gen; 1.3 liters of liquid hydrogen are obtained from each cylinder containing 200 cu. ft. of hydrogen gas. Liquid hydrogen may be stored in container (64) with the consumption of 800 cc.[30] of liquid hydrogen and 2000 cc. of liquid nitrogen per day. When the system is not in use, hydrogen slightly above atmospheric pressure is maintained in the lines. The liquefier has been installed for a period of eighteen months, during which time it has produced some 50 liters of liquid as required. It has always performed satisfactorily.

The design of this system was executed by the laboratory mechanicians, Mr. Charles Gallagher and Mr. Knut Wilhelmson.

Summary

A hydrogen liquefying system which depends upon commercial electrolytic hydrogen as the source of high pressure gas has been described. This involves the use of metal dewars, improved means of thermal isolation and heat exchange, and a means for producing lower fore-temperatures in the form of a charcoal desorption unit. The theory and economy of hydrogen liquefaction have been discussed.

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[30] By use of a copper plated container this figure can be reduced to 400 cc. per day. The monel surface catalyzes ortho-para conversion.

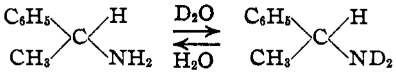
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND MILLS COLLEGE]

Stereochemistry of Deuterium Compounds. II. α-Methylbenzylamine

BY LEONA E. YOUNG AND C. W. PORTER

The change in the optical properties of 2-octanol, produced by the substitution of deuterium for hydrogen in the hydroxyl group, has been reported by us[1] and similar results have been obtained by Erlenmeyer and Schenkel with mandelic acid and with atrolactic acid.[2]

We have now measured the optical rotation of an asymmetric primary amine in which deuterium was substituted for hydrogen in the amino group. The compound used was α-methylbenzylamine (α-phenylethylamine). Equilibrium between light and heavy hydrogen atoms in the amino group is established rapidly when the amine is treated with deuterium oxide. If, then, the equilibrium mixture of light and heavy water is removed by distillation and the amine is again treated with pure deuterium oxide the substitution becomes more nearly complete. The number of times the process must be repeated to accomplish complete substitution depends upon the amount of deuterium oxide used in each treatment. The deutero-amine may then be reconverted into the ordinary form by a similar series of treatments with ordinary water.



There is perhaps a slow exchange in other positions in the molecule but the difference in rates between the exchange on the nitrogen atom and an exchange elsewhere in the molecule is enormous. We experienced no difficulty in obtaining constant values for the rotations after five or six treatments, using each time approximately two equivalents of deuterium oxide or of water.

The amine was made from acetophenone by treatment with formamide.[3] It was resolved through the fractional crystallization of the salt formed with *l*-malic acid.[4] The dextro form of the amine was obtained from the first crop of crystals in a nearly pure state. The levo form of the amine was obtained optically pure through the procedure described in the experimental part. The rotations, boiling points and densities of the amines are shown in the table. The formula RNH_2 stands for α-methylbenzylamine.

Compound	α^{20}_{5461}	Density at 24°	B. p. (corr.), °C.
RNH_2	−45.39°		
	+44.66°	0.9458	187.4
↓			
RND_2	−43.77°		
	+42.88°	.9615	188.4
↓			
RNH_2	−45.34°		
	+44.54°	.9458	187.4

In each case the deuterium compound has the lower rotation, the average difference between the corresponding forms being 1.65°. The read-

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[1] Young and Porter, THIS JOURNAL, **59**, 328 (1937).

[2] Erlenmeyer and Schenkel, *Helv. Chim. Acta*, **19**, 1199 (1936).

[3] Ingersoll, Brown, Kim, Beauchamp and Jennings, THIS JOURNAL, **58**, 1808 (1936).

[4] (a) Ingersoll, *ibid.*, **47**, 1168 (1925); (b) Lovén, *J. prakt. Chem.*, [ii], **72**, 307 (1905); (c) Ingersoll, *Org. Syntheses*, **17**, 80 (1937).

ings were made with the pure liquids (no solvent) in 10-cm. tubes. The light source was a mercury vapor arc with a Wrattan filter.

Experimental Part

Preparation of α-Methylbenzylamine.—Formic acid (366 g. of 85% acid) was added slowly to commercial ammonium carbonate (359 g.). The solution was then heated slowly in a distilling flask until the temperature of the liquid reached 165°. The portion that distilled off below this temperature was discarded. To the reagent in the flask was added 200 g. of acetophenone. The mixture was heated gradually to 175°. The portion of the ketone which distilled during this preliminary heating was returned to the reaction flask and the temperature of the mixture was maintained at 180 to 185° for four and one-half hours. The amine was isolated by the procedure described by Ingersoll[4c] (p. 76). The compound was purified by redistillation from ether and solid potassium hydroxide in an atmosphere of dry nitrogen free from carbon dioxide. The yield was 74% of the theoretical amount.

This amine absorbs carbon dioxide with unusual rapidity. It would serve as an excellent reagent for the removal of traces of carbon dioxide from air, oxygen, or nitrogen. A crystalline carbonate forms within a few minutes if a drop of the amine is exposed to the atmosphere of the laboratory. A small amount of the carbonate dissolved in the amine produces a large effect upon the optical rotation of the compound (lowers the rotation). Great care must be exercised to exclude carbon dioxide and moisture when the pure amine is required.

Resolution of *d*-*l*-α-Methylbenzylamine.—*l*-Malic acid (160 g.) dissolved in 290 g. of water was added to 147 g. of the racemic amine in 319 g. of water. The mixture became warm and clear. It was stirred and cooled rapidly to room temperature, then immersed in an ice-bath and stirred until the mixture had reached the temperature of the bath. The salt which crystallized under these conditions was separated from the mother liquor with a suction filter and recrystallized twice from water. The melting point of the dried salt was 184° (corr.). The salt was added to a solution of 188 g. of barium octahydrate in 800 cc. of water and the liberated amine was removed by distillation with steam. The distillate was made alkaline with potassium hydroxide and the amine was extracted with ether. The ether extract was dried over solid potassium hydroxide and the ether was removed by distillation in an atmosphere of dry nitrogen. The boiling point of the amine was 187.4°. In a 10-cm. tube its optical rotation was +44.66°.

Formation of Dextro-α-methylbenzylamine-d_2.—A 15-cc. portion of *d*-α-methylbenzylamine was mixed with 3 g. of deuterium oxide. After standing for three hours the water was distilled off. The small portion of the amine which was carried over with the steam was separated and returned to the reaction flask. This process was repeated until on drying with potassium hydroxide, and redistilling, there was no further change in optical rotation. The boiling point of the deuterium derivative was 188.4°. The rotation was +42.88°.

Regeneration of the Ordinary Amine.—The deuterium compound was mixed with 3-g. portions of water, distilled, dried and treated again with water until no further change in optical rotation was observed. The value of the rotation returned to that of the original hydrogen compound.

Isolation of *l*-α-Methylbenzylamine.—The mother liquor from which the dextro form of the amine had been removed, contained mainly the *l*-malic acid salt of *l*-α-methylbenzylamine, but this was contaminated with the *l*-malic acid salt of *d*-α-methylbenzylamine. This mixture was treated with 300 g. of $Ba(OH)_2 \cdot 8H_2O$ and distilled with steam. Through extraction with ether 60 g. of amine was obtained. The pure levo amine was obtained from this sample by treatment with 135 g. of *d,l*-malic acid in 300 cc. of water. The salt consisting of *d*-malic acid with the *l*-amine is the least soluble of all possible combinations in this mixture and it precipitates on standing at room temperature. The salt was recrystallized twice from water. It was decomposed by steam distillation from barium octahydrate solution, extracted with ether, dried and distilled in an atmosphere of nitrogen free from carbon dioxide. The boiling point of the *l*-α-methylbenzylamine was 187.4°, its optical rotation was −45.39°.

Formation of *l*-α-Methylbenzylamine-d_2.—The procedure was the same as in the case of the dextro compound. The optical rotation was −43.77°.

Regeneration of the Levo Form of the Ordinary Amine.—The procedure was similar to that employed in the case of the dextro compound. The rotation of the resulting hydrogen derivative was −45.34°.

All optical measurements were made with the pure liquid amines in 10-cm. tubes and with monochromatic light of 5461 Å.

Summary

The optical rotations of the dextro and levo forms of α-methylbenzylamine differ from those of the corresponding forms of α-methylbenzylamine-d_2 by 1.65°, the deuterium compound having the lower rotation in each case.

The density of α-methylbenzylamine at 24° is 0.9458, that of α-methylbenzylamine-d_2 is 0.9615. The normal boiling points are 187.4 and 188.4°, respectively.

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