$[\alpha]^{25}D$ 10.0° (c 2.4, $CHCl_3$) was saponified to regenerate (+)-*n*-butyl-*t*-butylcarbinol, b.p. 76° (23 mm.), $n^{20}D$ 1.4310, $\alpha^{25}D$ +17.12° (neat, l 0.5), d^{26} 0.823. The value for the pure isomer of *n*-butyl-*t*-butylcarbinol is taken as $\alpha^{25}D$ +34.24° (neat, l 1). Since the carbinol isolated from the reduction of *n*-butyl *t*-butyl ketone had a rotation of $\alpha^{25}D$ −3.78° (neat, l 1) the asymmetric reduction is 11.0%. In addition, the acetate of the carbinol obtained by asymmetric reduction was prepared, $\alpha^{25}D$ −2.60° (neat, l 1). Compared to the acetate of the 95.9% resolved carbinol described below, this indicates an asymmetric reduction of 11.1%, in excellent agreement.

The acetate, benzoate, and *p*-nitrobenzoate were prepared from the *n*-butyl-*t*-butylcarbinol, $\alpha^{25}D$ −32.8° (neat, l 1); acetate, b.p. 87° (20 mm.), $n^{20}D$ 1.4191, d^{26} 0.851 g./ml., $\alpha^{26}D$ −11.25° (neat, l 0.5). *Anal.* Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 71.26; H, 11.91. Benzoate, b.p. 98° (0.5 mm.), $n^{20}D$ 1.4887, d^{25} 0.936 g./ml., $\alpha^{25}D$ −7.29° (neat, l 0.5). *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.25; H, 9.77. *p*-Nitrobenzoate, b.p. 144–145° (0.5 mm.), $n^{25}D$ 1.5070, $\alpha^{29}D$ −12.50°. *Anal.* Calcd. for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90. Found: C, 65.32; H, 7.78.

(+)-1-Bromo-2-methylbutane was prepared by the method of Brauns,[27] 50 g. (41% yield), b.p. 60.8° (100 mm.), $n^{20}D$ 1.4453, $\alpha^{24}D$ +4.22° (l 1, neat), 84% optical purity. A second preparation gave 104 g. (43% yield), b.p. 57–58° (100 mm.). $\alpha^{26.5}$ +4.66°. 93% optical purity.

(+)-1-Iodo-2-methylbutane was prepared by treating the Grignard reagent prepared from the chloride[7a] with iodine in 57% yield, $n^{20}D$ 1.4955–1.4969, $\alpha^{21}D$ +8.65° (l 1, neat), 98.5% optical purity.[27] A second preparation gave 182 g. (46% yield), b.p. 70° (53 mm.), $n^{20}D$ 1.4969–1.4972, $\alpha^{25}D$ +16.8 (l 2, neat), optical purity[27] 96.5%.

---

[27] D. H. Brauns, *J. Res. Nat. Bur. Standards*, **18**, 315 (1937).

Stanford, Calif.

[Contribution from the Department of Chemistry, Duke University]

The Elimination Reaction of Alpha and Beta Deuterated *n*-Octyl Bromides with Potassium Amide in Liquid Ammonia[1]

By Seta Mahakian Luck, Douglas G. Hill, A. Theodore Stewart, Jr., and Charles R. Hauser

Received November 29, 1958

The olefin produced by the reaction of *n*-octyl bromide-1-d_2 with potassium amide in liquid ammonia is shown to be formed exclusively by the β-elimination of hydrogen bromide, not partly through α-elimination of deuterium bromide as reported earlier. The olefin formed by the reaction of *n*-octyl bromide-2d_2 with this reagent arises not only from the β-elimination of deuterium bromide, but apparently also through a little α-elimination of hydrogen bromide as observed previously. This might be ascribed to an isotope effect.

It has previously been shown[2] that the olefins produced by the reactions of 2-ethylbutyl bromide-1d_2 and 2-ethylbutyl bromide-2d_1 with potassium amide in liquid ammonia and ether were formed exclusively from the anticipated β-elimination of hydrogen bromide and deuterium bromide, respectively.

However, the olefins formed from *n*-octyl bromide-1d_2 and *n*-octyl bromide-2d_2 with this reagent[2] appeared to arise not only from β-elimination, but also through some α-elimination accompanied by a 1,2-shift of hydrogen or deuterium from the β- to the α-carbon atom.

Evidence has now been obtained invalidating[3] the small extent of α-elimination reported for *n*-octyl bromide-1d_2 but supporting that for *n*-octyl bromide-2d_2.

Results with *n*-Octyl Bromide-1d_2 (I).—This deuterio halide was prepared by a modification of the method described previously[2] (equation 1).

$$n\text{-}C_6H_{13}CH_2CO_2C_2H_5 \xrightarrow[CH_3CO_2D]{Na} n\text{-}C_6H_{13}CH_2CD_2OD \xrightarrow{HBr} n\text{-}C_6H_{13}CH_2CD_2Br \quad (1)$$

The yield of the deuterio alcohol in the first step of this method was improved over that obtained earlier by the use of a larger excess of the sodium and carefully prepared deuterioacetic acid.

The deuterio halide I was prepared three times, but only one of these preparations contained the desired two deuterium atoms per molecule corresponding to formula I. The other two preparations contained less than two deuterium atoms per molecule indicating the presence of not only compound I but also *n*-octyl bromide-1d_1 and perhaps a little undeuterated *n*-octyl bromide.

The pure halide I was allowed to react with potassium amide in a mixture of liquid ammonia and ether and in liquid ammonia alone. The reaction medium appeared to be homogeneous under the former condition and non-homogeneous under the latter condition. The olefinic product was separated from the amine product[4] and isolated by distillation. The two other halide preparations were treated similarly.

In Table I are summarized the physical constants and deuterium contents of the three preparations of the halide and of the corresponding olefinic products. It can be seen from the notes to this table that the refractive indexes of the deuterated halide and olefin are in close agreement with those of *n*-octyl bromide and octene-1, respectively.

It can be seen from Table I that the pure halide I having two deuterium atoms per molecule (prepn. 1) gave an olefin that likewise had two deuterium atoms per molecule both under the homogeneous and non-homogeneous conditions. Similarly each of the two other halide preparations having less than

---

[1] Supported in part by the National Science Foundation.

[2] D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, This Journal, **74**, 5599 (1952).

[3] Preliminary mention of this was made in note 13 of a paper by D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge and C. R. Hauser, *ibid.*, **76**, 5129 (1954).

[4] Whereas such branched halides as 2-ethylbutyl bromide yield predominantly the olefin with potassium amide in liquid ammonia, *n*-octyl bromide gives mainly the corresponding primary amine or derivative.

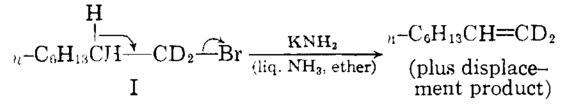
TABLE I

OLEFINIC PRODUCTS FROM THREE PREPARATIONS OF DEUTERIO HALIDE I AND POTASSIUM AMIDE

Deuterio halide I					Olefinic product				
	B.p.					B.p.			
Prepn.	°C.	Mm.	$n^{25}D$ [a]	D per molecule (±0.02D)	Reacn. medium (liq.)	°C.	Mm.	$n^{20}D$ [b]	D per molecule (±0.02D)
1	112.5–113.0	49	1.4498	2.00	NH_3, ether	63.0	108	1.4088	2.00
1	112.5–113.0	49	1.4498	2.00	NH_3	64.5–65.0	112	1.4085	2.00
2	112.0–114.0	54	1.4503	1.73	NH_3, ether	63.0	108	1.4088	1.76
2	112.0–114.0	54	1.4503	1.73	NH_3	64.0	108	1.4088	1.73
3	92.0– 94.0	20	1.4510[c]	1.93	NH_3	119.0–122.0	Atm.	1.4073[d]	1.92

[a] Reported for *n*-octyl bromide, $n^{25}D$ 1.4503; Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. IV, p. 14. [b] Reported for octene-1, $n^{20}D$ 1.4087, ref. in note *a*, p. 11. [c] At 23.1°. [d] At 25°; reported for octene-1, $n^{25}D$ 1.4062, ref. in note *b*.

two deuterium atoms per molecule (preps. 2 and 3) produced an olefinic product that had essentially the corresponding amount of deuterium. It may be concluded, therefore, that these olefinic products were formed by exclusive β-elimination of hydrogen bromide (equation 2) and not partly through α-elimination of deuterium bromide as assumed previously.[5]



$$n\text{-}C_6H_{13}\overset{H}{C}H\text{—}CD_2\text{—}Br \xrightarrow[\text{(liq. NH}_3\text{, ether)}]{KNH_2} n\text{-}C_6H_{13}CH{=}CD_2 \text{ (plus displacement product)} \quad (2)$$

I

Results with *n*-Octyl Bromide-2d_2 (II).—This deuterio halide was prepared as represented by equation 3.

$$n\text{-}C_6H_{13}CO_2C_2H_5 \xrightarrow[CH_3CO_2D]{Na} n\text{-}C_6H_{13}CD_2OD \xrightarrow[\substack{2,\ Mg \\ 3,\ HCHO}]{1,\ HBr}$$

$$n\text{-}C_6H_{13}CD_2CH_2OH \xrightarrow{HBr} n\text{-}C_6H_{13}CD_2CH_2Br \quad (3)$$

The first step of this method, which is the same as that described previously,[2] was modified as mentioned above for the analogous reduction represented in equation 1. The lengthening of the carbon chain by a methylene group illustrated in equation 3 is considered superior to that employed earlier[2] involving carbonation and reduction.

The halide preparation obtained by this method contained 1.86 D per molecule. Thus, a maximum amount of 93% of *n*-octyl bromide-2d_2 (II) might have been present in the preparation and a minimum amount of 86%. In the former event the preparation would have contained 7% of undeuterated *n*-octyl bromide and in the latter event, 14% of *n*-octyl bromide-2d_1 (III).

$C_6H_{13}CHDCH_2Br$ III

This halide preparation was allowed to react with potassium amide under the homogeneous and nonhomogeneous conditions described above for halide I. The olefinic products obtained under these two conditions were isolated by distillation. They contained 1.04 D and 1.06 D per molecule, respectively. The average of these two values, 1.05 D per molecule, is slightly higher than the maximum value which might result through exclusive β-elimination as discussed below.

The olefinic product might have contained a maximum of one deuterium atom per molecule if the halide preparation had consisted of 86% of bromide II and 14% of bromide III and if these halides underwent exclusive β-elimination of deuterium bromide and hydrogen bromide, respectively. Actually the olefinic product from such a halide preparation might be expected to contain slightly less than one deuterium atom per molecule, since bromide III should have undergone partly the β-elimination of deuterium bromide. Shiner[6] has observed that deuterio isopropyl bromide undergoes, with alcoholic sodium ethoxide at 25°, the β-elimination of hydrogen bromide and deuterium bromide in the rate ratio of 6.7. If a ratio of 6 is employed in the present case, the presence of 14% of bromide III would lead to the formation of an olefinic product having 0.98 D per molecule, which is 7% below the average value found. The experimental error for these determinations is considered to be only 0.02 D per molecule.

These results indicate that bromide II underwent a maximum β-elimination of deuterium bromide of 93% and that it exhibited at least 7% α-elimination of hydrogen bromide accompanied by the 1,2-shift of deuterium from the β- to the α-carbon atom. This supports the earlier observation when 8% α-elimination was reported.[2]

Although the main constituent in the halide preparation besides bromide II was presumably bromide III, an appreciable amount of undeuterated *n*-octyl bromide might also have been present. To the extent that the last compound was present, the indicated α-elimination should have been greater, since this compound could produce only undeuterated octene-1. The maximum extent of α-elimination of bromide II would be about 13%.

Such an α-elimination with *n*-octyl bromide-2d_2 (II) might be regarded as an isotope effect since it was not observed with the isomeric *n*-octyl bromide-1d_2 (I). In line with this, the yield of the olefinic product from bromide I was greater than that from bromide II being, under the homogeneous conditions, 13 and 6%, respectively.

However, before this isotope effect can be considered definitely established, the pure bromide II should be studied.[7]

---

(5) The apparent α-elimination reported earlier appears to have stemmed from incomplete separation of the ether from the olefinic product, the yield of which is low. In the present work sufficient olefinic product was prepared for proper purification (see Experimental and Table I).

(6) V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

(7) The present results might be accounted for through exclusive β-elimination if the halide preparation had contained an appropriate amount of the γ-deuterated bromide, $C_5H_{11}CHDCHDCH_2Br$, which might conceivably have arisen through hydrogen–deuterium exchange during the reduction of ethyl *n*-heptanoate (see equation 3). Such a hydrogen–deuterium exchange has been observed in the presence of

Experimental[8,9]

1-Bromoöctane-1d_2 (I) was prepared by a modification of the earlier procedure.[2]

Commercial acetic anhydride (1000 ml.) was heated under total reflux for several hours with 300 ml. of dry benzene in a 120-cm. glass-helix packed heated column of 13–14 theoretical plates. Maintaining a reflux ratio of approximately 6:1, the benzene–water azeotrope and the ensuing distillate were discarded until the highest steady distillation temperature was reached,[10] b.p. 138.5° and 139.2° in two different experiments; reported[11] b.p. 139.55° at 760 mm. (cor.). Approximately 500–600 ml. of pure acetic anhydride was obtained, $n^{20}\mathrm{D}$ 1.3903, $n^{25}\mathrm{D}$ 1.3886, $n^{31}\mathrm{D}$ 1.3860; reported $n^{20}\mathrm{D}$ 1.3901,[12] $n^{25}\mathrm{D}$ 1.3885,[13] $n^{31}\mathrm{D}$ 1.3863.[13]

To 510 g. (5.0 moles) of the purified acetic anhydride contained in a round-bottom flask equipped through a ground glass joint with a reflux condenser, were added 100 g. (5.0 moles) of deuterium oxide (99.5%) in a dry-box over phosphorus pentoxide. The mixture was heated cautiously[14] on a steam-bath for 14 hours, excluding atmospheric moisture. The deuterolysis of the anhydride was completed by adding 0.4 ml. of concentrated sulfuric acid and refluxing the mixture for 5 hours to give deuterioacetic acid, b.p. 50° at 57 mm., $n^{25.4}\mathrm{D}$ 1.3731; reported b.p. 48° at 60 mm.,[15] $n^{20}\mathrm{D}$ 1.3721.[16] The yield was essentially quantitative.[17]

In a modification of the Prins reduction,[18] about 10 ml. of deuterioacetic acid was added to a stirred solution of 200 g. (1.16 moles) of ethyl caprylate (b.p. 95.5° at 15 mm., $n^{25}\mathrm{D}$ 1.4160) and a pinch of dry phenolphthalein in 2.3 liters of anhydrous ether at −5°, followed by 134 g. (5.8 gram atoms) of sodium in 1-cm. cubes under a dry nitrogen atmosphere. The remainder of the deuterioacetic acid, total 355 g. (5.8 moles), was then added at a rate (3 hours) such that the temperature remained below 0° and the phenolphthalein remained colorless (kept acidic). After stirring under slight nitrogen pressure for three days and adding more ether occasionally, 870 ml. of water was added carefully with cooling and the mixture was stirred until all the sodium acetate was dissolved. The ether layer was washed with 25% ammonium hydroxide followed by water, dried over Drierite, and the solvent removed. Distillation gave 142.3 g. (94.8%) octanol-1-1d_2, b.p. 104–108° at 28 mm., $n^{20.5}\mathrm{D}$ 1.4285, $n^{25}\mathrm{D}$ 1.4267; reported b.p. 98° at 19 mm.,[19] $n^{20.5}\mathrm{D}$ 1.43035,[19] $n^{25}\mathrm{D}$ 1.4274.[20]

Octanol-1-1d_2 (142.3 g., 1.096 moles) was converted in 85% yield to 1-bromoöctane-1d_2 (I) with gaseous hydrogen bromide as described previously.[2] The physical constants and deuterium analyses for several preparations of this bromide are given in Table I.

Reaction of 1-Bromoöctane-1d_2 (I) with Potassium Amide.—A solution of approximately 0.23–0.25 mole of potassium amide in 250 ml. of anhydrous liquid ammonia was prepared from 0.25 g. atom of potassium in the usual manner.[21] To the stirred reagent was added over a period of about 2 minutes a solution of 44 g. (0.23 mole) of 1-bromoöctane-1d_2 (I) in 80 ml. of anhydrous ether. After stirring for one hour,[22] excess solid ammonium chloride was added. The reaction mixture was worked up to give 4.02 g. (13%) of octene-1-1d_2 b.p. 63.0° at 108 mm. (see Table I).

The reaction was also carried out by adding bromide I directly to the reagent without first dissolving it in ether. The yield of the purified deuterio olefin was 7%.

1-Bromoöctane-2d_2 (II).—Heptanol-1-1d_2 was prepared in 94% yield as described for octanol-1-1d_2 employing 198 g. (1.25 moles) of ethyl *n*-heptanoate (b.p. 75–78° at 15 mm., $n^{15}\mathrm{D}$ 1.4148), 145 g. (6.25 gram atoms) of sodium and 375 g. (6.25 moles) of deuterioacetic acid. The deuterated alcohol boiled at 82–85° at 16–18 mm., $n^{22.4}\mathrm{D}$ 1.4228, reported[21] $n^{25}\mathrm{D}$ 1.4222.

Heptanol-1-1d_2 (135 g., 1.17 moles) was converted by hydrogen bromide[2] in 92% yield to 1-bromoheptane-1d_2, b.p. 71.5–73.5° at 17–20 mm., $n^{25}\mathrm{D}$ 1.4480; reported b.p. 70.6° at 19 mm., $n^{25}\mathrm{D}$ 1.4480.[23]

1-Bromoheptane-1d_2 (192 g., 1.07 moles) was converted to its Grignard reagent employing 28.2 g. (1.16 gram atoms) of magnesium. This Grignard reagent was then treated with gaseous formaldehyde as described for the synthesis of cyclohexylcarbinol[24] to form octanol-1-2d_2 in 83% yield. The product boiled at 96–100° at 19 mm., $n^{25}\mathrm{D}$ 1.4273. See octanol-1-1d_2 above for the reported physical constants.

Octanol-1-2d_2 (116 g., 0.89 mole) was converted by hydrogen bromide[2] in 92% yield (158 g.) to 1-bromoöctane-2d_2 (II), b.p. 89.0–93.0° at 20 mm., $n^{25}\mathrm{D}$ 1.4501, reported[25] $n^{25}\mathrm{D}$ 1.4503. The product contained 1.86 ± 0.02 D per molecule.

Reaction of 1-bromoöctane-2d_2 (II) with potassium amide was carried out essentially as described above for bromide I.

The olefinic product obtained in 6% yield employing ether as solvent boiled at 63.5–64.0° at 103 mm., $n^{25}\mathrm{D}$ 1.4062, reported[26] $n^{25}\mathrm{D}$ 1.4062. Its deuterium content was 1.04 ± 0.02 D per molecule.

The olefinic product obtained in 3% yield without employing ether as solvent boiled at 64.5° at 110 mm., $n^{20}\mathrm{D}$ 1.4089,[26] $n^{25}\mathrm{D}$ 1.4065; reported $n^{25}\mathrm{D}$ 1.4087,[26] $n^{25}\mathrm{D}$ 1.4062.[26] Its deuterium content was 1.06 ± 0.02 D per molecule.

DURHAM, N. C.

---

sodium ethoxide; W. G. Brown and K. Eberly, THIS JOURNAL, **62**. 113 (1940). However, appreciable hydrogen–deuterium exchange seems unlikely under the present conditions, since care was taken to maintain an acidic medium throughout the reduction.

(8) Boiling points are uncorrected. Reported physical constants in the case of the deuterated compounds are for the undeuterated analogs. Refractive indices were measured on a thermostated Abbé refractometer.

(9) Deuterium analysis was accomplished by combustion of the purified deuterio compounds over hot copper oxide and measurement of the deuterium oxide content of the resulting purified water by the interferometer method; see ref. 2; R. H. Crist, G. M. Murphy and H. C. Urey, *J. Chem. Phys.*, **2**, 112 (1934); I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," edited by H. C. Urey and G. M. Murphy, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, 1st ed., pp. 348–370.

(10) This treatment was assumed to have rid the anhydride of any moisture and acetic acid that might have been present.

(11) K. J. P. Orton and M. Jones, *J. Chem. Soc.*, **101**, 1721 (1912).

(12) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. I, p. 7.

(13) J. H. Walton and L. L. Withrow, THIS JOURNAL, **45**, 2689 (1923).

(14) Care should be taken that the deuterolysis of the anhydride does not become too violent.

(15) See ref. 12, p. 6.

(16) Beilstein's "Handbuch der organischen Chemie," Julius Springer, Berlin, 1942, Vol. E II, 2, p. 98.

(17) In most experiments the deuterioacetic acid was not distilled but was used directly in the Prins reduction assuming that it had been formed quantitatively from the anhydride.

(18) H. J. Prins, *Rec. trav. chim.*, **42**, 1050 (1923).

(19) Reference 12, Vol. IV, p. 13.

(20) L. M. Ellis and E. E. Reid, THIS JOURNAL, **54**, 1674 (1932).

(21) See C. R. Hauser and T. M. Harris, *ibid*, **80**, 6360 (1958).

(22) Blank experiments with undeuterated *n*-octyl bromide indicated that the reaction was essentially complete after this time.

(23) Reference 12, Vol. I, p. 329.

(24) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 2nd. ed., John Wiley and Sons, Inc., New York, N. Y., 1932, p. 188.

(25) Reference 12, Vol. IV, p. 14.

(26) Reference 12, Vol. IV, p. 11.