

alkali. As the reaction proceeds, however, the production of organic acid through path A uses up the available alkali, thus slowing down the production of I, and allowing path B to proceed. Path A thus could be considered to proceed from $f = 0$ to some intermediate fraction (Fig. 6) at which point path B becomes more important. If the slow step of the reaction occurs before the

formation of the intermediate $\text{RC}\overset{\text{O}}{\parallel}\text{CHCl}_2$, then from

Fig. 6 it can be seen that Compound I should possess a smaller molar radioactivity than the reactant, whereas the molar radioactivity of the haloform III should be greater than that of the reactant.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

Stereospecific *trans* Radical Addition of DBr to the 2-Butenes. Syntheses of *erythro*- and *threo*-3-Deuterio-2-bromobutanes^{1,2}

BY PHILIP S. SKELL AND RICHARD G. ALLEN

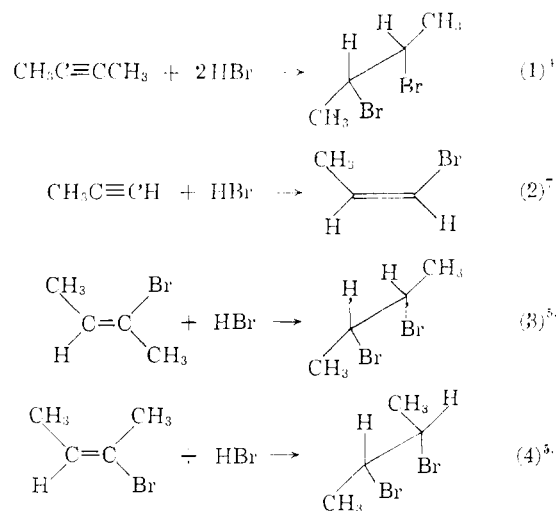
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Pure *erythro*- and *threo*-3-deuterio-2-bromobutanes can be synthesized by radical chain additions of deuterium bromide to *trans*- and *cis*-2-butene, respectively. Structures and purity were determined by alkaline dehydrohalogenation, *erythro*-yielding *trans*-2-butene and 2-deuterio-*cis*-2-butene, *threo*-yielding *cis*-2-butene and 2-deuterio-*trans*-2-butene. The mechanistic implications are considered.

Introduction

Optically active alkyl halides have been employed frequently in mechanism studies. Unfortunately there is no satisfactory criterion for establishing the optical purity of the alkyl halides prepared from optically pure alcohols. Since it has not been possible to prepare the pure enantiomers, in most instances the starting materials have been of uncertain purity, and the mechanistic conclusions may be ambiguous. There are often advantages in working with diastereoisomers employing, for example, infrared spectral analysis, since isomer purity can be determined without resorting to the tedium of exhaustive resolution. If these diastereomers are deuterium-labeled at one of the asymmetric centers removed from the reactive site, they should prove to be as valuable as the pure unlabeled enantiomorphs. Convenient synthetic routes to these substances have not been hitherto reported.

Radical chain addition reactions to acyclic olefins have been observed to be stereospecific only for hydrogen bromide,³⁻⁸ which adds to olefins in *trans* processes.



Both Epstein⁵ and Goering and Larsen⁶ failed to obtain stereospecific *trans* additions to the isomeric 2-bromo-2-butenes, the products containing 5–10% of the 2,3-dibromobutane which would have resulted from *cis* addition. Although the isomer contamination may be attributed to isomerization of the starting olefin, it would also be reasonable to interpret the results in terms of a combination of stereospecific and non-stereospecific processes in approximately 4:1 ratio.

Results and Discussion

Since the 2-butenes are less readily isomerized than the 2-bromo-2-butenes, the addition of deuterium bromide to the 2-butenes promised to be a more favorable system to study.

At temperatures between -78 and -60° , illumination of a mixture of *cis*- or *trans*-2-butene and deuterium bromide initiates very rapid chain reactions to produce the 3-deuterio-2-bromo-

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research & Development Command, under contract No. AF 49(638)-457.

(2) This paper was presented before the Organic Section of The American Chemical Society at the Chicago Meeting, September, 1958.

(3) P. S. Skell, R. C. Woodworth and J. H. McNamara, THIS JOURNAL, **79**, 1253 (1957).

(4) C. Walling, M. S. Kharasch and F. R. Mayo, *ibid.*, **61**, 1711 (1939).

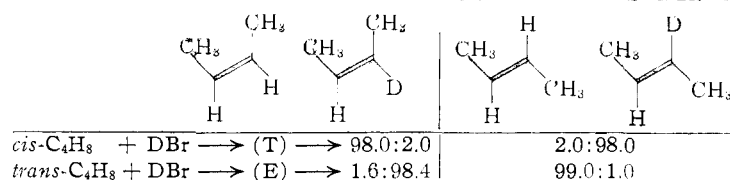
(5) M. Epstein, University of Syracuse, Thesis, 1951.

(6) H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957).

(7) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

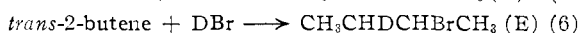
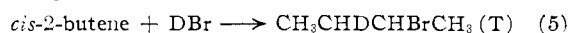
(8) Similar additions have been observed with substituent cyclohexenes: (a) H. L. Goering, P. I. Abell and B. F. Aycocock, *ibid.*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (c) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956); (d) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

CHART I
OLEFIN PRODUCT RATIOS FROM DEHYDROHALOGENATION OF 3-DEUTERIO-2-BROMOBUTANES



butanes in 95–99% yields. Unreacted olefins recovered from reactions stopped short of completion were found to be unisomerized.

Vapor phase chromatography failed to reveal contamination in the 2-bromobutanes. Nonetheless, the product obtained from *cis*-2-butene (T) had an infrared spectrum differing distinctly from the product obtained from *trans*-2-butene (E).



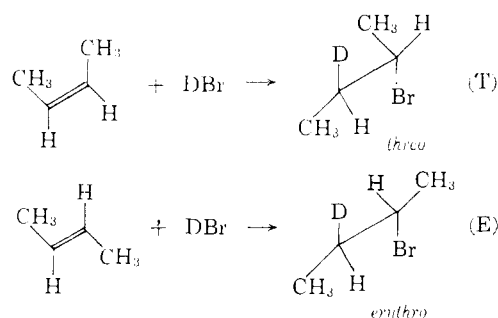
Unfortunately the non-congruous bands were not intense absorptions and overlapped one another so that it was not possible to use the spectra for estimating the degree of intercontamination of the isomers (T) and (E).

The contamination of (T) and (E) by undeuterated material was readily determined to be 1.6% for the (T) isomer, for the 12.67μ band of ordinary secondary $\text{C}_4\text{H}_9\text{Br}$ is sufficiently removed from the 12.23μ band of (T). The secondary $\text{C}_4\text{H}_9\text{Br}$ content of (E) could not be estimated as readily because the 12.47μ band of (E) tended to obscure the 12.67μ band, but the estimated extent of contamination is consistent with the 1.6% determined for (T). The secondary $\text{C}_4\text{H}_9\text{Br}$ probably results from the hydrogen bromide contaminant of the deuterium bromide. Elsewhere, data leading to the rate ratio $k_{\text{H}}/k_{\text{D}} = 1.54$ for the hydrogen bromide–2-butene reaction will be reported. Thus, if the secondary $\text{C}_4\text{H}_9\text{Br}$ is obtained from HBr addition only, it follows that the ratio DBr/HBr is 99. Since the starting deuterium oxide was 99.5 atom % D, either a small H contamination was introduced, or another isotope effect is involved in the preparative reaction.

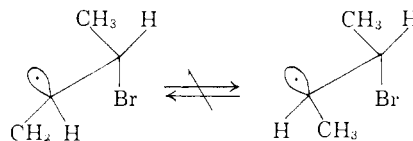
To determine the extent of intercontamination and to assign structures to (T) and (E), the isomers were subjected to alkaline dehydrohalogenation with ethanolic potassium ethoxide solution. The products 1-butene, *cis*-2-butene and *trans*-2-butene, were detected by vapor phase chromatography and separated to obtain samples of the pure olefins for infrared examination. The 3-deuterio-1-butene was not examined further. From the spectra of the 2-butenes it was readily apparent that isomer intercontamination was not greater than that anticipated from the olefin impurities (1 mole %) and the hydrogen bromide contaminant in the deuterium bromide. The results are summarized in Chart I.

Failure to observe isomer intercontamination proves that both hydrohalogenation and dehydrohalogenation are stereospecific. Since this is most certainly a *trans* elimination, it is possible to assign the *threo* structure to isomer (T) from *cis*-2-butene, and *erythro* to isomer (E) from *trans*-2-

butene. The reactions of deuterium bromide with the 2-butenes afford good synthetic routes to the pure diastereomeric *erythro*- and *threo*-3-deuterio-2-bromobutanes, the course of the reaction being stereospecific and *trans*.



Since the additions of deuterium bromide to the isomeric 2-butenes are stereospecific *trans* processes, it is tempting to rationalize these results with the simplest conclusion, that additions of a bromine atom to *cis*-2-butene produces a *threo* radical, and *trans*-2-butene the *erythro* radical, and that these radicals do not interconvert before abstracting a deuterium atom from deuterium bromide. However, this conclusion is *not* warranted



on the basis of the evidence here presented, for alternative constructs can also explain the experimental results. It is hoped that experiments in progress will clarify the detailed structures of the intermediate radicals.

Experimental

Preparation of Deuterium Bromide.—In an evacuated 12-l. flask, 31.88 g. of boron tribromide and 8.43 g. of 99.5% D_2O were mixed. An immediate exothermic reaction took place.

The deuterium bromide produced was taken into a high vacuum line and purified by distillation at 10^{-5} mm. through a -78° trap, collecting the purified deuterium bromide at -195° .

Purification of *cis*- and *trans*-2-Butene.—Phillips 99 mole % *cis*- and *trans*-2-butene were purified by distillation through a -78° trap in a high vacuum line collecting a center cut at -195° . Approximately 1% impurity was detected by vapor phase chromatographic analysis of these purified butenes.

Optical Density-Pressure Data for *cis*- and *trans*-2-Butene.—The following optical density-pressure curves were determined for pure *cis*- and *trans*-2-butene in a 5.0-cm. gas infrared cell, with compensation for the NaCl optics using a Perkin-Elmer model 21 infrared recording spectrophotometer.

<i>trans</i> -2-Butene		<i>cis</i> -2-Butene	
Press., mm.	O.d. at 10.37 μ	Press., mm.	O.d. at 14.90 μ
122.0	1.354	121.0	0.894
65.5	0.794	61.3	.532
27.5	.371	33.0	.301
10.0	.112	11.2	.107

Preparative Vapor Phase Chromatographic Separation of the Butenes.—The butene mixtures were separated by vapor phase chromatography using column A, 15 ft. by 10 mm. packed with 33% dipropylene glycol dibenzoate on firebrick at 24–25° and a helium flow rate of 40 cc. per minute. The *cis*-, *trans*- and 1-butene fractions were collected by passing the column exit gases through traps at –195°. Since the *cis*- and *trans*-2-butene peaks overlapped slightly, the fractions collected were passed through the column individually a second time and collected to ensure their purity from intercontamination. Retention times are: 1-butene, 18.0 min.; *trans*-2-butene, 22.0 min.; *cis*-2-butene, 25.5 min. The samples were shown to be free of structural isomer contamination by analytical v.p.c. and examination of the infrared spectra.

Reaction of DBr with *cis*-2-Butene to Produce threo-3-Deuterio-2-bromobutane (T).—Into a 141-ml. evacuated reaction flask on a vacuum line was condensed 40.7 mmoles of DBr and 36.3 mmoles of *cis*-2-butene. The reactants were warmed to –78°, mixed, and kept in the dark for 30 minutes. A distillation at –78° recovered 0.08 g. of high boiling material. The recovered *cis*-2-butene-DBr mixture was then irradiated by a General Electric Reflector Sunlamp at a distance of one inch for a total irradiation time of 7 minutes. The temperature of the reaction mixture was kept between –78 and –60° by alternating irradiation with cooling to –78°.

The reaction mixture was distilled collecting the product of the reaction at –78° and the excess reactants at –195°. The product was distilled at 10⁻⁶ mm. two more times collecting it at –78° and any reactants at –195°. Vapor phase chromatography showed no butenes in the material collected at –195°. The purified product (4.73 g., 94.5% of theoretical yield) had a vapor pressure of 28.1 mm. at 8.0° and 45.4 mm. at 17.8° n_{D}^{25} 1.4348.

The product gave only one peak when passed through a 9-foot vapor phase chromatographic column B (6 feet dipropylene glycol dibenzoate 33%, 3 feet carbowax 1000, 33% on firebrick) at 120° using a flow rate of 40 cc. of helium per minute; retention time 28 minutes.

Reaction of DBr with *trans*-2-Butene to Produce erythro-3-Deuterio-2-bromobutane (E).—In a similar experiment 37.2 mmoles of DBr and 29.0 mmoles of *trans*-2-butene was irradiated for 7 minutes at –78 to –60°. The purified product (4.01 g., 99.5% of theoretical yield) had a vapor pressure of 29.8 mm. at 9.5° and 42.5 mm. at 16.2°, n_{D}^{25} 1.4345.

Vapor phase chromatographic column B gave only one peak at 120° and 40 cc. of helium per minute flow rate; retention time 28 minutes.

Dehydrohalogenation of the threo Isomer (T).—In a 100-ml. flask equipped with a reflux condenser was placed 50 ml. of 1 M potassium ethoxide and 2.0 g., 14.5 mmoles, of the *cis*-2-butene-DBr addition product (T). The reaction flask was heated to 70 \pm 3° for 3.5 hours. A slow stream of nitrogen swept the gases evolved from the top of the reflux condenser into a trap immersed in frozen pentane, –130°.

The gases collected were taken into a vacuum line and purified by distillation through a –78° trap. The collected olefins (6.15 mmoles) were separated into *cis*-, *trans*-, and 1-butene fractions by preparative scale vapor phase chromatography.⁹ The infrared spectrum of the *cis*-2-butene fraction (34.2 mm.) had an optical density at 14.90 μ of 0.31 which is equivalent to 33.5 mm. of *cis*-2-butene, or 98.0% of the total sample. The 2.0% remainder must be 2-deuterio-*cis*-2-butene which does not absorb at this wave length. The *trans*-2-butene fraction (130 mm.) had an optical density of 0.03 at 10.37 μ which is equivalent to 2.6 mm. or 2.0% *trans*-2-butene in the sample. The remaining 98.0% was assumed to be 2-deuterio-*trans*-2-butene which does not absorb at this wave length.

Dehydrohalogenation of the erythro Isomer (E).—By a similar procedure 1.8 g. (13.0 mmoles) of the *trans*-2-butene-DBr addition product (E) was dehydrohalogenated.⁹ Preparative vapor phase chromatographic separation of the collected olefins (2.3 mmoles) and infrared analysis showed the *cis*-2-butene fraction (130 mm.) to have an optical density at 14.90 μ of 0.021 which is equivalent to 2 mm. of *cis*-2-butene, 1.6% in the sample. The remaining 98.4% was assumed to be 2-deuterio-*cis*-2-butene. The *trans*-2-butene fraction (99.5 mm.) had an optical density at 10.36 μ of 1.15 which is equivalent to 98.5 mm. or 99% *trans*-2-butene in the sample. The remaining 1.0% must be 2-deuterio-*trans*-2-butene.

Infrared Spectra.—The following infrared spectra were obtained for the pure gases in a 5-cm. cell vs. a NaCl plate using NaCl optics, recording wave length in microns. The instrument used was a Perkin-Elmer model 21 infrared recording spectrophotometer.

2-Deuterio-*trans*-2-butene: 3.23(w), 3.42(vs), 3.48(vs), 3.66(vs), 4.47(m), 4.50(m), 5.25(vw), 6.78(s), 6.90(s), 6.95(m), 7.17(m), 7.24(w), 7.64(w), 8.58(vw), 8.70(vw), 9.11(m), 9.24(m), 11.20–11.37(s), 11.47(vs); 2-deuterio-*cis*-2-butene: 2.34(vw), 3.33(s), 3.39(s), 3.43(vs), 3.48(s), 3.67(vw), 4.43(m), 4.46(m), 5.26(vw), 6.01(m), 6.07(m), 6.52(w), 6.82(m), 6.88(s), 7.17(s), 7.22(s), 7.42(m), 7.48(m), 7.53(m), 8.67–8.87(w), 9.04(m), 9.11(m), 9.69(w), 9.95(m), 10.13(m), 11.28(m), 11.43(m), 11.83(w); 3-deuterio-1-butene: 3.26(s), 3.34(vs), 3.47(vs), 4.62(m), 4.67(m), 5.43(w), 5.48(w), 6.07(m), 6.83(m), 7.10(m), 7.73(w), 9.97(s), 10.85(vs), 10.95(vs), 11.68(w), 13.75–14.17(vw).

The following liquid spectra were obtained neat in a 0.0235-mm. cell vs. a NaCl plate.

threo-3-Deuterio-2-bromobutane: 3.39(vs), 3.44(vs), 3.49(s), 3.67(vw), 4.56(vw), 4.62(w), 4.66(w), 4.70(vw), 6.88(vs), 7.24(vs), 7.50(w), 7.70(s), 8.27(s), 8.58(w), 8.82(s), 8.88(m), 8.95(m), 9.25(m), 9.57(m), 9.72(m), 10.00(m), 10.21(s), 10.50(m), 11.60(w), 11.94(s), 12.23(m), 13.90(s); erythro-3-deuterio-2-bromobutane: 3.39(vs), 3.44(vs), 3.49(s), 3.67(vw), 4.58(w), 4.67(m), 4.71(w), 6.87(vs), 7.24(vs), 7.63(m), 7.71(m), 7.83(s), 8.28(s), 8.62(s), 8.82(s), 8.87(s), 8.99(m), 9.11(w), 9.19(vw), 9.33(m), 9.57(w), 9.65(w), 9.97(m), 10.38(s), 11.90(s), 12.04(m), 12.47(w), 14.00(s).

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(9) Dehydrohalogenation on a small scale under identical conditions produced 97.5% and 96.0% C₄H₈ from (T) and (E), respectively. Analytical vapor phase chromatography, which will be described in a forthcoming publication, indicates the percentage composition of *cis*-, *trans*- and 1-butenes to be 9.8, 65.4 and 24.8 from (T), and 33.4, 31.4 and 35.2 from (E).