[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Optically Active α-Bromopropionitrile

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In an earlier communication,[3] preliminary experiments on the preparation of optically active α-bromopropionitrile were reported. We have now obtained further information concerning the magnitude of the optical rotation of this substance, as well as certain of its other physical properties. Data concerning molecules of this type, in which all four groups attached to the asymmetric carbon are cylindrically symmetrical, are of interest in connection with recent theories[4,5,6,7,8] of optical activity.

Preparation

dl-α-Bromopropionic acid was partially resolved by means of its cinchonine salt,[9] a sample having $[\alpha]^{25}\mathrm{D}$ $-13.79°$ being obtained. Complete resolution of this substance is very tedious, and was unnecessary for our purposes, since the value found by Ramberg,[10] $[\alpha]^{25}\mathrm{D}$ $-28.5°$, for the apparently optically pure compound permits calculation of the composition of our sample. This acid was converted to (−)-α-bromopropionyl chloride by treatment with thionyl chloride. The acid chloride had a rotation $\alpha^{20}\mathrm{D}$ $-19.90°$. The only density value[11] available for this substance is 1.697 at 11°; using this value we obtain $[\alpha]^{20}\mathrm{D}$ $-11.7°$. (−)-α-Bromopropionamide was obtained from the chloride by the action of ammonia in dry benzene[12]; $[\alpha]^{24}\mathrm{D}$ $-12.9°$ (0.0972 g. in 25 cc. benzene). It was observed that recrystallization of the amide from water resulted in practically complete racemization.

(−)-α-Bromopropionitrile was obtained by dehydration of the amide with phosphorus pentoxide at a temperature not exceeding 120°. The more drastic conditions employed by Moureu and Brown[13] were avoided to minimize racemization. The nitrile was redistilled over phosphorus pentoxide, and finally fractionated from the dehydrating agent *in vacuo* using a 19-in., vacuum-jacketed column packed with glass helices. The sample collected distilled from 44.5 (15 mm.) to 43.2° (13.7 mm.); $[\alpha]^{21}\mathrm{D}$ $-7.35°$.

In order to obtain an indication of the extent of racemization during the preparation of the nitrile, some of it was converted to the thyl eester of the acid through the intermediate stage of the imino ether. This method seemed to offer the best chance of conversion without extensive racemization. Twelve grams (0.09 mole) of the nitrile and 4.1 g. (0.09 mole) of absolute alcohol were dissolved in 20 cc. of absolute ether, and the solution was saturated with dry hydrogen chloride at 0°. After a day and a half crystals of α-bromopropionimino ethyl ether hydrochloride separated from the reaction mixture. The solvent was removed by distillation *in vacuo;* the crystals remaining were dissolved in ice-water and the solution immediately and continuously shaken with ether to remove the ester as it was formed by the hydrolysis of the imino ether hydrochloride. The ether solution was dried over sodium sulfate, the ether removed by distillation, and the residual ester fractionated *in vacuo;* yield 7.5 g. (46% of the theoretical); b. p. (21 mm.) 60–61°, $[\alpha]^{23}\mathrm{D}$ $-5.09°$.

Physical Properties

Melting Point.—The fusion curve of the nitrile was observed in an apparatus similar to that described by Skau.[14] The shape of the curve indicated that the sample was quite pure, and, since unequal amounts of the two enantiomorphs were present, that there was no racemic compound formation. The fusion temperature was found to be −63.4° (cor.).

Density.—The density of the *dl*-nitrile was determined from 0 to 75°. The results can be expressed by the equation (t = °C.).

$$d_t = 1.5777 - 1.557 \times 10^{-3}t - 0.80 \times 10^{-6}t^2 + 3.2 \times 10^{-9}t^3 \quad (1)$$

Refractive Dispersion.—A Pulfrich refractometer was employed to determine the refractive dispersion of *dl*-α-bromopropionitrile in the visible spectrum from 0.5 to 50°. The data were fitted to an equation of the form recommended by Tilton[15] (λ = wave length in microns):

$$n^2 = a^2 - k\lambda^2 + \frac{m}{\lambda^2 - l^2} \quad (2)$$

The constants for this equation listed in Table I reproduce the data within the experimental accuracy from λ 0.7065 to λ 0.4047.

TABLE I

THE CONSTANTS OF EQUATION (2)

Temp., °C.	a^2	k	m	l^2
0.5	2.1207	0.00642	0.01291	0.02544
25.0	2.0851	.00232	.01314	.02094
50.0	2.0469	.00203	.01339	.01683

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[1] The material in this paper constitutes part of a dissertation submitted by Kenneth L. Berry to Yale University in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

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[10] Ramberg, *ibid.*, **370**, 234 (1909).

[11] Collet, *Bull. soc. chim.*, [3] **15**, 717 (1896).

[12] Bischoff, *Ber.*, **30**, 2312 (1897).

[13] Moureu and Brown, *Bull. soc. chim.*, [4] **27**, 907 (1920).

[14] Skau, *Proc. Am. Acad. Arts and Sci.*, **67**, 551 (1933).

[15] Tilton, *Bur. Standards J. Research*, **17**, 646 (1936).

The Lorenz–Lorentz molecular refractivities for the sodium D line were found to be $R_{0.5} = 23.67$, $R_{25} = 23.75$, $R_{50} = 23.81$. The value obtained by adding atomic and group refractivities[16] is 23.56.

Optical Rotation and Rotatory Dispersion.—Three different samples of α-bromopropionitrile have been prepared, one dextro-rotatory and two levo-rotatory. If the assumption is made that no racemization occurred during the preparation, and if the rotation given by Ramberg[10] is taken as correct for the optically pure acid, the rotations calculated from these three samples for the optically pure nitrile are $[\alpha]^{25}\mathrm{D}$ +12.5, −15.3, −15.5°, respectively. If racemization took place, these figures represent lower limits. The last of these samples was converted back to ethyl (−)α-bromopropionate as described above. From the observed rotation of the ester thus obtained, and the rotation given by Ramberg[10] for the apparently nearly optically pure ester, one calculates for the rotation of the optically pure nitrile $[\alpha]^{25}\mathrm{D}$ −23.1°. If racemization took place in the formation of the ester, this figure is an upper limit. We may thus state that for the optically pure nitrile $-23.1° \leqslant [\alpha]^{25}\mathrm{D} \leqslant -15.5°$.

α-Bromopropionitrile apparently undergoes slow autoracemization. A dry sample which had an original rotation of $\alpha^{25.8}\mathrm{D}$ −8.15° was sealed in an ampoule and stored in the dark. After fourteen months the rotation was $\alpha^{25}\mathrm{D}$ −1.90°, and after eighteen and a half months −1.76°. There was some indication that this racemization is catalyzed by traces of moisture.

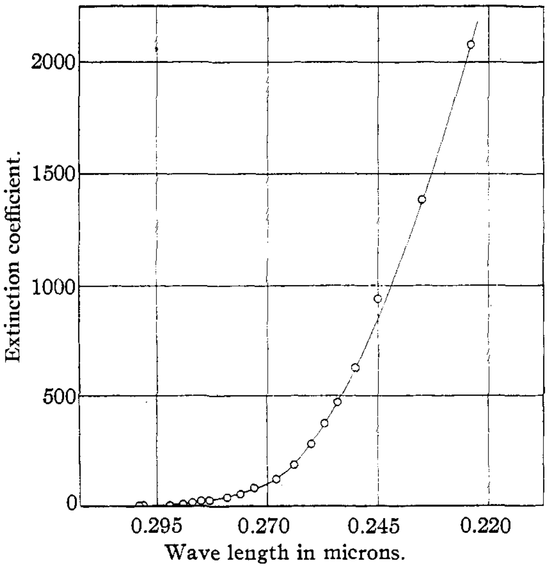

Fig. 1.—The near-ultraviolet absorption of α-bromopropionitrile.

The rotatory dispersion in the visible spectrum was measured on the second sample mentioned above by the method of Perkin[17]; the lines from multichromatic light sources were resolved by a direct-vision spectroscope mounted in front of the eyepiece of the polarimeter. Measurements were made from λ 0.6563 to λ 0.4358, and 0.4 to 69.5°. After the measurements at the higher temperatures, the rotation was again observed at 25° to be sure that racemization had not taken place. The observed rotations were multiplied by the appropriate factor calculated from the optical purity of the acid used as starting material. The specific rotations can be fitted to a two-constant Drude equation

$$[\alpha] = \frac{A}{\lambda^2 - \lambda_0^2} \qquad (3)$$

the constants having the values given in Table II. The constant λ_0^2 is seen to be independent of temperature.

TABLE II

THE CONSTANTS OF THE DRUDE EQUATION (3)

Temp., °C.	A	λ_0^2
0.4	4.192	0.0702
25.0	4.266	.0689
50.0	4.286	.0699
69.5	4.300	.0694

Near Ultraviolet Absorption.[18]—The absorption of *dl*-α-bromopropionitrile in 95% alcohol solution between λ 0.420 and λ 0.220 was measured with a Bausch and Lomb sector photometer employing a tungsten spark source of radiation. In Fig. 1 extinction coefficients are plotted against wave lengths in microns. Unfortunately the position of maximum absorption could not be located. The constant λ_0 in equation (3) would appear to correspond to this intense absorption band.

Summary

Optically active α-bromopropionitrile has been prepared; its refractive and rotatory dispersion in the visible spectrum and its near ultraviolet absorption have been determined.

NEW HAVEN, CONN. RECEIVED JULY 30, 1941

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[16] "Organic Chemistry, An Advanced Treatise," edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739.

[17] Perkin, *J. Chem. Soc.*, 616 (1906).

[18] The authors are indebted to Dr. Margaret McLean for this absorption spectrum.