(−) 1, in agreement with experiment. In this model the steric interactions with substituents on the C-1 of the olefin are similar to those in Brown's rectangular model and the old predictions for internal *cis* alkenes are preserved. Morrison[23] has pointed out that the present model is also more successful than Brown's original model in accounting for the asymmetric reduction of ketones by hydroboration.

Experimental Section

1-Butyne-1-*d*.—A solution of 61 g (1.1 moles) of 1-butyne (Matheson Co., 95% pure) in 50 ml of diglyme at Dry Ice temperature was added to the cold Grignard reagent prepared from 48.6 g (2.0 g-atoms) of magnesium and 218 g (2.0 moles) of ethyl bromide in 800 ml of diglyme. After stirring overnight the mixture was cooled to 0° and quenched with 40 g of deuterium oxide. The butyne-1-*d* (41 g, 0.75 mole, 68% yield) was distilled directly from the reaction vessel into a Dry Ice trap. The product had an acetylenic C–D band at 2600 cm^{-1} in the infrared and showed the absence of the corresponding C–H. A concentrated solution in CCl_4 showed a weak band at 1970 cm^{-1} assigned to triple-bond stretching.

***cis*-1-Butene-1-*d*.**—A solution of 156 g (1.1 moles) of boron fluoride etherate in 25 ml of diglyme was added to a well-stirred mixture of 28.4 g (0.75 mole) of sodium borohydride and 140 g (2.0 moles) of 2-methyl-2-butene (Matheson Coleman and Bell Co.) in 500 ml of freshly distilled (from sodium) diglyme maintained at 0°. After 4 hr at 0° the temperature was lowered to −15° and a solution of 41 g (0.75 mole) of 1-butyne-1-*d* in 40 ml of diglyme at Dry Ice temperature was added in several portions. The mixture was stirred overnight and excess hydride was decomposed with ethylene glycol. The organoborane was decomposed with 240 ml of glacial acetic acid and the resulting 1-butene-1-*d* (28 g, 0.49 mole, 65% yield) was distilled directly into a Dry Ice trap. The infrared spectrum showed double-bond absorption at 1615 and vinyl C–D at 2250 cm^{-1}. The nmr spectrum gave $J = 10.4$ cps for the vinyl protons characteristic of *cis*-vinylic hydrogens.

1-Butanol-1-*d*.—To a solution of 28.4 g (0.75 mole) of sodium borohydride in 1 l. of diglyme was added 272 g (2.0 moles) of α-pinene (99.8% pure by gc, $[\alpha]^{22}\text{D}$ +41.1°, 80% optically pure)[24] followed, at 0°, by 155.8 g (1.1 moles) of boron fluoride etherate. After 4 hr at 0° the reaction mixture was cooled to −15° and 28 g (0.49 mole) of *cis*-1-butene-1-*d* was added. After standing overnight excess hydride was decomposed with ethylene glycol and the organoborane was oxidized at 30–50° with 330 ml of 3 *N* NaOH and 330 ml of 30% hydrogen peroxide. The mixture was extracted with ether. Distillation of the extract gave 27 g (0.34 mole, 70% yield) of **1**, most of which was converted to the hydrogen phthalate[25] and recrystallized five times from cyclohexane–benzene: mp 74.0–75.0°, $[\alpha]^{22}\text{D}$ 0.437 ± 0.009° (*c* 24.0, acetone), pure by gc on a silicone oil column.

Cleavage of the ester with lithium aluminum hydride gave pure (gc) 1-butanol-1-*d*, having 1.0 deuterium by nmr and $[\alpha]^{21}\text{D}$ −0.210 ± 0.006° (neat).

Registry No.—**1**, 10060-19-2; 1-butyne-1-*d*, 10036-58-5; *cis*-1-butene-1-*d*, 10036-59-6.

[23] J. D. Morrison, *Surv. Prog. Chem.*, **3**, 170 (1966), and personal communication.

[24] F. H. Thurber and R. C. Thielke [*J. Am. Chem. Soc.*, **53**, 1030 (1931)] report $[\alpha]\text{D}$ +51.1° for α-pinene purified *via* the nitrosochloride.

[25] A. Streitwieser, Jr., *ibid.*, **77**, 1117 (1955).

Stereochemistry of the Primary Carbon. XVII. Absolute Configuration of 1-Butanol-1-*d*[1]

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Received October 6, 1966

(*S*)-(+)-1-Butanol-1-*d* was converted by reactions of known stereochemistry to (*R*)-(−)-1-bromopentane-2-*d* which was also related to (*S*)-(−)-pentane-2-*d* *via* asymmetric hydroboration reactions on 1-pentene-2-*d*. The configurations previously assigned to the deuterio alcohols on the basis of mechanisms are confirmed by these interconversions.

1-Butanol-1-*d* is significant among primary alcohols whose optical activity results from hydrogen–deuterium asymmetry. It was the first such alcohol shown to have measurable optical activity[3] and its configuration has been related to those of benzyl-α-*d* alcohol and a number of derivatives.[4] The absolute configurations of these compounds, however, rests entirely on an *assumed* mechanism for the asymmetric reduction by which the alcohols are synthesized[4] and on Brewster's *empirical* rules for relating structure and stereochemistry.[5] In the present paper 1-butanol-1-*d* is configurationally related to pentane-2-*d*. The existing assignments are confirmed.

The reaction sequence used is summarized in Chart I in which all rotations are given as specific rotations relative to the value, $[\alpha]\text{D}$ 0.47°, obtained for 1-butanol-1-*d* prepared by enzymatic reduction by Mosher, *et al.*[6] Assuming that this value represents optical purity, all of the numbers in Scheme I correspond to optically pure compounds of the indicated configuration.

The 1-butanol-1-*d* was converted to the *p*-nitrobenzenesulfonate ester and allowed to react with sodiomalonic ester. The formation of the butylmalonic ester undoubtedly occurs with complete inversion of configuration as shown. This ester had no observable rotation but hydrolysis gave caproic-β-*d* acid that was optically active. The Cristol–Firth modification[7] of the Hunsdiecker reaction gave the corresponding 1-bromopentane-2-*d*. Reduction of this halide to the hydrocarbon with lithium aluminum hydride did not give consistent results; so the amyl bromide was synthesized by an alternant route. Methyl valerate was treated with sodium methoxide in methanol-*d* to ex-

[1] (a) This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. (b) Paper XVI: A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

[2] U. S. Public Health Service Postdoctoral Research Fellow, 1963–1964.

[3] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **75**, 5014 (1953).

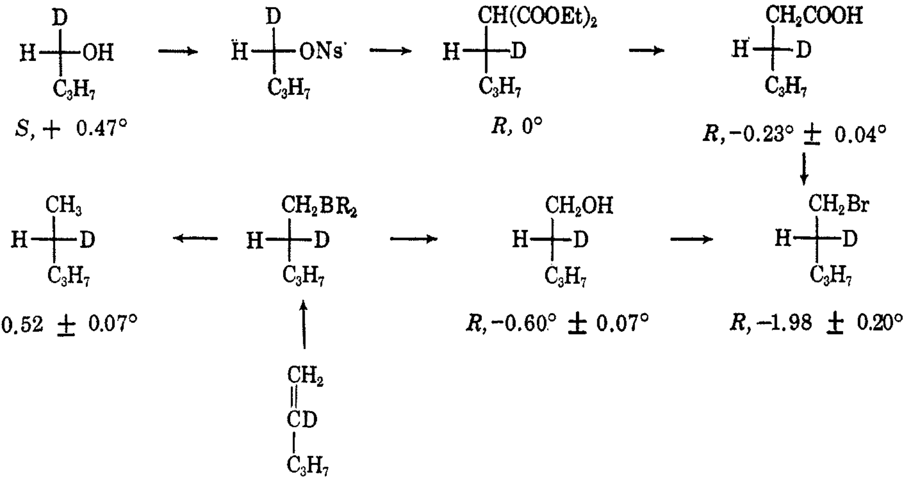
[4] A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

[5] J. H. Brewster, *Tetrahedron Letters*, No. 20, 23 (1959).

[6] V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Am. Chem. Soc.*, **88**, 3595 (1966).

[7] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

SCHEME I^a



^{a} Rotations are $[\alpha]\text{D}$ corrected to optical purity.

change the α hydrogens. Reduction with lithium aluminum hydride gave 1-pentanol-2-d_2, which was converted to the acetate and pyrolyzed to give 1-pentene-2-*d*.

The olefin was used with Brown's[8] asymmetric hydroboration reaction using diisopinocampheylborane to give the corresponding amylborane which in one experiment was protonolyzed with acetic acid to give pentane-2-*d* and in another was oxidized with hydrogen peroxide to give 1-pentanol-2-*d*. The stereochemistry is set during the reduction; hence, the (−)-pentane-2-*d* and (−)-1-pentanol-2-*d* produced are configurationally related by this sequence of reactions. The alcohol was converted to 1-bromopentane-2-*d* with phosphorus tribromide.

From the optical rotations obtained and estimates of the probable errors, optically pure pentane-2-*d* is deduced to have $[\alpha]\text{D}$ $-0.52 \pm 0.07°$. Our earlier preparation from (R)-(−)-2-pentanol by reduction of the methanesulfonate with lithium aluminum deuteride[9] gave a value of $[\alpha]\text{D}$ $-0.42 \pm 0.03°$ and showed that (−) hydrocarbon has the *S* configuration as shown; thus, (+)-1-butanol-1-*d* has the *S* configuration. The configurations are also summarized in Scheme I. These rotations for pentane-2-*d* are consistent, since 20% racemization is expected during the sulfonate reduction.[10] This comparison provides evidence that the enzymatically prepared 1-butanol-1-*d*[6] is indeed optically pure.

The hydroboration reaction with diisopinocampheylborane of *cis*-1-butene-1-*d* gave 1-butanol-1-*d* with 56% asymmetry at C-1;[1b] the accepted mechanism of this reaction carries the corollary that exactly the same degree of asymmetric induction should occur at C-2. The pentane-2-*d* obtained from 1-pentene-2-*d* in this reaction had $[\alpha]^{21}\text{D}$ $-0.19°$. The α-pinene used was 75.8% optically pure; correction for optically pure α-pinene gives $[\alpha]\text{D}$ for pentane-2-*d* of $-0.25°$. From the rotation of pentane-2-*d* of $[\alpha]\text{D}$ $0.52 \pm 0.07°$ deduced for optical purity, the hydroboration reaction is $48 \pm 7\%$ stereospecific. This degree of asymmetric induction for 1-pentene is comparable with the 56% found for 1-butene and is evidence for internal consistency of the results. This result was confirmed by reduction of 1-pentene with diisopinocampheyldeuterioborane which gave pentane-2-*d* (corrected to optically pure α-pinene) having $[\alpha]\text{D}$ $+0.25°$. This rotation has the same magnitude but opposite sign from the preparation above, as expected.

We conclude that the configurations assigned previously[4] to 1-butanol-1-*d* and to other compounds configurationally related to it (*e.g.*, benzyl-α-*d* alcohol, 1-phenylbutane-1-*d*, *etc.*) are correct but that the magnitudes of the rotations for optical purity must be increased by a factor of 2.5 to accord with the preparation by Mosher, *et al.*,[6] of optically pure 1-butanol-1-*d*.

Experimental Section

Optical rotations at the sodium D line were taken with a Rudolph precision polarimeter. Many individual readings were taken and rotations were frequently measured in more than one tube and with more than one observer. The mercury line rotations cited were taken with a Bendix photoelectric polarimeter and the italicized D line rotations were extrapolated by assuming proportionality to the reciprocal squares of the wavelengths. The deuterated compounds were characterized by nmr and infrared spectra and their purity was monitored by glpc.

Hexanoic-3-*d* Acid.—Butanol-1-*d* was prepared by reduction of butyraldehyde with deuterated isoborneol prepared by reduction of camphor with lithium aluminum deuteride[11] and had $\alpha^{24}\text{D}$ $+0.097 \pm 0.013°$ (l 1), 75 atom % D (nmr). To a mixture of 27 g of *p*-nitrobenzenesulfonyl chloride in methylene chloride maintained below 0° was added 8.2 g of this alcohol and 30 ml of pyridine. After 3 hr the mixture was poured into ice water and the washed and dried organic layer was evaporated. The resulting oil was crystallized twice from benzene–hexane yielding 15.2 g (50%) of light lemon crystals of the *p*-nitrobenzenesulfonate, mp 61–62°.

The reaction with sodiomalonate was carried out similar to Lawesson and Busch.[12] To a cooled mixture of 2.4 g of sodium hydride (Metal Hydrides, Inc., 54% dispersion in oil) in 50 ml of dry tetrahyrofuran maintained under an argon atmosphere was added 9.0 g of redistilled diethyl malonate. After hydrogen evolution ceased, 15 g of the above butyl-1-*d* *p*-nitrobenzenesulfonate was added and the mixture was stirred for 7 hr. Water was added and the mixture was extracted with ether. The washed and dried extract was distilled giving 8.0 g (67%) of diethyl (butyl-1-*d*)malonate, bp 91–93° (2 mm), which was shown to be pure by glpc. This ester had no observable rotation.

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(8) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

(9) Paper XV: A. Streitwieser, Jr., and M. R. Granger, *J. Org. Chem.*, **32**, 1528 (1967).

(10) G. K. Helmkamp and B. F. Rickborn, *ibid.*, **22**, 479 (1957).

(11) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957).

(12) S. O. Lawesson and T. Busch, *Acta Chem. Scand.*, **13**, 1717 (1959).

The hydrolysis procedure was adapted from Vliet, Marvel, and Hsueh.[13] A mixture of 7.5 g of the above ester and 7.5 g of potassium hydroxide in 10 ml of water was refluxed gently for 2 hr. An additional 10 ml of water was added and ethanol was distilled. The mixture was then refluxed with aqueous sulfuric acid and extracted with ether. The washed and dried extract was distilled, benzene was added and distilled off, and the residue was distilled through a small column yielding 2.4 g (60%) of caproic-β-*d* acid, bp 97–98° (6–7 mm), α^{28}D $-0.055 \pm 0.009°$ (*l* 1).

Butanol-1-*d* having αD $+0.076 \pm 0.005°$ (*l* 2, 25 atom % D) was carried through this same sequence to prepare caproic-β-*d* acid, αD $-0.030 \pm 0.002°$ (*l* 1).[14]

1-Bromopentane-2-*d*.—The procedure was adapted from Cristol and Firth.[7] A slurry of 6.1 g of red mercuric oxide and 4.2 g of the caproic-β-*d* acid, αD $-0.041 \pm 0.008°$ (*l* 1), in 50 ml of dry carbon tetrachloride was protected from light and refluxed with 2 ml of bromine in 10 ml of carbon tetrachloride for 1 hr. The mixture was poured into dilute sodium hydroxide and filtered through a Super Cel mat. The washed and dried organic layer was distilled through a small column giving crude 1-bromopentane-2-*d* which was purified on a glpc column yielding 2.6 g (47%), α^{22}D $-0.452 \pm 0.007°$ (*l* 1).

In the preliminary experiments,[14] caproic-β-*d* acid, αD $-0.030°$, (*l* 1) gave 1-bromopentane-2-*d* having αD $-0.359 \pm 0.003°$ (*l* 1).

1-Pentene-2-*d*.—Methyl valerate (79 g, 0.68 mole) was refluxed overnight with 100 g (3.3 moles) of methanol-*d*,[15] in which 0.4 g of sodium had been dissolved. The mixture was diluted with dilute hydrochloric acid and ice and extracted with ether. Distillation of the washed and dried extract gave an 85% recovery of the ester. The treatment was repeated until the nmr spectrum showed the absence of α protons. The methyl valerate-α-d_2 was reduced with lithium aluminum hydride in ether in the usual way to give 1-pentanol-2-d_2; this alcohol was treated with equivalent amounts of acetyl chloride and pyridine to give 1-pentyl-2-d_2 acetate, bp 146–147°. This ester was pyrolyzed by dropping through a Vicor tube packed with glass helices and heated to 550°. From 10 g of ester there was obtained 3 g of recovered ester and 3 g of 1-pentene-2-*d* whose nmr spectrum showed one deuterium atom.

Pentane-2-*d* from 1-Pentene-2-*d*.—To a mixture of 47.7 g (0.35 mole) of α-pinene ([α]D $+38.75°$, 75.8% optically pure) and 4.97 g (0.131 mole) of sodium borohydride in 225 ml of freshly distilled diglyme maintained at 0° was added 48.8 ml (0.175 mole) of boron fluoride diglymate. After several hours at 0°, 7 g of 1-pentene-2-*d* in diglyme was added. The mixture was maintained at 0° for 2 hr and stirred at room temperature for 8 hr. After decomposition of excess hydride with ethylene glycol, 45 ml of glacial acetic acid was added and the mixture was stirred for 2 hr. Distillation gave pentane-2-*d* which was purified by bulb-to-bulb distillation; gc showed the absence of pinene but the infrared showed the presence of a small amount of acetic acid. Measurement of rotation gave α^{21}D $-0.12 \pm 0.01°$ (*l* 1), $[\alpha]^{21}$D $-0.19°$.

1-Pentanol-2-*d*.—The preceding hydroboration preparation was followed except that decomposition of the organoborane was accomplished with 50 ml of 30% hydrogen peroxide. Extraction with ether and distillation gave 1-pentanol-2-*d* whose gc showed contamination by pinene and other impurities. Purification by chromatography on silica gel and gc (Carbowax) gave 0.9 g of product having a C–D band at 2120 cm^{-1} and α_{546} $-0.205°$, α_{578} $-0.190°$ (*l* 1) ([α]D $-0.22 \pm 0.01°$).

1-Bromopentane-2-*d* from 1-Pentanol-2-*d*.—The deuterio alcohol was diluted with two parts of 1-pentanol prepared by reduction of valeric acid with lithium aluminum hydride. The total of 3 cc was warmed with 5 g of phosphorus tribromide. After addition of water the amyl bromide layer was separated, washed, dried, and distilled giving 62% of product, bp 126–127°, 99.9% pure by glpc. The C–D band was at 2130 cm^{-1}; α_{546} $-0.343°$, α_{578} $-0.300°$ (*l* 1) [(α)D $-0.245°$). Correcting for fully deuterated material gives [α]D $-0.74 \pm 0.02°$.

Pentane-2-*d* from 1-Pentene.—To a solution of 1.5 g (0.036 mole) of lithium aluminum deuteride and 13.1 g (0.096 mole) of α-pinene (pure by glpc, $[\alpha]^{22}$D $+45.9°$, 90% optically pure) in diglyme was added 14 ml (0.048 mole) of boron fluoride diglymate. After several hours at 5–10°, the mixture was cooled to 0° and 3.2 g (0.046 mole) of 1-pentene was added. After stirring overnight the mixture was decomposed first with ethylene glycol followed by glacial acetic acid. Distillation and redistillation gave 1.0 ml of product which was further purified by washing with cold concentrated H_2SO_4 and finally by glpc (PBG). The pentane-2-*d* showed a C–D band at 2145 cm^{-1} and 0.70 ± 0.05 atom of deuterium per molecule in the nmr.

The ORD curve taken on a Cary 60 spectropolarimeter gave a normal Drude plot with λ_0 155 mμ and $[\alpha]^{25}$D $+0.158°$.

Registry No.—(*S*)-(+)-1-Butanol-1-*d*, 10035-71-9; *p*-nitrobenzenesulfonate, 10035-72-0; diethyl (butyl-1-*d*)-malonate, 10035-73-1; caproic-β-*d* acid, 10035-74-2; 1-bromopentane-2-*d*, 10035-75-3; 1-pentyl-2-d_2 acetate, 10035-76-4; 1-pentanol-2-*d*, 10035-77-5; pentane-2-*d*, 10035-83-3.

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[13] E. B. Vliet, C. S. Marvel, and C. M. Hsueh, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 416.

[14] These preliminary experiments were performed by V. Sarich.

[15] A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

Radical Reactions of Tetrafluorohydrazine. IV. Addition to Acetylenes[1a]

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Received December 1, 1966

Tetrafluorohydrazine reacts with acetylenes to produce α-fluoro-α-difluoramino fluorimines. These products appear to be produced by rearrangement of the original adduct, the α,β-bis(difluoramino)ethylenes.

Following the discovery that tetrafluorohydrazine (N_2F_4) reacts smoothly with a wide variety of olefins to produce the corresponding vicinal bis(difluoramines),[2,3] the behavior of acetylenes in this reaction was examined. Two objectives were involved: the synthesis of vinyl difluoramines and of tetrakis(difluoramines). However, a brief examination of this reaction revealed the instability of vinyl difluoramines which precluded the further addition of N_2F_4.

Tolane, acetylenedicarboxylic ester, and isopropenyl acetylene were investigated. Allene was also studied briefly and, since it yielded products analogous to those derived from acetylenes, its reaction will be described. Finally, β-bromostyrene reacted with N_2F_4 to produce a product related to acetylene addition products. In general, it was found that the reaction of acetylenes

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[1] (a) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama under Contract Numbers DA-01-021 ORD-5135 (1959) and DA-01-021 AMC-11536(Z). (b) Deceased. (c) To whom correspondence should be directed.

[2] R. C. Petry and J. P. Freeman, Abstract S-46, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[3] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, *Sec A*, 582 (1966). For leading references and pertinent work, see A. L. Logothetis, *J. Org. Chem.*, **31**, 3686 (1966); A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966).