ruvamide-1-C^{14}, as prepared by the method of Anker,[10] were often seriously contaminated with labeled impurities. A chromatographic procedure for the purification of labeled pyruvic acid was devised to facilitate the use of this compound.

After hydrolysis of the labeled pyruvamide to pyruvic acid by heating in 1 *N* HCl for 1 hour at 100°, the material was absorbed on a column of Dowex-1 chloride. The labeled pyruvic acid was chromatographically eluted with gradually increasing concentrations of HCl in an apparatus of the type described by Busch, *et al.*[11] Each successive fraction of the chromatogram was analyzed for pyruvic acid.[12] In these studies with the chromatographic purification of labeled pyruvic acid, approximately 10–40% of the C^{14} in the total sample, depending upon the purity of the pyruvamide used, was eluted with water only from the column of Dowex-1 Cl, 50–85% was recovered in the pyruvic acid peak (5-ml. fractions 25–33), and 5% in the fractions (35–42) following pyruvic acid. At least two other minor C^{14} fractions, preceding and following the pyruvic acid peak, were observed. The fractions containing the labeled pyruvic acid were combined, evaporated at reduced pressure to a small volume and stored in the frozen state. The purified preparations were essentially free of labeled impurities (less than 1%) as shown by volatility studies. Per mole of labeled pyruvic acid, the stored solutions contained approximately ten moles of HCl. When the final acid concentration was adjusted to 1 molar, the preparations were stable over a period of 6 months.

(10) H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1948).

(11) H. Busch, R. B. Hurlbert and V. R. Potter, *ibid.*, **196**, 717 (1952).

(12) T. E. Friedman and G. E. Haugen, *ibid.*, **147**, 415 (1943).

McArdle Memorial Laboratory, Medical School
University of Wisconsin
Madison, Wisconsin

cis–trans Isomerization of 1-Bromo-1-propene and Related Compounds

By Kenneth E. Harwell[1] and Lewis F. Hatch

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Chavanne[2] prepared both *cis*- and *trans*-1-bromo-1-propene in 1914. The configuration of the isomers was assigned on the basis of the lower boiling isomer (*cis*) dehydrobrominating seven times faster at 70° than the higher boiling isomer. Chavanne also noted that on standing at room temperature the density of each isomer approached a common, intermediate value after five days and this action was correctly interpretated as a *cis–trans* isomerization. The observation that the 1-bromo-1-propenes isomerize at room temperature was largely ignored in subsequent investigations of these compounds.[3] Some very precise work has been reported on what may have been a mixture of the two isomers.

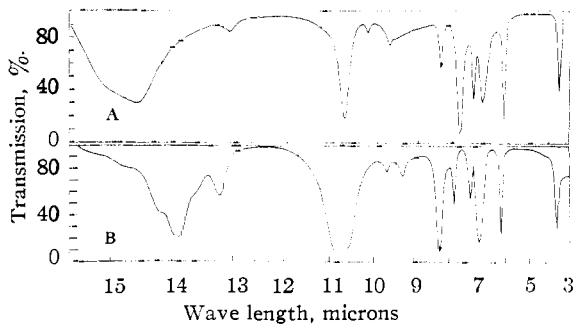

Fig. 1.—Infrared spectra: A, *cis*-1-bromo-1-propene; B, *trans*-1-bromo-1-propene.

(1) Jefferson Chemical Co., Austin, Texas.

(2) G. Chavanne, *Compt. rend.*, **158**, 1698 (1914).

It became necessary to learn more about the isomerization of the 1-bromo-1-propenes when it was planned to use them in the synthesis of a number of related compounds which also exhibit *cis–trans* isomerization.[4] The 1-bromo-1-propenes were prepared along with 2-bromopropene by the dehydrobromination of 1,2-dibromopropane using sodium phenolate. The *cis* and *trans* isomers were separated by low temperature (−18°, −13°) distillation and were stored at temperatures below zero. At these temperatures isomerization in the dark is negligible over a period of a few days.

The characterization and purity of the 1-bromo-1-propenes and the various other *cis–trans* isomers studied were determined by their infrared spectra.[5] All of the *trans* isomers (of 1-bromo-1-propene, 1,3-dibromopropene, 3-bromo-2-propen-1-ol, 1-bromo-3-chloro-1-propene and 1-chloro-1-propene) showed the hydrogen out-of-plane bending band at 10.75 μ which is characteristic of compounds having a halogen and an alkyl or haloalkyl group attached to the carbon–carbon double bond.[6] The *cis* isomers showed a moderately strong, broad hydrogen out-of-plane bending band between 13 and 15 μ which is characteristic of the *cis* configuration. This band was absent in the corresponding *trans* isomers.

The isomeric compounds also showed a consistent shift in the in-plane bending band of the ethylenic hydrogens between the *cis* and *trans* isomers. These bonds are all strong and rather sharp in shape.

	cis	*trans*
1-Bromo-1-propene	7.78	8.32
1,3-Dibromopropene	7.74	8.05
3-Bromo-2-propen-1-ol	7.77	8.10
1-Bromo-3-chloro-1-propene	7.77	8.10
1-Chloro-1-propene	7.65	8.13

Infrared spectra provided an excellent method of analysis for the *cis* and *trans* isomers. The infrared spectra of *cis*- and *trans*-1-bromo-1-propene are shown in Fig. 1 and these show a small amount of cross-contamination. The wave lengths used for analysis were 7.78, 7.87, 8.32 and 8.70 μ. The 2-bromopropene which sometimes occurred in these mixtures was determined from its absorption at 8.70 and 11.2 μ. Analytical standards were selected distillation fractions showing no detectable absorption from other compounds.

To determine the effect of temperature on the rate of isomerization, samples were taken immediately from the distillation column, sealed in glass ampoules, wrapped in metal foil to protect them from light, and placed in a constant temperature bath. Samples were taken from the bath periodically and analyzed immediately by their infrared spectra. Runs were made starting with the *cis*

(3) M. S. Kharasch, H. Engelman and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1938).

(4) L. F. Hatch and K. E. Harwell, This Journal, **75**, 6004 (1953).

(5) We are indebted to Robert E. Kitson of E. I. du Pont de Nemours & Co., Kinston, North Carolina, for the interpretation of the spectra.

(6) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

and with the *trans* isomer to permit approach to equilibrium concentration from both directions. Representative data are given in Table I. The isomerization at 100° was so fast that accurate rate data could not be obtained.

These data follow the kinetics of a set of reversible first order reactions. The rate constants for the reactions *cis* ⇄ *trans* were calculated from the standard rate equation[7] and using the equilibrium constant at the various temperatures. The individual constants at several temperatures are given in Table II. The energy of activation calculated from these data by the Arrhenius equation[8] is 22,700 ± 300 cal./mole. The equilibrium constant (k_{eq} = 0.472, *cis* ⇄ *trans*) was essentially the same at each temperature.

TABLE I

ISOMERIZATION OF *cis*- AND *trans*-1-BROMO-1-PROPENE

0°, Dark					
Time, min.	0	775	2897	5453	
Mole % *trans*	0.0	0.0	0.0	0.0	
Mole % *cis*	23.9	23.1	24.7	25.6	
40°, Dark					
Time, min.	33	273	978	1004	2488
Mole % *trans*	0.0	10.1	19.5	21.1	29.2
Time, min.	0	180	755	1458	
Mole % *cis*	23.9	34.6	56.1	62.4	
66.7°, Dark					
Time, min.	0	25	65	133	
Mole % *trans*	0.0	9.5	26.3	29.1	
Time, min.	0	10	39	120	
Mole % *cis*	20.4	25.0	62.5	63.6	
100°, Dark					
Time, min.	0	10	34	73	242
Mole % *trans*	0.5	26.2	30.0	29.4	29.6
Time, min.	0	5	20	40	
Mole % *cis*	23.9	68.5	68.8	68.2	

Several samples were run without the metal foil wrapping to ascertain the effect of light on the isomerization rate. At 40° the isomerization rate was increased approximately 20% by exposure of the samples to 1600 foot-candles from a tungsten lamp. Since the isomerization is negligible at 0° the effect of light alone could be studied at this temperature. When exposed to 400 ft.-candles from a fluorescent type lamp at 0° the *cis* isomer did not isomerize a measurable amount in 58 hours. Under the same conditions the *trans* isomer isomerized at a constant rate of 0.344 mole %/hour. In all the runs exposed to light, parallel control runs were made in the dark.

A number of runs were made at 40° in the dark with various substances added to obtain information on the question of catalysis. In all cases, a parallel control run was made with the same material but having nothing added, and in all cases the control samples isomerized at the same rate as found in the temperature studies.

A small amount of pure mercury was shaken with freshly distilled (isomerizable) *cis*- and *trans*-1-bromo-1-propene and no isomerization was found after 47 hours. The mercury would presumably remove any free bromine or bromine atoms. When this inhibited material was redistilled it isomerized at its original rate. Another sample, shaken with a concentrated aqueous solution of sodium thiosulfate and dried over calcium chloride showed no isomerization after 47 hours. The addition of 2% ethyl alcohol also stopped the isomerization. A small amount (1 to 2%) of liquid bromine was added to two previously inhibited samples, one by mercury and one by ethanol, but neither isomerized following this addition. This behavior indicates that a further study should be made of bromine-catalyzed isomerization of compounds of this type.

It has been suggested that the isomerization is catalyzed by bromine, perhaps released during distillation or on exposure to light. But it has not been established whether or not a catalyst is necessary for this isomerization under the conditions used here, or what the nature of the catalyst is if one is involved. One isomer isomerized readily in the presence of light at 0°, whereas the other one did not, or its rate values were so small as to be obscured by experimental error. This photochemical behavior would, on the basis of thermodynamic reasoning, require a catalytic agent other than 1-bromo-1-propene.

The isomerization rate of the 1-bromo-1-propenes appeared quite reproducible regardless of whether or not the samples were distilled at different rates or were from different preparations.

Some less detailed isomerization data on several derivatives of the 1-bromo-1-propenes are given in Table II. These compounds were studied using the same procedures described for the 1-bromo-1-propenes. Some other similar compounds whose isomerization properties and conditions have been described previously are 1,2-dibromo-1-propene,[9] 1,2-dichloroethylene,[10-13] 1,2-dibromoethylene[9,13,14] and 1,2-diiodoethylene.[15] The "light" in Table II was in all cases 400 ft.-candles from a fluorescent lamp.

Experimental

1-Bromo-1-propene.—A mixture of the two isomers of 1-bromo-1-propene and 2-bromopropene was obtained by the treatment of 1,2-dibromopropane with sodium phenolate in ethanol.[2,4] The 2-bromopropene (b.p. 47° (745 mm.), $n^{20}D$ 1.4448; lit.[3] b.p. 48.4° (748 mm.), $n^{20}D$ 1.4440) was separated by distillation at atmospheric pressure. The two isomers of 1-bromo-1-propene were separated using a Podbielniak Hyper-Cal 100-plate column at a pressure of 25 mm. The kettle temperature was not permitted to exceed 0°.

cis-1-**Bromo-1-propene**: b.p. −18° (25 mm.), d^0_4 1.4641, d^{25}_4 1.4171; lit.[16] b.p. 58–58.8° (752 mm.), d^{25}_4 1.4157.

trans-1-**Bromo-1-propene**: b.p. −13° (25 mm.), d^0_4 1.4471, d^{25}_4 1.4062; lit.[2] b.p. 63.25° (760 mm.), $d^{15.75}_4$ 1.4169.

1,3-Dibromopropene.—The 1,3-dibromopropenes were prepared by brominating a mixture of the 1-bromo-1-propenes with N-bromosuccinimide following the procedure pre-

(7) Samuel Glasstone, "Textbook of Physical Chemistry," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1070.

(8) Reference 7, pp. 1088-1089.

(9) R. M. Noyes and R. G. Dickinson, THIS JOURNAL, **65**, 1427 (1943).

(10) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

(11) R. G. Dickinson, R. F. Wallis and R. E. Wood, *ibid.*, **71**, 1238 (1949).

(12) J. L. Jones and R. L. Taylor, *ibid.*, **62**, 3480 (1940).

(13) A. R. Olsen and W. Marony, *ibid.*, **56**, 1322 (1934).

(14) H. Van De Valle, *Bull. soc. chim. Belges*, **27**, 209 (1913).

(15) R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

(16) M. T. Rogers, *ibid.*, **69**, 1243 (1947).

TABLE II
ISOMERIZATION PROPERTIES OF SOME *cis–trans* ISOMERS

Compound	Conditions	Isomerization rate, min.$^{-1}$
A, *cis*-1-Bromo-1-propene	0°, dark	0.341×10^{-5}
	0°, light	Apx. same
	40°, dark	0.403×10^{-3}
	66.7°, dark	0.0126
	100°, dark	Apx. 0.25
trans-1-Bromo-1-propene	0°, dark	0.801×10^{-5}
	0°, light	Greater than 0.80×10^{-5}
	40°, dark	0.910×10^{-3}
	40°, light	Greater than 0.910×10^{-3}
	66.7°, dark	0.0302
	100°, dark	Apx. 0.6
B, *cis*-1-Chloro-1-propene	139°, light	0
trans-1-Chloro-1-propene	139°, light	0
C, *cis*-1,3-Dibromopropene	30°, light, dark	0
trans-1,3-Dibromopropene	30°, light, dark	0
D, *cis*-3-Bromo-2-propen-1-ol	30°, light, dark	0
trans-3-Bromo-2-propen-1-ol	30°, light, dark	0
E, *cis*-1-Bromo-3-chloro-1-propene	0°, dark	0
	40°, dark	Less than *cis*-BrCH=CH—CH_3
	40°, light	Increased
trans-1-Bromo-3-chloro-1-propene	0°, dark	0
	40°, dark	Less than *trans*-BrCH=CH—CH_3
	40°, light	Increased
F, 3-Bromo-1-chloro-2-fluoro-1-propene	Room temp., light	Isomerizes

viously described.[4] A sample of the pure *cis* isomer was obtained by distillation and a pure sample of the *trans* isomer was obtained by recrystallization at −78°.

3-Bromo-2-propen-1-ols.—The 3-bromo-2-propen-1-ols were prepared by hydrolysis of a mixture of the 1,3-dibromopropenes with an excess of 5% aqueous sodium carbonate solution at 75° for 24 hours as previously described.[4] The isomers were separated by distillation.

1-Bromo-3-chloro-1-propene.—The 1-bromo-3-chloro-1-propenes were prepared by the action of an excess of concentrated hydrochloric acid on a mixture of the 3-bromo-2-propen-1-ols at 65° for 5 hours.[4] The isomers were separated by distillation through a 100-plate column.

Isomerization, Thermal.—Approximately 0.5 ml. of freshly distilled isomer was injected into a 1-ml. Pyrex ampoule with a hypodermic syringe and the ampoule sealed while surrounded by Dry Ice. Each ampoule was then wrapped in aluminum foil to exclude light. Six or seven ampoules were usually filled at the same time and with the same material. The group was then placed in a constant temperature bath and individual ampoules withdrawn at appropriate intervals of time and their contents immediately analyzed by infrared spectra.

Isomerization in the Presence of Light.—The procedures used for the isomerizations in the presence of light were identical with those in the dark except that the ampoules were not wrapped and their contents were exposed to light of measured intensity. In the 40° runs a 250 watt tungsten spot lamp was used to provide the light (1600 ft.-candles) and in the 0° runs the illumination was provided by a 40 watt fluorescent lamp (400 ft.-candles). The light intensity at the surface of the ampoules was measured by a photoelectric exposure meter.

Infrared Spectra.—A Perkin–Elmer model 12 infrared spectrometer was used throughout the work. Liquid samples were analyzed in a cell having sodium chloride windows, and with a spacing of 0.025 mm.

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DEPARTMENT OF CHEMISTRY AND
DEFENSE RESEARCH LABORATORY
THE UNIVERSITY OF TEXAS
AUSTIN, TEXAS

The Preparation of Long Chain Alkylamine Hydrochlorides[1a]

BY BROWN L. MURR AND CHAS. T. LESTER[1b]

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The observation by Cummings that certain alkylamine salts inhibited the *in vitro* growth of tubercle bacilli and certain pathogenic fungi[2] led us to prepare a number of such compounds. These compounds are all salts of primary aliphatic amines, containing nine or more carbons, with the amino group on the 1-, 2- or 3-position.

The 1-aminoalkanes were prepared from the appropriate acid amide, either by reduction with lithium aluminum hydride[3] or by a Hofmann rearrangement.[4] This latter reaction we found even more sensitive to reaction conditions than we expected despite some literature warning concerning its sensitivity.[5] The 2- and 3-aminoalkanes were prepared from the appropriate methyl and ethyl ketones by means of a Leuckart[6] reaction. The amines prepared are listed in Tables I and II. Although all the 1-amino compounds have been previously reported, they are included for comparison.

The complete details of the testing will be reported elsewhere. Maximum *in vitro* activity ap-

(1) (a) Taken in part from the M.S. Thesis of B. L. Murr, Emory University, 1953, and supported in part by a grant from the National Tuberculosis Association and in part by a grant from the U. S. Public Health. Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., Dec., 1953. (b) To whom inquiries should be addressed.

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(3) W. G. Brown in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(4) E. S. Wallis and J. F. Lane in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 267.

(5) L. Jeffreys, *Am. Chem. J.*, **22**, 14 (1899).

(6) M. L. Moore in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 301.