[Contribution from the Department of Chemistry, Duke University]

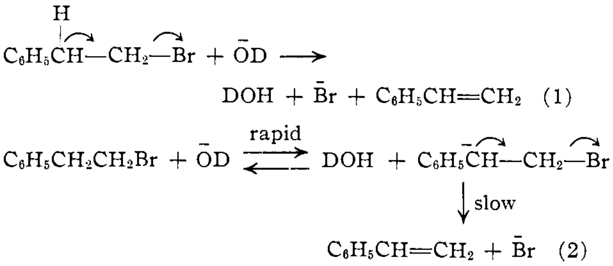
Mechanism of β-Elimination with Alkyl Halides and Bases Using Deuterium as Tracer[1]

By Douglas G. Hill, Beverly Stewart, Simon W. Kantor, William A. Judge and Charles R. Hauser

Received May 13, 1954

The β-elimination reactions of β-phenylethyl bromide with sodium deuteroxide in CH_3OD and D_2O and of 2-ethylbutyl bromide-2d_1 with potassium amide in liquid ammonia are shown to take place without being accompanied by hydrogen–deuterium exchange and deuterium–hydrogen exchange, respectively. These results support the bimolecular mechanism E2 in which the proton (or deuteron) and halide ion are eliminated simultaneously.

The β-elimination reaction of β-phenylethyl bromide, which exhibits second-order kinetics with sodium ethoxide,[2] has been shown to take place with sodium hydroxide and sodium deuteroxide in aqueous ethanol containing 34 mole % of exchangeable deuterium without being accompanied by hydrogen–deuterium exchange.[3] This result has now been confirmed with sodium deuteroxide in CH_3OD and D_2O in which medium the possible hydrogen–deuterium exchange should be more readily detected. Even under these conditions the halide recovered after partial β-elimination contained no deuterium. These results are in agreement with the bimolecular mechanism (E2)[4] involving the simultaneous removal of the proton and halide ion (equation 1) but not with the alternative mechanism in which the proton is first removed in a rapid and reversible acid–base reaction (equation 2).[5] Had the second mechanism been operative, the intermediate carbanion should have acquired some deuterium from the solvent since, although the by-product, DOH, is a stronger acid than D_2O,[6] the latter was present in excess. Of course the failure to observe hydrogen–deuterium exchange does not rule out a third possible mechanism, involving the relatively slow removal of the proton and relatively rapid elimination of halide ion, which evidently operates in certain *cis* eliminations.[7] However, this mechanism seems unlikely in most *trans* β-elimination reactions of halides which are concerted processes.[8]



$$C_6H_5\overset{H}{C}H{-}CH_2{-}Br + \bar{O}D \longrightarrow DOH + \bar{Br} + C_6H_5CH{=}CH_2 \quad (1)$$

$$C_6H_5CH_2CH_2Br + \bar{O}D \xrightleftharpoons{\text{rapid}} DOH + C_6H_5\bar{C}H{-}CH_2{-}Br \xrightarrow{\text{slow}} C_6H_5CH{=}CH_2 + \bar{Br} \quad (2)$$

Since hydrogen compounds are more acidic than corresponding deuterium compounds,[6] a more conclusive isotopic test would be to determine whether deuterium–hydrogen exchange occurs during β-elimination of deuterium halide from a β-deuterated halide by an undeuterated base and its conjugate acid. For this purpose 2-ethylbutyl bromide-2d_1 (I) was prepared as represented by transformation A. The α-hydrogen of ethyl diethylacetate was substituted by deuterium by allowing the ester to react with a slight excess of sodium triphenylmethide in ether for 24 hours at room temperatures and then adding excess deuterium oxide. Evidently this acid–base reaction proceeds slowly, since in an earlier experiment[9] the deuterated ester containing only 0.72 D per molecule was obtained on adding the deuterium oxide after two hours. At this time some of the reagent was still present as indicated by the red color. As can be seen from transformation A the deuterated ester was converted through the alcohol to bromide without loss of deuterium. The slightly low value for deuterium in the intermediate alcohol may be ascribed to the incomplete combustion of this compound (some tar remained in the combustion tube).

Transformation A

$$(C_2H_5)_2CHCOOC_2H_5 \xrightarrow{(C_6H_5)_3CNa} [(C_2H_5)_2CCOOC_2H_5]Na \xrightarrow{D_2O} \underset{(0.98\ \mathrm{D/mole})}{(C_2H_5)_2CDCOOC_2H_5} \xrightarrow[\mathrm{AcOH}]{\mathrm{Na}} \underset{(0.96\ \mathrm{D/mole})}{(C_2H_5)_2CDCH_2OH} \xrightarrow{\mathrm{HBr}} \underset{\substack{\mathrm{I}\\(0.98\ \mathrm{D/mole})}}{(C_2H_5)_2CDCH_2Br}$$

The isotopic test with deuterated bromide I was carried out with potassium amide in liquid ammonia with which the undeuterated halide has been shown to yield mainly 2-ethylbutene-1 and only a little 2-ethylbutylamine.[10] The reaction was stopped before completion by the addition of solid ammonium chloride, and some of the halide recovered and analyzed for deuterium. The deuterium

---

[1] Supported in part by the Office of Naval Research.

[2] E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

[3] P. S. Skell and C. R. Hauser, This Journal, **67**, 1661 (1945).

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 423.

[5] Although the carbanion shown in equation 2 is not an intermediate, the corresponding carbanions from β-phenylethyl methyl ether and β,β-diphenylethyl methyl ether appear to be intermediates in β-eliminations with these ethers and potassium amide. The evidence will be published later.

[6] In general hydrogen compounds are several times more acidic than the corresponding deutero compounds; see especially C. L. Wilson, *J. Chem. Soc.*, 1550 (1936), and W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934).

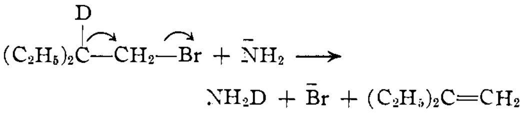
[7] S. J. Cristol, N. L. Hause and J. S. Meek, This Journal, **73**, 674 (1951); S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

[8] *Cf.* S. J. Cristol, *ibid.*, **69**, 338 (1947); C. G. Swain and R. W. Eddy, *ibid.*, **70**, 2989 (1948); C. K. Ingold and co-workers, *J. Chem. Soc.*, 2093 (1948).

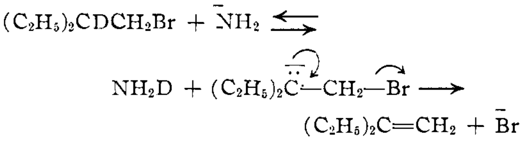
[9] D. G. Hill, W. A. Judge, P. S. Skell, W. W. Kantor and C. R. Hauser, This Journal, **74**, 5599 (1952).

[10] R. N. Shreve and L. W. Rothenberger (*Ind. Eng. Chem.*, **29**, 1361 (1937)) reported a 75% yield of the olefin and a 4% yield of the amine. We obtained a 55% yield of the olefin and some amine and recovered halide on stopping the reaction after only 14 minutes (see Experimental).

content of the recovered halide was 0.97 D per molecule which is within the limits of experimental error[11] for that of the original halide (0.98 D per molecule). This lack of deuterium–hydrogen exchange[12] furnishes strong evidence for the simultaneous elimination of the deuteron and halide ion (equation 3), for if the intermediate carbanions were formed (equation 4) it should have acquired hydrogen from the medium[6] unless of course the less likely third possible mechanism mentioned above were operative. The similar β-elimination of deuterium bromide from *n*-octyl bromide-2*d*₂ without deuterium–hydrogen exchange was reported recently,[9] although this β-elimination appeared to be accompanied by some α-elimination and rearrangement[13]; moreover, the main reaction involved displacement to form the corresponding amine.



$$(C_2H_5)_2\overset{D}{\overset{|}{C}}\text{—}CH_2\text{—}Br + \bar{N}H_2 \longrightarrow NH_2D + \bar{B}r + (C_2H_5)_2C{=}CH_2 \quad (3)$$



$$(C_2H_5)_2CDCH_2Br + \bar{N}H_2 \rightleftarrows NH_2D + (C_2H_5)_2\overset{\overline{\cdot\cdot}}{C}\text{—}CH_2\text{—}Br \longrightarrow (C_2H_5)_2C{=}CH_2 + \bar{B}r \quad (4)$$

The deuterium content of the olefin from this reaction was 0.03 D per molecule which may be considered as zero within the limits of experimental error.[11,14] This result confirms the experimental evidence presented recently[9] that the olefin from 2-ethylbutyl bromide with potassium amide is formed exclusively through β-elimination as has been assumed, not by α-elimination accompanied by the shift of the deuterium (or hydrogen) from the β- to the α-carbon atom.

Experimental[15]

Methanol-*d*.—Commercial sodium methoxide (containing small amounts of sodium hydroxide and sodium carbonate) supplied by the Mathieson Co. was freed from traces of methanol by heating at 170° for 6 hours *in vacuo*. Titration of the resulting free-flowing powder indicated a purity of 87% sodium methoxide. To 125 g. of this reagent (containing approximately 2 moles of sodium methoxide) was added 42.2 g. (2.1 moles) of deuterium oxide (99.8%) and the resulting paste was stirred and refluxed for 4 hours. The liberated deuteromethanol was driven off *in vacuo* (1 mm.) and collected in a Dry Ice trap, the residue finally being heated at 180° for 3.5 hours; total deuteromethanol, 61.5 g. (93%). Drying over calcium oxide followed by potassium carbonate gave 44.2 g. (67%) of pure deuteromethanol, b.p. 66–67°, $n^{19.5}$D 1.3281 (reported for methanol, n^{25}D 1.3276).[16]

β-Phenylethyl Bromide with Sodium Deuteroxide in Methanol-*d*.—To a solution of sodium methoxide prepared from 3.0 g (0.13 mole) of sodium in 42.0 g. (1.27 moles) of methanol-*d* was added 6.0 g. (0.30 mole) of deuterium oxide. The resulting solution had the following composition (moles): 1.27, CH_3OD; 0.13, NaOD; and 0.17, D_2O. To this well-stirred solution was added 24.1 g. (0.13 mole) of β-phenylethyl bromide (b.p. 90–90.5° at 10 mm., n^{21}D 1.5566) and the stirring continued for 2.17 hours. Water was added and the mixture extracted with ether. The solvent was distilled from the dried ethereal solution and the residue fractionated to give 2.9 g (22%) of styrene, b.p. 54.5–55° at 29 mm., $n^{24.5}$D 1.5430 (lit. values: b.p. 52–53° 28 mm. n^{20}D 1.5462)[17] and 13.2 g. (55%) of β-phenylethyl bromide, b.p. 91–91.5° at 10.5 mm., $n^{24.5}$D 1.5539. This recovered bromide did not contain any deuterium (D analysis, 0.00 ± 0.02 atom % D per molecule). The method used for deuterium analysis has been described.[9]

Ethyl Diethylacetate-2*d*₁.—To a solution of 0.89 mole of sodium triphenylmethide[18] in 1800 ml. of ether in a 2-l. standard taper bottle was added under nitrogen 123 g. (0.85 mole) of ethyl diethylacetate (b.p. 150–151°, n^{25}D 1.4014), and the mixture allowed to stand at room temperature with occasional shaking. The deep red color of the reagent was only partly discharged after 4 hours. After 24 hours when the mixture had become gray, 19 ml. (0.95 mole) of 99.8% deuterium oxide was added in an atmosphere of nitrogen. The deuterium oxide had been measured and transferred to the dropping funnel in a dry-box. The mixture was shaken, and allowed to stand 5 hours. The ether solution was decanted from the solid and washed with cold water. After drying over Drierite, the solvent was distilled on the steam-bath and the residue cooled in an ice-bath. The liquid was decanted from the solid triphenylmethane and distilled to give 81 g. (68%) of the deuterated ester, b.p. 150–152°. containing 0.98 D per molecule.

2-Ethylbutanol-2*d*₁.—To a stirred solution of 116 g. (0.75 mole) of ethyl diethylacetate-2*d*₁ and a little phenolphthalein powder as indicator in 2.5 l. of anhydrous ether, cooled with an ice–salt-bath, was added gradually during 2 hours 230 g. (3.75 moles) of redistilled glacial acetic acid (b.p. 117°) and 86.3 g. (3.75 moles) of sodium, keeping the mixture slightly acidic and below 10°.[19] The mixture was stirred 60 hours and then shaken with cold water. After removing the ether from the organic layer and refluxing the residue with methanolic (270 ml.) potassium hydroxide (42 g.), there was obtained 49 g. (53%) of 2-ethylbutanol-2*d*₁, b.p. 144–146°, containing 0.96 D per molecule; reported b.p. for the undeuterated alcohol, 147–147.6°.[20]

2-Ethylbutyl Bromide-2*d*₁.—2-Ethylbutanol-2*d* (41 g., 0.4 mole) was treated with hydrogen bromide (prepared from 0.62 mole of bromine and tetralin) at 100° as described previously for *n*-dodecyl alcohol.[21] After removing unreacted alcohol by extraction with cold 95% sulfuric acid, water was added, followed by ammonium hydroxide until basic to phenolphthalein. The organic layer was dried over Drierite and distilled to give 43 g. (66%) of the deuterated bromide, b.p. 143–145°, n^{22}D 1.4495, containing 0.98 D per molecule; reported b.p. for the undeuterated bromide, 143–144°, n^{25}D 1.4490.[20]

2-Ethylbutyl Bromide-2*d*₁ with Potassium Amide in Liquid Ammonia.—To a stirred solution of 0.3 mole of potassium amide in 250 ml. of liquid ammonia[9] was added within 1.5 minutes 36.5 g. (0.22 mole) of 2-ethylbutyl bromide-2*d*₁. After 10 minutes, excess (21 g.) solid ammonium chloride was added, followed by crushed ice and water, and most of the ammonia allowed to evaporate while the flask was immersed in an ice–salt-bath (in order to minimize

---

(11) The probable limits of experimental error in the method employed were recently (ref. 9) estimated to be ±0.02 D per molecule.

(12) In an earlier experiment with a mixture of the deuterated and undeuterated bromide (ref. 9), the deuterium content of the recovered halide was actually greater than that of the original mixture; this increase in deuterium content resulted presumably from the preferential β-elimination of hydrogen halide in the undeuterated molecule.

(13) In a further study in this Laboratory of the elimination reaction of *n*-octyl bromide-1*d*₂ with potassium amide in the absence of ether, exclusive β-elimination was observed. A thorough investigation of the reaction is being undertaken.

(14) If the trace of deuterium in the olefin is considered as real it is probably to be accounted for by a rearrangement of deuterium from the β- to the α-carbon atom in the conversion of the alcohol to the bromide (see transformation A). This would form the tertiary halide, $(C_2H_5)_2CBrCH_2D$, in which the hydrogen would enter into β-elimination preferentially to deuterium.

(15) Melting points and boiling points are uncorrected.

(16) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, p. 291, Oxford Press, 1953.

(17) I. M. Heilbron, *ibid.*, Vol. IV, p. 379.

(18) "Organic Syntheses," Collective Vol. II, p. 607.

(19) *Cf.* H. J. Prins, *Rec. trav. chim.*, **42**, 1050 (1923), and ref. 9.

(20) H. A. Shonle, J. H. Waldo, A. K. Keltch and H. W. Coles, This Journal, **58**, 585 (1936).

(21) E. E. Reid, J. R. Ruhoff and R. E. Burnett, *Org. Syntheses*, **15**, 24 (1935).

loss of the volatile olefin). The organic layer was extracted with dilute hydrochloric acid, followed by water and dried over Drierite. It was distilled to give 4.7 g. (26%) of 2-ethylbutene-1, b.p. 62–64°, $n^{25}D$ 1.3960, and 2.7 g. (7.6%) of recovered 2-ethylbutyl bromide-2d_1, b.p. 70–75° at 59 mm., $n^{25}D$ 1.4495. The olefin contained 0.03 D per molecule, and the recovered halide, 0.97 D per molecule.

In a preliminary experiment with the undeuterated bromide (stopped after 15 minutes), there were obtained 12 g. (55%) of 2-ethylbutene-1, b.p. 65–70° (reported 66.2–66.7°[22]), $n^{25}D$ 1.3950, and 1.7 g. (4.2%) of recovered halide, b.p. 144–145°, $n^{25}D$ 1.4495. The yield of olefin calculated on the basis of the reacted halide was 61%. On making the acid extract alkaline and adding benzenesulfonyl chloride, there was isolated in approximately 15% yield N-2-ethylbutylbenzenesulfonamide, m.p. 151–152°.

---

[22] S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1751 (1939).

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Acid Dissociation Constants and Saponification Rate Constants for Some 1-Naphthoic and Thenoic Acid Derivatives

BY CHARLES C. PRICE,[1] EDWIN C. MERTZ[2] AND JOHN WILSON

RECEIVED MAY 13, 1954

Dissociation constants in 78% ethanol for several 1-naphthoic and thenoic acids are reported. The rates of saponification of the corresponding esters in 70% dioxane are also reported. These data are interpreted satisfactorily in terms of the Hammett equation only by referring the data to the unsubstituted 1-naphthoic or 2-thenoic acid, respectively, apparently due to important steric factors in the saponification reaction arising from the *peri*-hydrogen or the adjacent sulfur atom, respectively.

The work reported herein is part of a general program to evaluate the influence of substituents on reactivity in the naphthalene and thiophene nuclei.[3]

The data on acid dissociation constants in 78% ethanol and on ethyl ester saponification in 70% dioxane are summarized in Table II.

Experimental

The properties of the acids used for pK_a determination are summarized in Table I. The methods of preparation are described in the references cited.

TABLE I

PROPERTIES OF ACIDS AND ETHYL ESTERS

Acid	Acid M.p., °C.	Acid Liter.	Ester B.p. °C.	Ester B.p. Mm.	Ester $n^{20}D$ or m.p., °C.	Ester Lit. b.p. (mm.) or m.p., °C.
1-Naphthoic	161.5	161[a]	127–128	0.9	1.5940	
4-Cl-1-Naphthoic[b]	223.5–224	224[b]	156–157	1.3	m. 25.5–27	......
7-Cl-1-Naphthoic[c]	238–240	233.6,[c] 242[d]			m. 44.5	......
4-NO_2-1-Naphthoic[e]	223.5–224	227[e]			m. 57.5	58[e]
5-NO_2-1-Naphthoic[f]	237–238	239[f]			m. 92	92[m]
2-Thenoic	126–127	127[g]	71	1.0	1.5262	96 (18)[n]
5-CH_3-2-Thenoic	138–139.5	138.5[h]	87	1.0	1.5247	89 (5)[o]
5-NO_2-2-Thenoic	158	158[i]			m. 64	64[i]
5-Cl-2-Thenoic	145–146	147[j]	75	0.3	1.5376	......
3-Thenoic[k]	136	138[l]	82	2.3	1.5219	208 (73)[l]

[a] H. Gilman, N. B. St. John and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 425. [b] T. L. Jacobs, S. Winstein, J. W. Ralls and J. H. Robson, *J. Org. Chem.*, 11, 27 (1946). [c] T. L. Jacobs, S. Winstein, R. B. Henderson, J. Bond, J. W. Ralls, D. Seymour and W. H. Florsheim, *ibid.*, 11, 229 (1946). [d] C. D. Hurd, O. E. Fancher and W. B. Bonner, *ibid.*, 12, 369 (1947). [e] G. J. Leuck, R. P. Perkins and F. C. Whitmore, THIS JOURNAL, **51**, 1834 (1929). [f] A. G. Eckstrand, *J. prakt. Chem.*, [2] **38**, 159 (1888). [g] P. Schorigin, *Ber.*, **43**, 1942 (1910); H. D. Hartough and L. G. Conley, THIS JOURNAL, **69**, 3096 (1947), report m.p. 129–130°. [h] J. W. Schick and H. D. Hartough, *ibid.*, **70**, 1645 (1948). [i] O. Dann, *Ber.*, **76**, 419 (1943). [j] J. W. Schick and H. D. Hartough, THIS JOURNAL, **70**, 286 (1948). [k] We are indebted to Dr. E. E. Campaigne of Indiana University for a sample of this acid. [l] E. E. Campaigne and W. M. LeSuer, THIS JOURNAL, **70**, 1555 (1948). [m] A. G. Eckstrand, *Ber.*, **12**, 1395 (1879). [n] W. Schlenk and R. Ochs, *ibid.*, **48**, 679 (1915). [o] H. G. Gross and E. E. Campaigne, THIS JOURNAL, **71**, 3258 (1949).

The esters were prepared by Fisher esterification and their properties are also summarized in Table I.

The approximate dissociation constants for the acids were taken as the pH of a 0.005 N solution in 78.1% ethanol, exactly half-neutralized with sodium hydroxide. The value of the Hammett reaction constant[4] for dissociation in this solvent (σ 2.07) was determined from the pK_a for benzoic (6.37), *p*-toluic (6.74) and *p*-chlorobenzoic (5.94) acids, using as σ-constants Hammett's values (for *p*-methyl, σ -0.170; for *p*-chloro, σ 0.227). Results are summarized in Table II.

The saponification rate constants were determined as previously[3] and are also summarized in Table II.

The values in Table I labeled σ_a and σ_s are the values of Hammett's substituent constant σ, calculated from acid dissociation and saponification rate, respectively, referred back to benzene. The values labeled σ'_a and σ'_s are the same values referred back to the parent acid, 1-naphthoic or 2-thenoic, respectively.

Discussion

As might have been expected because it is to be considered an *ortho*-substituted ester, the ester of 1-

---

[1] Department of Chemistry, University of Pennsylvania, Phila. 4, Pa.

[2] AEC Fellow 1948–1950; American Cyanamid Fellow 1950–1951. Abstracted from the Ph.D. dissertation of E. C. M., June, 1954.

[3] For the preceding paper, see C. C. Price and R. H. Michel, THIS JOURNAL, **74**, 3652 (1952).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 184–192.