Amines Derived from Dihalopropenes. III.[1a] Dehydrobromination of *cis*- and *trans*-N-(3-Bromoallyl)-*n*-butylamine[1b,c]

ALBERT T. BOTTINI, BARBARA J. KING, AND JAMES M. LUCAS

Chemistry Department, University of California, Davis, California

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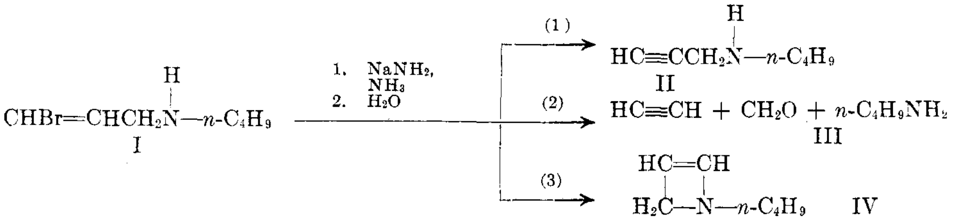
The reactions of *cis*- and *trans*-N-(3-bromallyl)-*n*-butylamine (*cis*- and *trans*-I) with sodium amide in liquid ammonia were investigated because it appeared that these reactions could proceed by one or more of at least three routes. These routes included β-elimination (1), which would yield N-*n*-butylpropargylamine (II), β-fragmentation (2), which would yield acetylene, formaldehyde, and *n*-butylamine (III), and cyclization (3), which would yield N-*n*-butylazetine (IV).



Path 1 appeared to be the most probable for *cis*-I because of the favorable *trans* arrangement of the bromine and the β-hydrogen, but the large rate difference observed for *cis*- and *trans*-dehydrohalogenations across double bonds[2] indicated that path 1 might not be the most favorable for *trans*-I. A β-fragmentation reaction of *trans*-I appeared to be plausible because of the *trans* arrangement of the bromine and the carbon–carbon bond that would be broken,[3] and because 3-chloroallyl alcohol has been observed to yield the products expected of a β-fragmentation reaction.[4a] When this work was undertaken, the cyclization reaction 3 could not be ruled out as a possibility because of the formation of allenimines (2-methyleneaziridines) by the reaction of N-(2-bromoallyl)alkylamines with sodium amide in liquid ammonia.[5] Allenimines are now known to be formed *via* an elimination–addition mechanism involving an allenic amine intermediate.[6]

1,3-Dibromopropene was prepared by treatment of 1-bromopropene with N-bromosuccinimide. *cis*-Enriched 1,3 - dibromopropene and *trans* - 1,3-dibromopropene were separated as described by Hatch and Harwell,[7] and *cis*-enriched I and *trans*-I were prepared by reaction of *n*-butylamine with the corresponding dibromide. *cis*- and *trans*-I, when treated with sodium amide in liquid ammonia, yielded only N-*n*-butylproparglyamine (II), the product of β-elimination. Yields were good, and no evidence was obtained by use of gas-liquid partition chromatography (GLPC) that indicated formation of any III or IV. Thus, no evidence was obtained to indicate that the β-fragmentation reaction 2 or the ring-closure reaction 3 occurs under the reaction conditions.

It seems reasonable that the rapid dehydrobromination of *trans*-I to II can occur by either a *cis*-dehydrobromination across a double bond or by initial isomerization of *trans*-I to *cis*-I followed by *trans*-dehydrobromination. It is noteworthy that certain vinyl halides, when treated with a strong base, undergo *cis*-dehydrohalogenation across the double bond,[8a] and that sodium amide in liquid ammonia is capable of causing rapid *cis*-type dehydrobromination across an aromatic bond.[8b]

trans-I is stable when treated with sodium hydroxide in aqueous dioxane at 77.2°; under similar conditions, *cis*-I dehydrobrominates rapidly. The reaction of *cis*-I and sodium hydroxide in 50% aqueous dioxane follows good second-order kinetics at 61.4 and 77.2°. The second-order rate constants and the thermodynamic data are given in Table I. In the absence of sodium hydroxide, both *cis*- and *trans*-I were found to be stable at 77.2° in aqueous dioxane for forty-eight hours. Heating an aqueous dioxane solution of *trans*-I containing an excess of sodium hydroxide at 100° for forty-eight hours yielded 8% of the theoretical amount of bromide ion. Because of the small yield, the path by which the bromide ion was produced from *trans*-I was not determined.

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[1] (a) Paper II, A. T. Bottini and V. Dev, *J. Org. Chem.*, **27**, 968 (1962); (b) taken in part from the M.S. thesis of J. M. L., University of California, Davis, 1961; (c) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

[3] A. T. Bottini, C. A. Grob, and E. Schumacher, *Chem. Ind.* (London), 757 (1958).

[4] (a) L. F. Hatch and A. C. Moore, *J. Am. Chem. Soc.*, **66**, 285 (1944), reported that treatment of *trans*-3-chloroallyl alcohol[4b] with sodium hydroxide solution at temperatures between 102 and 117° gave acetylene and formate but no propargyl alcohol. Under the same conditions, *cis*-3-chloroallyl alcohol[4b] gave fair to good yields of propargyl alcohol. It is doubtful that any significant amounts of acetylene and formate were formed by decomposition of propargyl alcohol[4c]; (b) L. F. Hatch and R. H. Perry, Jr., *ibid.*, **71**, 3262 (1949); (c) *cf.* A. F. Thompson, Jr., and C. Margnetti, *ibid.* **64**, 573 (1942).

[5] C. B. Pollard and R. F. Parcell, *ibid.*, **73**, 2925 (1951); A. T. Bottini and J. D. Roberts, *ibid.*, **79**, 1462 (1957).

[6] A. T. Bottini and R. E. Olsen, *ibid.*, **84**, 195 (1962).

[7] L. F. Hatch and K. E. Harwell, *ibid.*, **75**, 6002 (1953).

[8] (a) L. K. Montgomery and J. D. Roberts, *ibid.*, **82**, 4750 (1960); (b) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956); J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, and D. A. Semenow, *ibid.*, **78**, 611 (1956).

TABLE I

BIMOLECULAR RATE CONSTANTS AND THERMODYNAMIC DATA FOR DEHYDROBROMINATION OF *cis*-I BY SODIUM HYDROXIDE IN 50% AQUEOUS DIOXANE

Temp., °C.	Initial concentrations, M (*cis*-I)	NaOH	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$	ΔE^*, kcal./mole	$\Delta S^*_{61.4°}$, e.u.
61.4	0.0175	0.0387	1.29 ± 0.06	23.7	−5.9
77.2	.0173	.0387	6.40 ± 0.08		
61.4	.0177	.0645	1.25 ± 0.06	24.2	−4.5
77.2	.0176	.0645	6.44 ± 0.09		

The large difference in reactivity of sodium hydroxide with *cis*-I and *trans*-I allowed the isolation of essentially pure *trans*-I from a mixture of N-(3-bromoallyl)-*n*-butylamines that had been treated with sodium hydroxide in aqueous ethanol.

The difference in reactivity of *trans*-I with sodium amide in liquid ammonia and with sodium hydroxide in a partially aqueous solvent is reminiscent of the behavior of the bromotoluenes. For example, *p*-bromotoluene undergoes rapid dehydrobromination when treated with sodium amide in liquid ammonia at −33°,[8] but treatment with aqueous sodium hydroxide requires a temperature of 340° to effect dehydrobromination.[9]

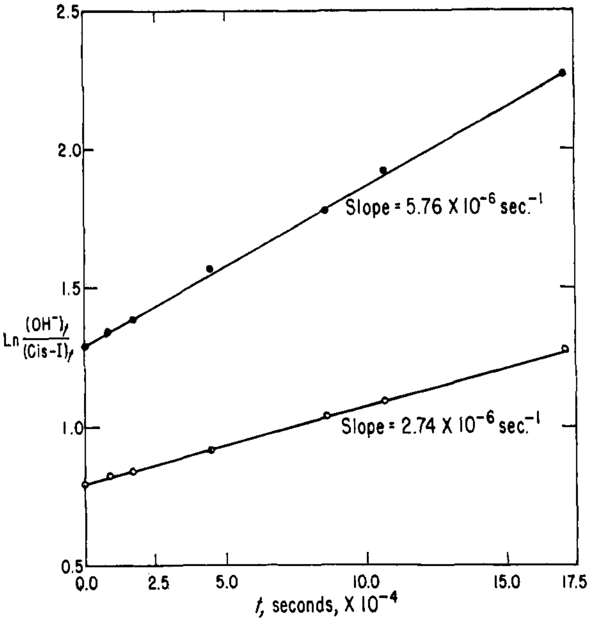

Fig. 1.—Dehydrobromination of *cis*-N-(3-bromoallyl)-*n*-butylamine (*cis*-I) in 50% aqueous dioxane at 61.4°. Initial concentrations: *cis*-I = 0.0175, NaOH = 0.0387 (○—○); *cis*-I = 0.0177, NaOH = 0.645 (●—●). The slope is equal to $k_2[(\text{OH}^-)_0 - (cis\text{-I})_0]$.

Experimental[10]

***cis*- and *trans*-1,3-Dibromopropene.**—Redistilled, commercial 1-bromopropene (Columbia Organic Chemical Co., Inc.) was converted to a mixture of *cis*- and *trans*- 1,3-dibromopropene, b.p. 62–69° (30 mm.), in 59% yield by the method used for the preparation of 4-bromo-2-heptene.[11] A mixture of 300 g. of the isomers was redistilled through a 1000 × 13 mm. column packed with glass helices, and the fraction with b.p. 60–61° (25 mm.), $n^{25}\text{D}$ 1.5525, was used for the preparation of *cis*-enriched I; lit.,[7] b.p. 60° (25 mm.), $n^{25}\text{D}$ 1.5516 for *cis*-1,3-dibromopropene. The fraction enriched with *trans*-I (55 g., b.p. 65–66° at 25 mm.) was taken up in ether and cooled to −77°. The crystalline material that separated was recrystallized from ether, allowed to melt, and freed of ether by vacuum distillation. The purified *trans*-I (9.0 g.) had $n^{25}\text{D}$ 1.5570; lit.,[7] b.p. 66° (25 mm.), $n^{25}\text{D}$ 1.5466.

***cis*-Enriched N-(3-Bromoallyl)-*n*-butylamine (I).**—To a stirred solution of 110 g. (1.50 moles) of *n*-butylamine and 150 ml. of ether held at 34–45° was added dropwise 100 g. (0.50 mole) of *cis*-enriched 1,3-dibromopropene. When the addition was complete, stirring at 45–50° was continued for 3 hr., and the reaction mixture was allowed to stand overnight. The amine hydrobromide, which began to separate during the addition of the dibromopropene, was removed by filtration, and the filtrate was washed with 1 *N* potassium hydroxide solution. The organic phase was dried over potassium hydroxide and distilled to yield 43 g. (45%) of *cis*-enriched I, b.p. 82–84° (7 mm.), $n^{25}\text{D}$ 1.4757.

Anal. Calcd. for $C_7H_{14}BrN$: C, 43.76; H, 7.34; N, 7.29. Found: C, 44.02; H, 7.51; N, 7.30.

The product, which consisted of 72% *cis*-I and 28% *trans*-I as determined by dehydrobromination with sodium hydroxide in aqueous dioxane, yielded a *p*-bromobenzenesulfonamide, which had a melting point of 49–50° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{17}Br_2NO_2S$: C, 37.98; H, 4.17. Found: C, 38.19; H, 4.55.

trans-I.—A. Using the method described for the preparation of *cis*-enriched I, 5.33 g. (0.027 mole) of *trans*-1,3-dibromopropene was converted to 2.32 g. (46%) of *trans*-I, b.p. 60–65° (2 mm.), $n^{25}\text{D}$ 1.4781.

Anal. Calcd. for $C_7H_{14}BrN$: C, 43.76; H, 7.34; N, 7.29. Found: C, 44.32; H, 7.46; N, 7.60.

The *p*-bromobenzenesulfonamide had a melting point of 144–146° after recrystallization from methanol.

Anal. Calcd. for $C_{13}H_{17}Br_2NO_2S$: C, 37.97; H, 4.17. Found: C, 38.22; H, 4.35.

The infrared spectrum of *trans*-I differed from that of *cis*-enriched I in that it possessed more intense bands at 942 cm.$^{-1}$, believed due solely to *trans*-I, and virtually no absorption at 1285 cm.$^{-1}$, the frequency of an intense band in the spectrum of *cis*-enriched I.

B. A mixture of 32.8 g. (0.175 mole) of unfractionated I, 20.5 g. (0.51 mole) of sodium hydroxide, and 460 ml. of 50% aqueous ethanol was heated at reflux for 16 hr. The reaction mixture was cooled and made acidic with hydrochloric acid. The resulting solution was concentrated to 150 ml. with a rotary film evaporator and made alkaline with sodium hydroxide solution. The alkaline solution was extracted twice with 50-ml. portions of ether, and the extracts were combined and dried with sodium hydroxide. Fractionation of the ether solution yielded 5.0 g. (27%) of N-*n*-butylpropargylamine (II), b.p. 62–65° (35 mm.), $n^{25}\text{D}$ 1.4382, and 6.8 g. (21% recovery) of *trans*-I, b.p. 62–64° (2 mm.). The infrared spectrum of *trans*-I was superimposable on that of *trans*-I prepared by method A, and the infrared spectrum of II was identical with that of II prepared by dehydrobromination of I with sodium amide in liquid ammonia.

Dehydrobromination of *cis*-Enriched I and *trans*-I with with Sodium Amide in Liquid Ammonia.—To a stirred slurry of 1.5 g. (0.039 mole) of sodium amide and 65 ml. of liquid ammonia was added dropwise 6.7 g. (0.035 mole) of *trans*-I (recovered from the reaction of I with sodium hydroxide), and the reaction mixture was stirred under reflux for 4 hr.

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[9] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1458 (1957).

[10] Boiling points are uncorrected. Infrared spectra were obtained using a Beckman IR-4 spectrophotometer. Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, California, and Drs. Weiler and Strauss, Oxford, England.

[11] F. L. Greenwood, M. D. Kellert, and J. Sedlak, *Org. Syn.*, **38**, 8 (1958).

Ether (20 ml.) and 1.0 ml. of water were added, and the mixture was allowed to stand overnight, during which time the ammonia evaporated. The ether solution was decanted from the solids in the flask, the solids were washed with 20 ml. of ether, and the ether solutions were combined and dried over sodium hydroxide. Most of the ether was removed by distillation through a short, packed column, and the residue was distilled through a semimicro Vigreux column to yield 1.4 g. (65% based on sodium amide) of N-*n*-butylpropargylamine, b.p. 68–70° (102 mm.), $n^{28}\text{D}$ 1.4382.

Anal. Calcd. for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.61; H, 11.72; N, 12.50.

Using essentially the same procedure, 40 g. (0.21 mole) of I (72% *cis* and 28% *trans*) and 9.0 g. (0.23 mole) of sodium amide in 400 ml. of liquid ammonia yielded 9.3 g. (73% based on sodium amide, 39% based on I) of N-*n*-butylpropargylamine, b.p. 66–68° (100 mm.), $n^{28}\text{D}$ 1.4384. The residue was not examined.

Using essentially the same procedure, but with a larger sodium amide/I mole ratio, 30 g. (0.16 mole) of I (72% *cis*-I) and 13.3 g. (0.34 mole) of sodium amide gave 13.5 g. (76%) of N-*n*-butylpropargylamine, b.p. 66–68° (100 mm.), $n^{28}\text{D}$ 1.4384.

The products from the three reactions had identical infrared spectra and identical retention times (344 sec.) on a 1.0 × 200 cm. column packed with nonyl phthalate on firebrick with a flow rate of 110 cc./min. of helium at 120°. GLPC analysis of the concentrated ether solutions from the reactions failed to show the presence of *n*-butylamine (III) or to indicate the presence of IV.

Dehydrobromination of N-(3-Bromoallyl)-*n*-butylamines with Sodium Hydroxide in Aqueous Dioxane.—The reactions of I (*cis* and *trans*) with sodium hydroxide in 50% aqueous dioxane were followed by measuring the bromide ion produced as a function of time. The bromide ion concentration in each aliquot was determined by adding excess standard silver nitrate solution to the cooled acidified aliquot, and titrating the excess silver nitrate with stan ard potassium thiocyanate solution.[12] Prior to carrying out kinetic runs, samples of *cis*-enriched I (0.0251 *M*) and sodium hydroxide (0.06 *M*) were heated at 77.2° for up to 96 hr. The concentration of bromide ion produced was found to remain constant at 0.0070 *M* after 48 hr. Similar treatment of *trans*-I yielded <3% of the theoretical amount of bromide ion in 48 hr. From this, the initial concentration of *cis*-I in *cis*-enriched I was estimated as 72% of the initial concentration of I. Treatment of a 0.0249 *M* solution of I (72% *cis*-I) containing no sodium hydroxide at 77.2° for 48 hr. failed to produce any bromide ion.

Setting the concentration of hydroxide ion, $(\text{OH}^-)_t$, at any time, *t*, equal to the initial hydroxide ion concentration less the bromide ion concentration at *t*, and setting the *cis*-I concentration, $(cis\text{-I})_t$, at *t* equal to the initial *cis*-I concentration less the concentration of bromide ion, good straight line plots were obtained when $\ln [(\text{OH}^-)_t/(cis\text{-I})_t]$ was plotted against *t*. Typical plots are shown in Fig. 1. The second-order rate constant, k_2, was calculated for each experimental point using the integrated rate expression for a second order reaction

$$k_2 = \frac{1}{[(\text{OH}^-)_0 - (cis\text{-I})_0]} \ln \frac{(cis\text{-I})_0\,(\text{OH}^-)_t}{(\text{OH}^-)_0\,(cis\text{-I})_t}$$

The average values for k_2 at 61.4 and 77.2°, together with the calculated Arrhenius energy of activation and the entropy of activation at 61.4° are given in Table I.

Treatment of a 50% aqueous dioxane solution 0.0115 *M* in *trans*-I and 0.065 *M* in sodium hydroxide at 100° for 48 hr. produced 8% of the theoretical amount of bromide ion.

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[12] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, 1940, pp. 42–46.

Isomerization of Bromochlorobenzene Using Aluminum Chloride Catalyst

FLOYD L. BEMAN

Edgar C. Britton Research Laboratory, The Dow Chemical Co., Midland, Michigan

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Leroy[1] (1887) and Copisarow[2] (1921) reported the isomerization and disproportionation of dibromobenzene. Fairbrother and Scott[3] reported the equilibrium constant for disproportionation in the system bromobenzene, benzene, dibromobenzene to be 0.040 at 25° using aluminum bromide as the catalyst.

The equilibrium mixture for the aluminum halide catalyzed isomerization of dichlorobenzene was reported by Angelkort[4] to be 10–15% *o*-, 55–60% *m*-, and 25–30% *p*-. A small amount of disproportionation was also reported. Spryskov and Erykalov[5] found the equilibrium to be 12% *o*-, 55% *m*-, and 33% *p*-.

It is the purpose of this paper to present data to establish the thermodynamic equilibrium for the bromochlorobenzene system catalyzed by aluminum chloride, and to delineate side reactions. Studies of the kinetics of this and related systems are being published currently by Crump and Gornowicz[6] and by Olah, *et al.*[7–9]

Experimental

All boiling points and melting points are uncorrected.

Materials.—The three bromochlorobenzene isomers were prepared and purified for use as infrared standards and to determine the physical properties. *o*-Bromochlorobenzene was synthesized from *o*-bromoaniline [Distillation Products Industries, white label] using the hot procedure Sandmeyer reaction described by Fry and Grote,[10] modified by the substitution of 10 *N* hydrochloric acid for acetic acid. Phenolic impurities were removed by washing the crude product with 2 *N* sodium hydroxide, after which the product was purified by fractional distillation. The product was distilled at 88°/20 mm. to give a yield of 31% based on bromoaniline, and was found to melt at −12.2° (reported freezing point −12.6° −12.1°).[11]

m-Bromochlorobenzene was synthesized from *m*-bromoaniline [Distillation Products Industries, white label] by the procedure described above. The product was distilled at 83°/20 mm. to give a yield of 27.8% based on *m*-bromo-

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[1] A. J. Leroy, *Bull. Soc. Chim. France*, [2] **48**, 211 (1887).

[2] M. Copisarow, *J. Chem. Soc.*, **119**, 442 (1921).

[3] F. Fairbrother and N. Scott, *Chem. Ind.* (London), 998 (1953).

[4] J. W. Angelkort, Canadian Patent 541,673 (1957).

[5] A. A. Spryskov and Yu. G. Erykalov, *Zh. Obsch. Khim.*, **29**, 2798 (1959).

[6] J. W. Crump and G. A. Gornowicz, *J. Am. Chem. Soc.*, in press.

[7] G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, Part 1, *J. Org. Chem.*, **27**, 3441 (1962).

[8] G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, Part 2, *J. Org. Chem.*, **27**, 3449 (1962).

[9] G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, Part 3, *J. Org. Chem.*, **27**, 3455 (1962).

[10] H. S. Fry and I. W. Grote, *J. Am. Chem. Soc.*, **48**, 711 (1926).

[11] Beilstein, 5, Suppl. I, p. 116.