Addition of Trichlorosilane to 4-Phenylbutene-1, Rate Study.—Into each of eight 1 × 20 cm. Pyrex tubes cooled in Dry Ice were sealed 0.01 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol and 2.0 ml. of an equimolar solution of trichlorosilane in 4-phenylbutene-1. The tubes were heated in a boiling water bath, cooled by Dry Ice, and analyzed immediately by v.p.c. The first tube was heated only 5 min., after which it contained little or no 4-phenylbutene-1, but *trans*-1-phenylbutene with a trace of another olefin which has not been identified. The successive tubes, each heated for a longer time, showed that the *trans*-1-phenylbutene and the unidentified olefin slowly disappeared as the relative amount of (1-phenylbutyl)trichlorosilane increased (see Fig. 2).

Addition of Trichlorosilane to *cis*-Pentene-2 and Pentene-1.—In a similar manner pentene-1 and *cis*-pentene-2 (1.00 ml.) were heated for 10 min. in sealed tubes at 100° with trichlorosilane (0.50 ml.) and 0.0025 ml. of 0.1 *M* chloroplatinic acid. Analysis by v.p.c. and infrared showed that all of the trichlorosilane was gone and that *n*-pentyltrichlorosilane was the only adduct. The distribution of isomers in the recovered olefins can be found in Table II.

Isomerization of 4-Phenylbutene-1.—4-Phenylbutene-1 (10 ml.) and 3.9 g. of 8% sodium on alumina were heated at 58° in a dry 20-ml. ampoule for 48 hr. The isomerization proceeded smoothly but slowly. V.p.c. analysis showed the presence of four olefins, two of which were 4-phenyl- and *trans*-1-phenylbutene. Ninety-one per cent of the total area was due to *trans*-1-phenylbutene. A 0.05-ml. sample of the mixture was chromatogrammed and the major compound collected to give a pure fraction having the infrared spectrum of a *trans* olefin and a refractive index of $n^{25}\mathrm{D}$ 1.5395.

Cleavage of (1-Phenylbutyl)trimethylsilane with Alcoholic Caustic.—All (phenylalkyl)silanes in this study were treated with alcoholic caustic to determine those compounds containing a silicon attached to a position α to a benzene ring.[23] (1-Phenylbutyl)trimethylsilane (15.4 g.), potassium hydroxide (34.2 g.), absolute ethanol (51 ml.), and water (3 ml.) were heated at reflux (108°) for 22 hr. The organic layer was separated, washed with water, dried with anhydrous sodium sulfate, and carefully distilled to give a 95% yield of *n*-butylbenzene, b.p. 185° at 746 mm., $n^{25}\mathrm{D}$ 1.4872, $d^{25}{}_4$ 0.8548. V.p.c. analysis before distillation showed that all of the (1-phenylbutyl)trimethylsilane had been cleaved. The infrared spectrum and v.p.c. retention time of this product were identical with those of an authentic sample of *n*-butylbenzene prepared by the reaction of *n*-butylbromide, bromobenzene, and sodium; b.p. 185° at 740 mm., $n^{25}\mathrm{D}$ 1.4873, $d^{25}{}_4$ 0.8585; lit.[12] b.p. 182.9° at 760 mm., $n^{20}\mathrm{D}$ 1.48975, $d^{20}{}_4$ 0.86017.

The other samples mentioned in this paper were subjected to treatment with alcoholic caustic as here described, but the products were identified only by their v.p.c. retention times.

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(23) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 143–146.

The Free-Radical Addition of Deuterium Bromide to *cis*- and *trans*-1-Deuterio-1-hexene[1]

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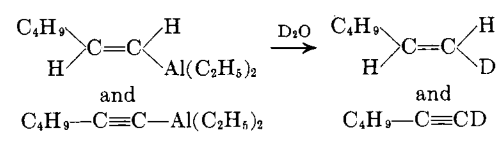
The radical-chain addition of deuterium bromide to a terminal olefin, 1-deuterio-1-hexene, is a stereospecific reaction.

The stereochemistry of free-radical additions of hydrogen bromide and deuterium bromide to olefins has aroused considerable interest. The interest in this topic has been generated by studies which have demonstrated that hydrogen bromide adds in a completely *trans* manner to 1-methylcyclohexene,[3] 1-bromocyclohexene,[4] and 1-chlorocyclohexene.[4] However, in the similar 1-bromocyclobutene, 1-bromocyclopentene, and 1-bromocycloheptene systems, even though a preference remains for *trans* addition, the reactions are no longer completely stereospecific.[5] In a somewhat more complex, but still similar system, 2-bromo-2-norbornene, reaction with hydrogen bromide gives predominantly *cis* addition.[6]

In acyclic systems radical additions of deuterium bromide to *cis*- and *trans*-2-butenes[7] are stereospecific and *trans*, and hydrogen bromide additions to 2-bromo-2-butenes are 90–95% *trans* additions, the source of the contaminating isomers being undetermined.[8]

Since all previous studies had been constrained to nonterminal olefins, the stereochemistry of additions to terminal olefins was investigated using 1-deuterio-1-hexene and deuterium bromide. The procedure of Wilke and Müller[9] for the synthesis of *trans*-1-deuterio-1-hexene was used with somewhat different results. Whereas Wilke and Müller found that the addition of diethylaluminum hydride to 1-hexyne, followed by deuterolysis, yields *trans*-1-deuterio-1-hexene, in our hands the reaction gave varying ratios of *trans*-1-deuterio-1-hexene and 1-deuterio-1-hexyne, which were dependent on the reaction temperature. Addition of diethylaluminum hydride to 1-hexyne at 35–45° gave a 44% yield of *trans*-1-deuterio-1-hexene and a 12% yield of 1-deuterio-1-hexyne. When the reaction was carried out at a lower temperature (5–15°), a 76% yield of *trans*-1-deuterio-1-hexene and 10% yield of 1-deuterio-1-hexyne was obtained. The 1-deuterio-1-hexyne was removed by shaking the product with aqueous ammoniacal silver nitrate solution.



The infrared spectrum[10] of the purified product was identical with that prepared by Wilke and Müller.[9] Although comparison with the spectrum of *cis*-1-deuterio-1-hexene failed to indicate the presence of this

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(1) This was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-457.

(2) The Pennsylvania State University, 1958–1959.

(3) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

(4) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

(5) P. I. Abell and C. Chiao, *ibid.*, **82**, 3610 (1960).

(6) N. A. LeBel, *ibid.*, **82**, 623 (1960).

(7) P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

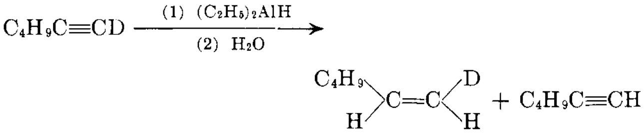
(8) H. L. Goering and D. W. Larsen, *ibid.*, **81**, 5937 (1959).

(9) G. Wilke and H. Müller, *Ann.*, **618**, 267 (1958).

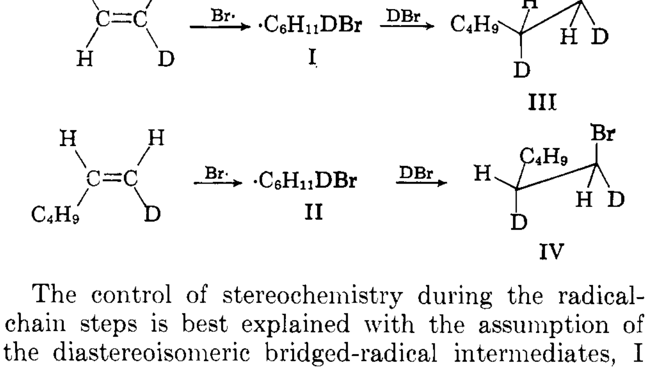
(10) E. G. Hoffmann, *ibid.*, **618**, 276 (1958).

isomer, a maximum of 6% of the *cis* isomer would have escaped detection.

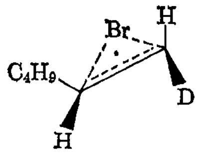
cis-1-Deuterio-1-hexene was prepared by addition of diethylaluminum hydride to 1-deuterio-1-hexyne. The addition was carried out at 10–20° and, after hydrolysis, resulted in a yield of 44% *cis*-1-deuterio-1-hexene and a 1% yield of 1-hexyne. Infrared analysis gave no indication of contamination of *cis*-1-deuterio-1-hexene with the *trans* isomer, but a maximum of 2% may have gone undetected.



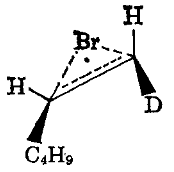
Irradiation of a mixture of deuterium bromide and *trans*-1-deuterio-1-hexene at −78 to −60°, using a medium-pressure mercury lamp, gave a 65% yield of alkyl bromide. Vapor phase chromatography demonstrated that the product was 39% secondary bromide and 61% primary bromide. Deuterium bromide was added to *cis*-1-deuterio-1-hexene in a similar manner to give hexyl bromide with a 21% secondary bromide–79% primary bromide composition. Vapor phase chromatographic separation of the primary hexyl bromides and comparison of their infrared spectra showed clearly that different primary bromides had been formed. The infrared comparison gave no indication of cross contamination; however, as much as 5% of the primary hexyl bromide formed from *cis*-1-deuterio-1-hexene may have gone undetected in the primary hexyl bromide prepared from the *trans* isomer. Similarly, as much as 9% of the primary hexyl bromide formed from *trans*-1-deuterio-1-hexene may have gone undetected in the primary hexyl bromide fraction prepared from the *cis* isomer. On the basis of this infrared evidence, and by analogy to the previously discovered stereospecific *trans* additions of hydrogen bromide and deuterium bromide to nonterminal olefins, it is postulated that the free-radical addition of deuterium bromide to *trans*- and *cis*-1-deuterio-1-hexene gives *threo*- and *erythro*-1,2-dideuterio-1-bromohexane (III and IV), respectively. Clearly, two different free-radical intermediates (I and II) are involved, and these radicals are converted to their respective products III and IV faster than conversion of one to the other. *There is no significant difference between free-radical additions of deuterium bromide to terminal and nonterminal olefins.*



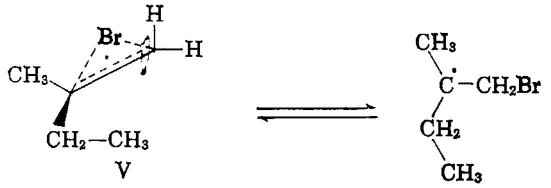
The control of stereochemistry during the radical-chain steps is best explained with the assumption of the diastereoisomeric bridged-radical intermediates, I and II. This type of intermediate has been demonstrated[11] to control optical stability in V. In the presence of 0.01 *M* Br_2, the dibromide obtained from this system has 50% the maximum activity. If trapping by bromine is a diffusion-controlled process, the half-life of V for racemization is ~10^{-6} sec. The half-life for interconversion of I and II may be longer since energetic considerations suggest it would be a more endothermic reaction. Under the conditions used in these experiments, deuterium bromide reacts with I and II faster than they are interconverted.



I



II



Experimental

***trans*-1-Deuterio-1-hexene.**—The procedure of Wilke and Müller[9] was followed for the addition of diethylaluminum hydride to 1-hexyne. However, the somewhat different results coupled with a different purification procedure warrant a complete description.

Diethylaluminum hydride (8.9 g., 0.10 mole) was added, with stirring, under nitrogen (0.002–0.004% oxygen), to 38.6 g. of 1-hexyne (0.470 mole), which was heated at 35–45° in an oil bath during the addition. After the addition was complete (3 hr.), the reaction mixture was stirred for an additional 1.5 hr. at 35–45°. The excess 1-hexyne was then distilled from the reaction mixture, using an oil bath temperature of 50° and a pressure of 2.5 mm.; 28.5 g. of 1-hexyne was recovered. The two-necked reaction flask, containing the diethylaluminum hydride–hexyne addition product, was designed so that by tilting the flask 120° it could be used as an addition funnel. The aluminum alkyl was then added, with stirring under nitrogen, to 200 ml. of carefully dried mineral oil and 12.5 g. (0.63 mole) of deuterium oxide. After the addition was complete (2 hr.), the reaction mixture was stirred for an additional 12 hr. Deuterium oxide and C_6 hydrocarbon were distilled from the reaction mixture at 10-mm. pressure, the temperature of the oil bath being increased gradually to 90°. The distillate was mixed with some dodecane to facilitate handling, dried, and distilled to yield 4.69 g. of product, b.p. 63–64°. Gas chromatographic analysis on a 3-ft. dioctyl phthalate column indicated the product was 79% 1-hexene and 21% 1-hexyne.

A subsequent run, similar in all respects, except for a lower temperature of 5–15° for the addition of diethylaluminum hydride to 1-hexyne, yielded 7.30 g., b.p. 63°. This product was 89% 1-hexene, thus indicating a 76% yield of *trans*-1-deuterio-1-hexene, and a 10% yield of 1-hexyne.

As an example of the purification of these mixtures, 2.72 g. (79% *trans*-1-deuterio-1-hexene, 21% 1-deuterio-1-hexyne), was shaken 4 hr. with a solution of 50 ml. of aqueous ammoniacal silver nitrate, prepared from 10 g. of silver nitrate. The reaction mixture was then subjected to a reduced pressure of 10 mm. at room temperature, and the *trans*-1-deuterio-1-hexene was condensed in a −78° trap. The crude *trans*-1-deuterio-1-hexene (1.81 g.) was distilled yielding 1.63 g., b.p. 62°. The absence of bands at 3.04, 3.86, and 11.00 μ in the infrared spectrum of the purified product demonstrates that no detectable amount (less than 1%) of 1-hexyne, 1-deuterio-1-hexyne, and 1-hexene were

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[11] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2850 (1963).

present. Furthermore, the spectrum of the purified product is identical with that of the *trans*-1-deuterio-1-hexene of Hoffmann.[10] However, comparison with the spectrum of *cis*-1-deuterio-1-hexene described below indicates that as much as 6% of the *cis* isomer may possibly be present without detection.

1-Deuterio-1-hexyne.—1-Hexyne (75.6 g., 0.92 mole) was added to a di-*n*-butyl ether solution of ethylmagnesium bromide, which had been prepared from 24.3 g. of magnesium (1.57 g.-atoms), 171 g. of ethyl bromide (1.57 moles), and 800 ml. of dry di-*n*-butyl ether. This addition required 2 hr. As a precaution against contamination of the final product with undeuterated 1-hexyne, 200 ml. of di-*n*-butyl ether was distilled *in vacuo* from the reaction mixture, b.p. 45° (20 mm.). After the reaction mixture cooled to room temperature, 100 g. of deuterium oxide (5.00 moles) was added, dropwise, to the reaction mixture. The 1-deuterio-1-hexyne and some di-*n*-butyl ether were distilled into −78° traps by subjecting the reaction mixture to 25° and 10 mm. pressure. The contents of the traps were combined and dried over anhydrous calcium sulfate. Distillation through a spinning-band column yielded 62.2 g. of 1-deuterio-1-hexyne (81.5% yield), b.p. 69.5–70.0°. Absence of a detectable absorption at 3.04 μ in the infrared demonstrates that less than 1% of the product is the undeuterated 1-hexyne.

***cis*-1-Deuterio-1-hexene.**—Diethylaluminum hydride (23 ml., 18.6 g., 0.216 mole) was added, with stirring under nitrogen, to 62.2 g. (0.748 mole) of 1-deuterio-1-hexyne. The addition was carried out at a temperature of 10–20° and required 3 hr. The excess of 42.6 g. of 1-deuterio-1-hexyne was recovered by distillation at reduced pressure (0.5 mm.), finally using an oil bath temperature of 30°.

The resulting aluminum alkyl was added, dropwise, with stirring under nitrogen, to a mixture of 130 ml. of redistilled pentane and 25 ml. of water. After the addition, which required 1 hr., the reaction mixture was stirred for an additional 2 hr. The pentane, *cis*-1-deuterio-1-hexene, and water were then removed from the reaction flask by distillation at reduced pressure. After drying over anhydrous magnesium sulfate, distillation through a spinning-band column yielded 7.82 g. (44.6%) of *cis*-1-deuterio-1-hexene. Infrared analysis of the product showed that it was contaminated with 2% 1-hexyne. In addition, the infrared spectrum, $\lambda_{\max}$ (neat, 0.025 mm.) 4.47 (w), 5.67 (w), 6.19 (m), 6.85 (s), 6.95 sh (m), 7.26 (m), 7.32 sh (w), 7.46 sh (w), 7.73 (w), 8.10 (w), 9.08 (w), 9.91 (w), 10.26 (w), 10.90 (w), 12.20 sh (m), 12.52 (s), and 13.60 (w) μ, gives no indication of *trans*-1-deuterio-1-hexene absorption at 10.21 μ (as much as 2% contamination may have gone undetected). Lack of absorption at 6.08 μ indicated that no 1-hexene was present (as much as 0.8% may have gone undetected).

Addition of Deuterium Bromide to *trans*-1-Deuterio-1-hexene.—In a Pyrex glass container a mixture of 20 mmoles of *trans*-1-deuterio-1-hexene and 27 mmoles of deuterium bromide (2% HBr) was degassed *in vacuo* and irradiated with an ultraviolet lamp under autogeneous pressures at temperatures varying between −78 and −60°. This temperature range was maintained by alternately irradiating 30 sec. and cooling in a Dry Ice bath 90 sec. Distillation *in vacuo* separated unreacted deuterium bromide.

The less volatile components were distilled at reduced pressure, yielding a total of 2.08 g. (65.1%) in two fractions: 0.26 g., b.p. 45–47° (17 mm.); and 1.82 g., b.p. 47–50° (17 mm.). Vapor phase chromatographic analysis using a 3-ft. column of dioctyl phthalate on crushed firebrick indicated 39% secondary bromide and 61% primary bromide. Separation, for infrared analysis, of *threo*-1,2-dideuterio-1-bromohexane and 1,1-dideuterio-2-bromohexane was accomplished by vapor phase chromatography, using a 3-ft. paraffin oil–crushed firebrick column: the infrared spectrum of *threo*-1,2-dideuterio-1-bromohexane, $\lambda_{\max}$ (neat, 0.025 mm.) 4.56 (w), 4.66 (w), 6.85 (x), 7.25 (m), 7.48 (w), 7.58 (w), 7.72 (w), 7.84 (w), 8.04 (w), 8.23 (w), 8.41 (s), 8.98 (w), 9.21 (w), 9.90 (w), 10.15 (w), 10.44 (w), 11.14 (w), 11.30 sh (w), 11.87 (w), 12.16 (w), 13.46 (w), 13.76 (w), 14.45 (w), and 14.88 (w) μ; the infrared spectrum of 1,1-dideuterio-2-bromohexane, $\lambda_{\max}$ (neat, 0.025 mm.) 4.53 (w), 4.71 (w), 6.85 (s), 7.01 (w), 7.25 (m), 7.46 (w), 7.82 (s), 8.15 (m), 8.44 (s), 8.87 (w), 8.97 (w), 9.20 (w), 9.63 (w), 9.89 (w), 10.30 (w), 10.76 (w), 11.96 (w), and 13.72 (m) μ.

Addition of Deuterium Bromide to *cis*-1-Deuterio-1-hexene.—Following the procedure described above, the reaction was carried out with 25.4 mmoles of *cis*-1-deuterio-1-hexene (contaminated by 10% undeuterated 1-hexene and some 1-deuterio-*n*-hexane) and 25.8 mmoles of deuterium bromide (2% HBr).

Distillation of the less volatile products yielded a total of 2.29 g. (54.2%) of alkyl bromides in two fractions: 0.15 g., b.p. 59–59.5° (33 mm.); and 2.14 g., b.p. 59.5–65.0° (33 mm.). In addition, 0.28 g. of volatile material condensed in the Dry Ice trap during the distillation. Vapor phase chromatographic analysis of the alkyl bromide fractions, using a 5-ft. Ucon polar–crushed firebrick column, indicated that 60% was primary bromide and 40% secondary bromide. Vapor phase chromatographic analysis of the material which condensed in the trap using the same 5-ft. Ucon polar column showed the composition to be 56% 1-deuterio-*n*-hexane (impurity in the starting olefin), 37% *cis*-1-deuterio-1-hexene, and 7% of a mixture of approximately equal amounts of 1-deuterio-*trans*-2-hexene and 1-deuterio-*cis*-2-hexene (the peaks for these two components were not resolved well in the analysis). Each of the components was assumed to be 90% deuterated corresponding to the deuteration of the starting olefin. The 2-hexene components most likely were generated during a small amount of thermal elimination which occurred during vacuum distillation of the hexyl bromides. The lack of absorption at 10.20 μ in the infrared spectrum of this volatile fraction showed that the recovered 1-deuterio-1-hexene was not isomerized to the *trans* isomer. Perhaps 2% of the *trans* isomer could have been present without detection.

Using the same conditions as above, the reaction was repeated with completely deuterated *cis*-1-deuterio-1-hexene (less than 0.8% 1-hexene). The *erythro*-1,2-dideuterio-1-bromohexane and 1,1-dideuterio-2-bromohexene, formed in ratio 0.79:0.21, were separated by vapor phase chromatography using a 3-ft. column of paraffin oil on crushed firebrick: the infrared spectrum of *erythro*-1,2-dideuterio-1-bromohexane, $\lambda_{\max}$ (neat 0.025 mm), 4.55 (w), 4.66 (w), 6.85 (s), 7.25 (m), 7.48 (w), 7.66 sh (w), 7.78 (m), 8.06 (w), 8.23 (w), 8.38 (s), 8.99 (w), 9.15 (w), 9.80 (w), 11.04 (m), 12.00 (w), 13.70 (w), 14.10 (w), and 14.60 (w) μ. Lack of an absorption peak or shoulder at 11.14 μ best indicated that there was no contamination of the *erythro* with the *threo* isomer. However, 9% or less of *threo* isomer in the *erythro* isomer could have gone undetected. The absorption at 11.04 μ in the infrared spectrum of the *threo* isomer gives no indication of intercontamination by the *erythro* isomer. As much as 5% *erythro* isomer may have gone undetected.