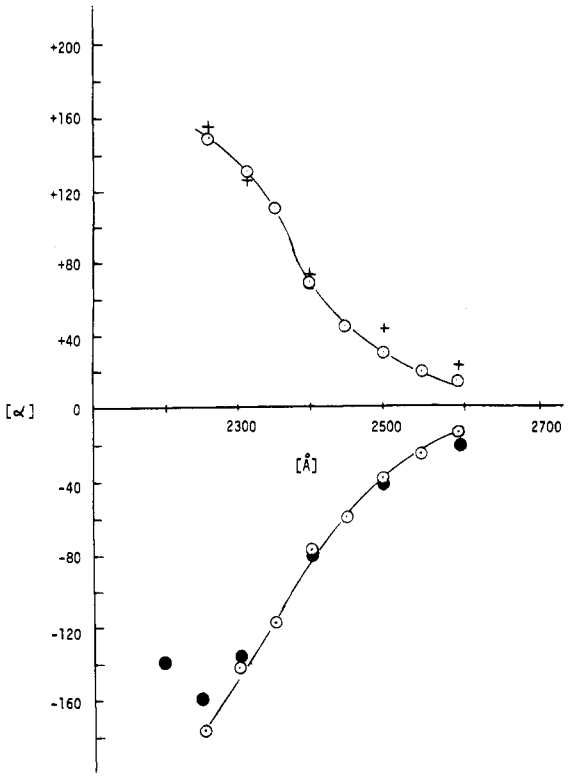


Figure 1. Circled dot, ⊙: for ORD curves for the following: (*R,R*)-(−)-2,3-dideuteriosuccinic acid from (*S,S*)-(−)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol ($[\alpha]^{20}_D$ −26.5°) corrected for optical purity and 14% (*R*)-(−)-deuteriosuccinic acid; (*S,S*)-(+)-2,3-dideuteriosuccinic acid from (*R,R*)-(+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol $[\alpha]^{20}_D$ +39.4°) corrected for 14% (*S*)-(+)-deuteriosuccinic acid. Solid circle, ●: for ORD curve for (*RR*)-(−)-2,3-dideuteriosuccinic acid obtained from *Pseudomonas saccharophila* by Portsmouth et al.[2] The plus sign indicates values calculated for dideuteriosuccinic acid (2[α] for monodeuteriosuccinic acid).

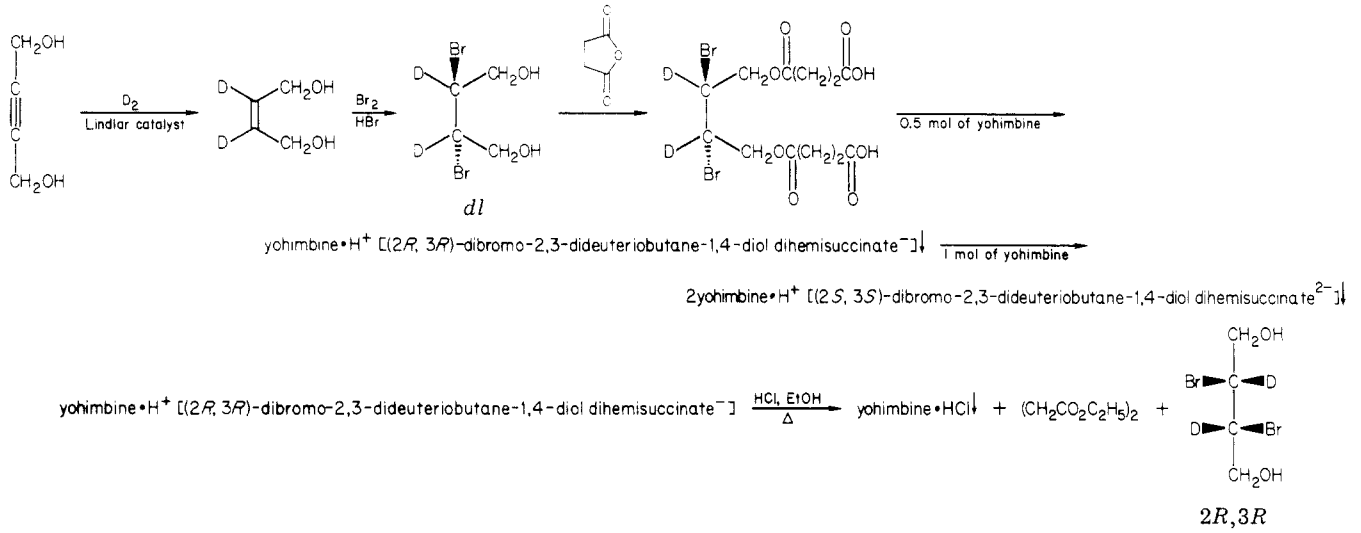
Thus reduction with lithium aluminum hydride occurs stereospecifically and with inversion of configuration. The yield is estimated at 70%.

The optical rotatory dispersion (ORD) curves for both enantiomers of 2,3-dideuteriosuccinic acid are reported in Figure 1. The rotations have been corrected for optical purity (based on Feit's rotations for the corresponding bromo alcohols) and the isotopic distributions noted above. The contributions of succinic-*d* acid (14%) was assumed to contribute half the rotatory power of the dideuteriosuccinic acid in these calculations. The ORD curve reported by Portsmouth et. al.[2] for (−)-2,3-dideuteriosuccinic acid has been included for comparison in Figure 1 (solid circles). Agreement between the two curves is very good. Comparison of the observed curve to that generated by assuming the rotation of the (+)-dideuteriosuccinic acid

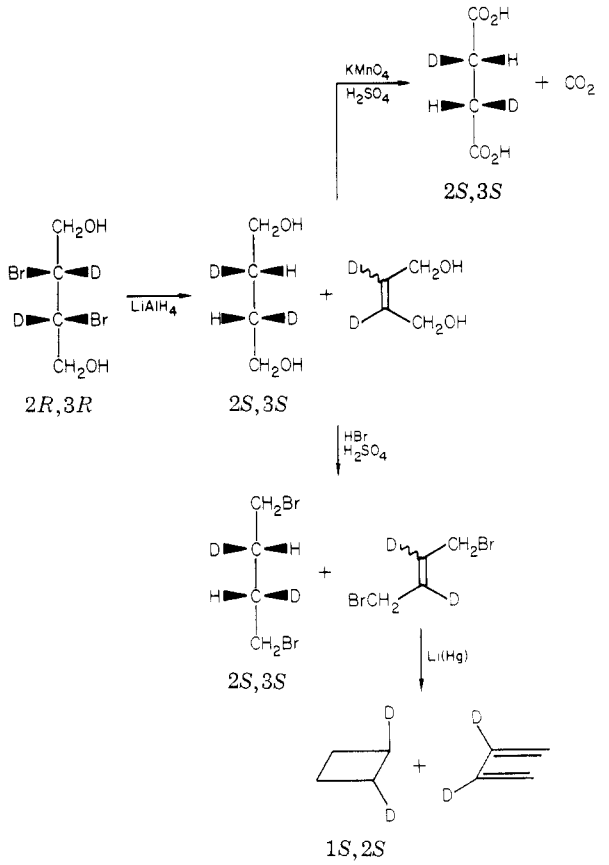
(1) For review, see: Agrigoni, D.; Eliel, E. L. *Top. Stereochem.* **1969**, *4*, 127. Sprecher, M.; Clark, M. J.; Sprinson, D. B. *J. Biol. Chem.* **1966**, *241*, 872. England, S.; Hanson, K. R. *Methods Enzymol.* **1969**, *13*, 567. Cornforth, J. W.; Rybock, G. *Biochem. Biophys. Res. Commun.* **1967**, *27*, 517. Sprecher, M.; Switzer, R. L.; Sprinson *J. Biol. Chem.* **1966**, *241*, 864.
(2) Portsmouth, D.; Stoolmiller, A. C.; Abeles, R. H. *J. Biol. Chem.* **1967**, *242*, 2751.
(3) Tchen, T. T.; Van Milligan, H. *J. Am. Chem. Soc.* **1960**, *82*, 4115. Corey, E. J.; Pasto, D. J.; Mock, W. L. *Ibid.* **1961**, *83*, 2957. Corey, E. J.; Mock, W. L. *Ibid.* **1962**, *84*, 685. Hunig S.; Muller, H. R.; Thiev. W. *Angew Chem., Int. Ed.,Engl.* **1965**, *4*, 271. Childs, C. R.; Block, K. *J. Org. Chem.* **1961**, *26*, 1630.
(4) Feit, P. W. *Ber.* **1960**, *93*, 116.
(5) Chickos, J. S. *J. Org. Chem.* **1979**, *44*, 780.
(6) Vogel, A. "Practical Organic Chemistry", 3rd ed.; Wiley: New York, 1958; p 280.

0022-3263/81/1946-3559$01.25/0

Scheme I



Scheme II



to be twice that of the (+)-monodeuteriosuccinic acid also gives very good agreement.

Control experiments on the reduction of *dl*-2,3-dibromobutane-1,4-diol indicated that some 2-butene-1,4-diol (20%) was also formed in the reaction. In sulfuric acid–potassium permanganate solution, this olefin was presumed oxidized to CO_2. In sulfuric acid–hydrobromic acid, this material could either be converted to 1,4-dibromo-2-butene and subsequently to butadiene upon treatment with lithium amalgam or completely destroyed, depending on the sequence and amounts of sulfuric and hydrobromic acids used. The ratio of substitution to elimination for reaction of the chiral deuterated dibromides was estimated as approximately 4/1 from the area ratio of cyclobutane to butadiene obtained by gas chromatography. The stereochemistry of 1,4-dibromo-2-butene was not determined since control experiments indicated that isomerization of the olefin in strong acid can occur. Previously, trans elimination of bromine has been observed in the reaction of *meso*-1,2-diphenyl-1,2-dibromoethane[7] with lithium aluminum hydride.

During the early stages of our study of the LAH reduction of 2,3-dibromobutane-1,4-diol and conversion to the dibromide, we obtained a higher boiling liquid in addition to the expected dibromobutane. This material was identified as 1,2,4-tribromobutane by comparison with an authentic sample. The rotation of 1,2,4-tribromo-2,3-dideuteriobutane ($[\alpha]^{20}_D$ −9.7°) clearly indicated that this material resulted from incomplete reduction of the starting material. The weakening of the reducing power of LAH in the presence of Lewis acids, particularly with regards to halogens, is well-known.[8] Increasing the LAH ratio from 1.6/1 to 2.5/1, however, completely eliminated the tribromide as a product.

Experimental Section

***cis*-2,3-Dideuteriobutene-1,4-diol.** 2-Butyne-1,4-diol (107 g), pyridine (300 mL), and the Lindlar catalyst[9] (4.2 g) were stirred in an atmosphere of D_2 gas generated from the electrolysis of deuterium oxide.[10] Stirring was continued until the uptake was complete (approximately 1 week). Warming the reaction flask increased the uptake to some extent. Preparation of the catalyst by other procedures[11] did not appear to influence the rate of reaction significantly. After the uptake of deuterium was reduced significantly, the reaction mixture was filtered, the pyridine removed on a rotatory evaporator, and the residue distilled under vacuum. *cis*-2,3-Dideuteriobutene-1,4-diol distilled as a colorless liquid: bp 87–91 °C (40 μm); yield 70 g; NMR (acetone-d_6) δ 4.12 (br s).

***dl*-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol.** *cis*-2,3-Dideuteriobutene-1,4-diol (140 g) was dissolved in 10% hydrobromic acid (250 mL) kept between 0 and 5 °C. Bromine was added dropwise until the brown color was no longer discharged. If crystallization had not spontaneously occurred, seeding with a small crystal of unlabeled dibromide was sufficient to achieve crystallization. The cold solution was filtered, washed with cold water, and allowed to air dry. *dl*-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol (155 g, 40%) was isolated as a solid, mp 88–90

(7) Trevoy, L. W.; Brown, W. C. *J. Am. Chem. Soc.* **1949**, *71*, 1675.
(8) Eliel, E. L. *Rec. Chem. Prog.* **1961**, *22*, 129.
(9) Lindlar, H. *Helv. Chim. Acta.* **1952**, *35*, 446.
(10) The deuterium was collected over mineral oil and passed through a liquid nitrogen trap before use.
(11) Baumgarten, H., Ed. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. 5, p 880.

°C (lit.[4] mp 90 °C). The air-dried material was used without further purification.

***dl*-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol 1,4-Dihemisuccinate.** *dl*-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol (140 g) and succinic anhydride (119 g) were stirred in pyridine (120 mL). A mildly exothermic reaction ensued, and the succinic anhydride slowly dissolved. The reaction was stirred overnight. Hydrolysis was achieved by pouring the mixture into cold 2.5 N HCl until the solution was acidic to litmus. A viscous oil separated immediately which upon vigorous stirring first appeared to harden and then finally crystallize over a period of 1 h. This precipitate was vigorously stirred in cold water to remove traces of pyridinium hydrocholoride (pyridinium hydrochloride caused the precipitation of yohimbine hydrochloride in the resolution step). The precipitate (233 g, 92%) was filtered and allowed to air dry; mp 96–98 °C (lit.[4] mp 96–98 °C).

Resolution of (+)-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol. Yohimbine (30 g) and *dl*-2,3-dibromo-2,3-dideuteriobutane-1,4-diol 1,4-dihemisuccinate (75 g) were dissolved in hot absolute alcohol (200 mL) and filtered. When the mixture was allowed to stand, a material slowly crystallized. The solid was washed with alcohol. On occasion additional solid precipitated when the mixture was allowed to stand. The combined solids (52 g) were slurried in 95% ethanol (300 mL), and sufficient hydrochloric acid in ethanol (prepared by saturating ethanol with hydrogen chloride gas) was added until the solution was strongly acidic to litmus. The slurry was refluxed for 3 h, cooled, and filtered. The recovered yohimbine hydrochloride was washed with ethanol and recycled by being stirred with strong aqueous base. The alcoholic solution was concentrated on a rotatory evaporator and then vacuum distilled to remove the diethyl succinate. Distillation was continued until the pot temperature reached 90 °C and no further diethyl succinate distilled over. After the residue was cooled, chloroform was added, and crystallization ensued. The solid was filtered and continuously extracted in a Soxhlet extractor with chloroform. The (+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol crystallized in the pot of the Soxhlet and was recovered by filtration. Recrystallization from ethyl acetate (twice) afforded (+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol: 6.7 g; mp 112–114 °C; $[\alpha]^{20}_D$ +39.4° (*c* 2.9 g/100 mL, methanol); on the basis of Feit's rotation of the unlabeled dibromobutanediol, the optical purity is estimated as 98.5%; NMR (acetone-d_6 δ 3.77 (d, 2 H), 4.1 (t, 1 H).

(2*S*,3*S*)-(−)-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol. The mother liquor recovered after isolation of the monoyohimbine diasteriomer of (+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol was heated, and additional yohimbine (60 g) was added. When the mixture was allowed to stand, a solid precipitated which was filtered. (−)-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol (8.4 g; mp 90–111 °C $[\alpha]^{20}_D$ −26.5° (*c* 3.56 g/100 mL, methanol)) was isolated as described above. The optical purity was estimated at 66%.

(2*S*,3*S*)-(+)-Dideuteriosuccinic Acid. (+)-2,3-Dibromo-2,3-dideuteriobutane-1,4-diol (17.6 g, $[\alpha]_D$ +39.4°) in tetrahydrofuran (150 mL) was added dropwise to lithium aluminum hydride (4 g) in tetrahydrofuran (50 mL) over a period of 1 h. The mixture was refluxed for 3 h, hydrolyzed with water (4 mL), 15% NaOH (4 mL), and water (12 mL), and then stirred overnight. The reaction mixture was filtered and evaporated. The last traces of tetrahydrofuran (which would interfere with the conversion to dibromobutane-d_2[6]) were removed by adding acetone, slurring, and evaporation on a vacuum line. A portion of the residue (1 g/9.5 g) was dissolved in 2 M H_2SO_4 and oxidized by adding solid potassium permanganate until the dark solution retained a violet color when spotted on filter paper. The ensuing reaction was exothermic, and gas evolution was observed. Sodium bisulfite was added next until all the precipitated MnO_2 dissolved, and the solution was repeatedly extracted with ether. Evaporation of the ether afforded (+)-dideuteriosuccinic acid: 207 mg (24%); mp 183–184 °C (recrystallized from ethyl acetate). The yield was not optimized. (2*R*,3*R*)-(−)-Dideuteriosuccinic acid was prepared in an analogous manner. A sample of (−)-2,3-dideuteriosuccinic acid (28 mg) was refluxed with excess acetic anhydride. Evaporation of the acetic anhydride followed by sublimation of the residue afforded (2*R*,3*R*)-dideuteriosuccinic anhydride, mp 118–119 °C. Mass analysis of the parent ion of the anhydride (*m*/*e* 102), when compared to the parent ion of the unlabeled anhydride (*m*/*e* 100), indicated 84.6% d_2 14% d_1, and 1% d_0. The relative amounts of d_1 and d_0 species are most likely attributed to the composition of the deuterium as generated by the electrolysis of D_2O.

(2*S*,3*S*)-1,4-Dibromo-2,3-dideuteriobutane. The residue from lithium aluminum hydride reduction of (+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol (8.5 g) was dissolved in a cold concentrated sulfuric (50 mL–hydrobromic acid (48%, 75 mL) mixture,[6] allowed to stand overnight, and then refluxed on a steam bath for 5 h. Addition of pentane followed by washing the organic layer with K_2CO_3 solution, evaporation, and vacuum distillation gave (2*S*,3*S*)-1,4-dibromo-2,3-dideuteriobutane and 1,4-dibromo-2,3-dideuteriobutene as a mixture [bp 60–65 °C (4mm); 5.9 g; 4/1 mixture] along with a higher boiling liquid: bp 60–65 °C (50 μm); 3.6 g. The higher boiling liquid was identified as 1,2,4-tribromo-2,3-dideuteriobutane by comparison with a sample of 1,3,4-tribromobutane (see below). A freshly distilled sample of 1,2,4-tribromo-2,3-dideuteriobutane exhibited a rotation of $[\alpha]^{20}_D$ −7.6° (*c* 0.24 g/mL, cyclohexane). Gas chromatography indicated the sample to be a mixture of (2*S*,3*S*)-1,4-dibromo-2,3-dideuteriobutane (22%) and 1,2,4-tribromo-2,3-dideuteriobutane (78%). Assuming the rotation of the former to be small and correcting the observed rotation gives $[\alpha]^{20}_D$ −9.7° for the latter.

(2*R*,3*R*)-1,4-Dibromo-2,3-dideuteriobutane was prepared in an analogous manner from lithium aluminum hydride reduction of (−)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol. Similar products were obtained.

(1*R*,2*R*)-Dideuteriocyclobutane. Cyclization of (2*S*,3*S*)-1,4-dibromo-2,3-dideuteriobutane isolated above as a mixture (5.9 g) with lithium amalgam in dioxane as previously reported[5,12] afforded a mixture of *trans*-1,2-dideuteriocyclobutane, butadiene-2,3-d_2, and some butane-2,3-d_2. The butadiene and butane were identified by comparison with authentic samples of unlabeled materials. Preparative gas chromatography on a squalene column at room temperature afforded pure *trans*-1,2-dideuteriocyclobutane: 0.6 g (16% from 2,3-dibromo-2,3-dideuteriobutane-1,4-diol); $[\alpha]^{20}_D$ −0.015 ± −0.011° (neat liquid). No absorption was observed at 565 cm^{-1} in the infrared spectrum, which is characteristic of the cis isomer.[5]

(1*S*,2*S*)-Dideuteriocyclobutane was prepared in an analogous manner from (2*R*,3*R*)-1,4-dibromo-2,3-dideuteriobutane.

1,3,4-Tribromobutane. Bromine was added to 3-buten-1-ol (1 g) in carbon tetrachloride (75 mL) at 0 °C until the color was no longer discharged. The solvent was distilled and the residue treated with a mixture of cold concentrated sulfuric acid–48% hydrobromic acid as before.[6] 1,3,4-Tribromobutane, was isolated: bp 60–63 °C (50 μm); 1.44 g η^{25}_D 1.5676 (lit.[13] η^{25}_D 1.6583, 1.5588); NMR ($CHCl_3$, $CDCl_3$) δ 4.4 (m, 0.95 H), 3.6 (m, 4 H), 2.43 (m 2 H). This material exhibited the same retention time on both Carbowax and didecylphthalate columns as did the 1,3,4-tribromo-2,3-dideuteriobutane isolated above. The NMR spectrum of 1,3,4-tribromo-2,3-dideuteriobutane also showed complex patterns at δ 3.6 and 2.4. The absorption at δ 4.4 was not observed.

***cis*- and *trans*-1,4-Dibromo-2-butenes.** A mixture of *cis*- and *trans*-1,4-dibromo-2-butenes could be prepared from commerically available *cis*-2-butene-1,4-diol (which contained some trans isomer) as previously described. The ratio of *cis*- to *trans*-dibromide isolated varied, depending on the ratio of acid to alcohol used. Refluxing on a steam bath for 3 h prior to workup did not appear to greatly affect the conversion to the unsaturated dibromide nor the cis/trans ratio. The *trans*-dibromide was isolated as a solid which crystallized from the mixture: mp 50–53 °C (lit[14] mp 53 °C); tetrabromide, mp 115–116 °C (lit.[14] mp 116 °C). The NMR spectra of both cis and trans isomers were very similar: NMR for *trans*-1,4-dibromo-2-butene ($CDCl_3$, Me_4Si) δ 3.91 (m, 2 H) 5.93 (m, 1 H).

Addition of concentrated sulfuric acid (50 mL) to a mixture of butene-1,4-diol (2.1 g) and butane-1,4-diol in an ice bath followed in turn by addition of this mixture to a cold concentrated sulfuric acid–48% hydrobromic acid mixture and reaction as before[6] afforded only 1,4-dibromobutane (2.2 g). No 1,4-di-

(12) Connor, D. S.; Wilson, E. R. *Tetrahedron Lett.* **1967**, 4925.
(13) Buchman, E. R.; Conly, J. C. *J. Am. Chem. Soc.* **1953**, *75*, 1990.
(14) Mislow, K. *J. Am. Chem. Soc.* **1953**, *75*, 2512.

bromo-2-butene could be detected in the NMR of the distillate.

Treatment of *trans*-1,4-dibromo-2-butene with lithium amalgam afforded butadiene.

Acknowledgment. We thank the Chemistry Department of Washington University for allowing us the use of their JASCO Model J20 spectropolarimeter and the NSF and the University of Missouri-St. Louis for financial support.

Registry No. 2-Butyne-1,4-diol, 110-65-6; *cis*-2,3-dideuteriobutane-1,4-diol, 56543-04-5; *dl*-2,3-dibromo-2,3-dideuteriobutane-1,4-diol, 78019-68-8; *dl*-2,3-dibromo-2,3-dideuteriobutane-1,4-diol 1,4-dihemisuccinate, 78019-69-9; (2*R*,3*R*)-(+)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol, 78087-06-6; (2*S*,3*S*)-(−)-2,3-dibromo-2,3-dideuteriobutane-1,4-diol, 78087-07-7; (2*S*,3*S*)-(+)-dideuteriosuccinic acid, 78087-08-8; (2*R*,3*R*)-(−)-dideuteriosuccinic acid, 78087-09-9; (2*R*,3*R*)-dideuteriosuccinic anhydride, 78019-70-2; (2*S*,3*S*)-1,4-dibromo-2,3-dideuteriobutane, 78087-10-2; 1,2,4-tribromo-2,3-dideuteriobutane, 78019-71-3; (2*R*,3*R*)-1,4-dibromo-2,3-dideuteriobutane, 78087-11-3; butadiene-2,3-d_2, 1983-06-8; butane-2,3-d_2, 78019-72-4; (1*R*,2*R*)-1,2-dideuteriocyclobutane, 78087-12-4; (1*S*,2*S*)-dideuteriocyclobutane, 78087-13-5; 3-buten-1-ol, 627-27-0; 1,3,4-tribromobutane, 38300-67-3; *cis*-1,4-dibromo-2-butene, 18866-73-4; *trans*-1,4-dibromo-2-butene, 821-06-7; *cis*-2-butene-1,4-diol, 6117-80-2; *trans*-2-butene-1,4-diol, 821-11-4; butane-1,4-diol, 110-63-4; 1,4-dibromobutane, 110-52-1; 1,3-butadiene, 106-99-0; (*R*)-(−)-deuteriosuccinic acid, 3038-36-6; (*S*)-(+)-deuteriosuccinic acid, 10013-03-3.

New Synthesis of Azetidine

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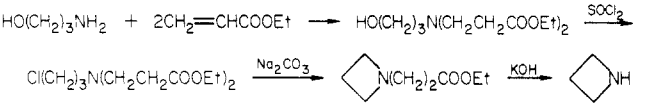
Unlike its smaller and larger homologues, azetidine is available commerically only in small quantities and is expensive.[1]

Although we were able to repeat the literature procedure[2] (Scheme I) and the reduction of tosylazetidine[3a] (Scheme II) on the scale described in the literature, we were unable to scale up either preparation significantly.

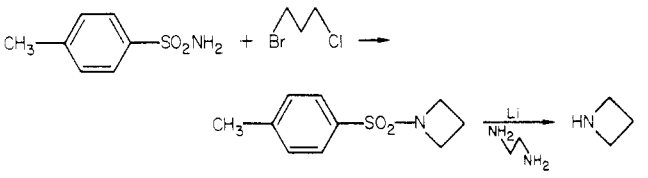
We report here a new synthesis which is convenient for the preparation of moderate quantities of azetidine. The procedure is shown in Scheme III.[4]

Reaction of acrolein with sodium azide in acetic acid[5] gave β-azidopropionaldehyde (1), which was reduced with sodium borohydride to 3-azidopropanol (2).[6] The very facile Staudinger reaction[7a] of 2 with triphenylphosphine in ether afforded the intermediate crystalline alcohol **3a** which on heating gave azetidine in 33% yield. The resulting azetidine contained some benzene, presumably as a result of a process involving a hydride (or proton) transfer

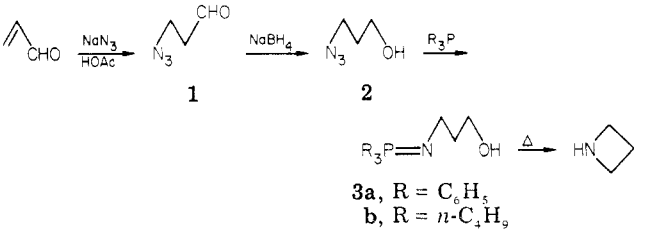
Scheme I. Azetidine Synthesis by the Literature Procedure[2]



Scheme II. Azetidine Synthesis by the Reduction of Tosylazetidine[3]

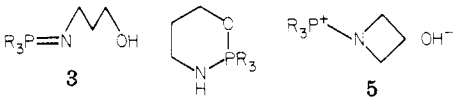


Scheme III



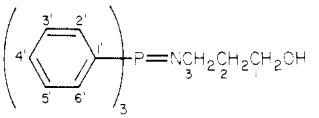
3a, R = C_6H_5
b, R = n-C_4H_9

Chart I



4a, R = C_6H_5
b, R = n-C_4H_9

Table I. NMR Data for 3a



^{1}H data		^{13}C data		
atom	shift, δ	atom	shift, δ	coupling const, Hz
H_1	3.94	C_1	65.42	J_{PNCCC} = 0
H_2	1.80	C_2	33.76	J_{PNCC} = 18.3
H_3	3.35	C_3	45.64	J_{PNC} = 6.1
$H_{2',6'}$	7.70	$C_{1'}$	132.80	J_{PC} = 6
$H_{3',4',5'}$	7.50	$C_{2',6'}$	132.20	J_{PCC} = 9.0
		$C_{3',5'}$	128.27	J_{PCCC} = 11.6
		$C_{4'}$	131.21	J_{PCCCC} = 2.7

Table II. NMR Data for 3b

$(CH_3CH_2CH_2CH_2)_3P{=}NCH_2CH_2CH_2OH$
4′ 3′ 2′ 1′ 3 2 1

^{1}H data		^{13}C data		
atom	shift, δ	atom	shift, δ	coupling const, Hz
H_1	3.84	C_1	67.70	J_{PNCCC} = 0
H_2	1.80	C_2	34.21	J_{PNCC} = 14.3
H_3	3.24	C_3	44.97	J_{PNC} = 3.0
$H_{1'}$	1.60	$C_{1'}$	27.85	J_{PC} = 65
$H_{2'}$	1.50	$C_{2'}$	24.22	J_{PCC} = 17.2
$H_{3'}$	1.40	$C_{3'}$	23.97	J_{PCCC} = 3.5
$H_{4'}$	0.96	$C_{4'}$	13.61	J_{PCCCC} ≈ 0

(1) See the Kodak Laboratory Chemicals catalog and the Tridom-Fluka catalog.
(2) Wadsworth, D. H. *Org. Synth.* **1973**, *53*, 13.
(3) (a) Gallegos, E. J.; Kiser, R. W. *J. Phys. Chem.* **1962**, *66*, 136. (b) For a review of this methodology see: Moore, J. A. In "Heterocyclic compounds with Three or Four-Membered Rings"; Weisberger, A., Ed.; Interscience: New York, **1964**; Chapter VII, p 898, trimethyleneimine. (c) Cf. also: White, J.; McGillivray, G. *J. Org. Chem.* **1974**, *39*, 1973.
(4) This process is similar to that reported for the synthesis of 2-phenylaziridine by: Blum, J.; et al. *J. Org. Chem.* **1978**, *43*, 4271.
(5) Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5248.
(6) Hassner, A.; Galle, J. E. *J. Org. Chem.* **1976**, *47*, 2273.
(7) (a) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437-472. (b) Another structural possibility is a pentacoordinate phosphorane $R_3P(OH)NCH_2CH_2CH_2$. Note the ionic structure proposed for the product of the reaction of 3-azidopropyl iodide with Ph_3P by Hassner and Galle;[6] in this case also a pentacoordinate phosphorane may be a possibility.

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