tion for the generous supply of ethylene oxide furnished for this investigation.

Summary

Three new β-amoxyethanols, six new β-amoxyethyl esters of *p*-nitrobenzoic acid and six new β-amoxyethyl esters of *p*-aminobenzoic acid have been prepared and some of their physical constants determined.

MORGANTOWN, WEST VIRGINIA RECEIVED JUNE 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Succinic-α-d,α'-d Acid and its Derivatives. II. Stereochemistry of the Type RR'CHD

BY MARLIN T. LEFFLER[1] AND ROGER ADAMS

The effect of deuterium upon the optical activity of organic molecules and the possibility of obtaining an answer to the question as to whether RR'CHD may be optically active has engaged the attention of investigators in several laboratories.[2]

Schoenheimer and Rittenberg[3] compared the optical activity of coprostanone-d_2 and coprostanone and noted that the difference in optical activity was very small, if at all appreciable. Erlenmeyer and Gärtner[4] were unable to resolve phenylpropionic-α-d,β-d acid of which they obtained an impure sample by reduction of cinnamic acid with deuterium iodide and phosphorus.

In the research now reported the reduction of diethyl fumarate and diethyl maleate was carried out using practically 100% deuterium in the presence of platinum catalyst. The resulting diethyl succinate-α-d,α'-d corresponds to the stereochemical R'CHD-CHDR' type, separable into a *meso* and a *racemic* modification. It is well known that the action of permanganate on maleic acid produces *meso*-tartaric acid while the *racemic* modification results from fumaric acid. Although the deuterium reduction of an ethylenic linkage probably does not follow the above "*cis*" addition, the reduction of diethyl maleate should still be capable of yielding a different form from that given by diethyl fumarate. As shown by the constants (Table I), the diethyl succinic-α-d,α'-d specimens from both sources appeared to be identical, nor was the presence of isomers in either sample noticed during the distillation of the ester.

The densities of diethyl succinate-α-d,α'-d (Table I) from different reductions of the same material show some variance, possibly due to varying amounts of hydrogen "impurity." In a previous paper[1b] it was pointed out that the observed densities of dimethyl succinate-α-d_2,α'-d_2 and succinic-α-d_2,α'-d_2 anhydride were lower than and did not agree with the calculated values. The calculation of these values was based primarily upon the assumption of identical molecular volumes for deuterium and hydrogen. Since that time it has been observed[5] that the molecular volumes of the two isotopes are not identical and may differ sufficiently to affect the densities of deuterium compounds. However, it is evident that this effect must vary with the substances in question, as the densities[6] of several deuterium compounds, of established purity, agree very well with the calculated values; others show less agreement. In any case, it is worth mentioning that the densities (Tables I, II) observed for diethyl succinic-α-d,α'-d and its derivatives show fair agreement with the theoretical values. It is entirely probable that the discrepancy which does exist may be due both to a difference in molecular volumes and to hydrogen "impurities."

Succinic-α-d,α'-d acid was prepared by the hydrolysis of the ester from both of the above-mentioned sources. These specimens of dideu-

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[1] (a) This is a portion of a thesis submitted in fulfilment of partial requirements for the degree of Doctor of Philosophy in Chemistry; (b) for previous paper in this field see McLean and Adams, THIS JOURNAL, **58**, 804 (1936).

A description of the investigation herewith reported was included in an address in connection with the Willard Gibbs Medal award to the senior author, May 23, 1936.

[2] After the preparation of this manuscript, an article by Biilmann, Jensen and Knuth, *Ber.*, **69**, 1031 (1936), reports the preparation of a deuterio camphane derivative which must be optically active due to the —CHD group. This paper will be discussed in a subsequent communication.

[3] Schoenheimer and Rittenberg, *J. Biol. Chem.*, **111**, 183 (1935).

[4] Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).

[5] Brickwedde and Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).

[6] Erlenmeyer, Lobeck, Gärtner and Epprecht, *Helv. Chim. Acta*, **19**, 336 (1936); Bowman, Benedict and Taylor, THIS JOURNAL, **57**, 960 (1935); Breuer, *ibid.*, **57**, 2236 (1935).

TABLE I

CONSTANTS OF DIETHYL SUCCINATE AND ITS DERIVATIVES

Compound		B. p., °C., at 40 mm. bath 155°	B. p. °C., at 16 mm., bath 125°	n^{20}_{D}	Density, d^{20}_{4} Found	Calcd.[c]
Diethyl succinate-*α-d,α′-d* (from fumarate)	(I)	126.0–126.5	106.0–106.5	1.4193	1.0533	1.0542
	(II)	....	106.0–106.4	1.4194	1.0527	1.0542
Diethyl succinate-*α-d,α′-d* (from maleate)	(I)	126.2–126.5	106.5–106.8	1.4198	1.0543	1.0542
	(II)	126.0–126.5	....	1.4196	1.0527	1.0542
Diethyl succinate (from fumarate)		126.0–126.4	....	1.4200[a]	1.0420[b]	....
Diethyl succinate (from maleate)		126.0–126.4	....	1.4199[a]	1.0421[b]	....

[a] The value reported in the literature is: n^{20}_{D} 1.42007 (Karvonen, *Ann. acad. sci. Fennicae*, 10A, 13 (1912)). [b] This density agrees with the previously reported value, d^{20}_{4} 1.042 ("Int. Crit. Tables," Vol. 1, 1926, p. 222). [c] The method of calculation was that employed previously.[1b]

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF HYDROGEN AND DEUTERIUM ANALOGS[a]

Compound (formula and name)	M. p., °C. (corr.)	Density, d^{181}_{4} Found	Calcd.[c]		Subst., mg.	CO_2, mg.	Water, mg.	% C	% hydrogen[b] isotopes		% H
Diethyl succinate-*α-d,α′-d*;[b]	....	(See Table I)		Found	3.890	7.79	2.77	54.61	8.95		..
$C_8H_{12}D_2O_4$ (from fumarate)				Calcd.	...	..	..	54.51	9.15	2.30	..
Diethyl succinate-*α-d,α′-d*;	....	(See Table I)		Found	3.911	7.81	2.76	54.46	8.87	18.30	..
$C_8H_{12}D_2O_4$ (from maleate)				Calcd.	...	..	..	54.51	9.15		..
Diethyl succinate;	....	(See Table I)		Found	3.988	8.05	2.84	55.05	..		7.97
$C_8H_{14}O_4$				Calcd.	...	..	..	55.08	..		8.10
Succinic-*α-d,α′-d* acid;	184.0–184.5	....		Found	3.720	5.48	1.73	40.17	6.69		..
$C_4H_4D_2O_4$ (from fumarate)				Calcd.	...	..	..	39.98	6.71	2.69	..
Succinic-*α-d,α′-d* acid;	184.0–184.5	....		Found	3.743	5.52	1.73	40.22	6.65	18.69	..
$C_4H_4D_2O_4$ (from maleate)				Calcd.	...	..	..	39.98	6.71		..
Succinic acid; $C_4H_6O_4$	184.5–185	....		Found	3.708	5.55	1.67	40.82	..		5.04
				Calcd.	...	..	..	40.66	..		5.13
Succinic-*α-d,α′-d* anhydride;	119.3–119.6	1.2560	1.2588	Found	3.604	6.25	1.33	47.29	5.86		..
$C_4H_2D_2O_3$ (from fumarate)				Calcd.	...	..	..	47.04	5.92	3.02	..
Succinic-*α-d,α′-d* anhydride;	119.3–119.6	1.2563	1.2588	Found	3.800	6.56	1.41	47.08	5.89	19.02	..
$C_4H_2D_2O_3$ (from maleate)				Calcd.	...	..	..	47.04	5.92		..
Succinic anhydride;[d]	119.3–119.6	1.2340	....	Found	3.817	6.71	1.36	47.94	..		3.99
$C_4H_4O_3$				Calcd.	...	..	..	47.99	..		4.03

[a] In order to obtain satisfactory analyses on the acids and the anhydrides, only copper oxide was used in a combustion tube of twice the ordinary length. [b] A mixed melting point of the d_2-acid from fumarate and maleate showed no depression. A mixture containing approximately 50% of either the d_2-acid from fumarate or from maleate and succinic acid melted at 184–185°. [c] The method of calculation was that used previously.[1b] [d] Mixtures containing varying amounts of succinic anhydride and either of the d_2-anhydrides melted at 119.3–119.6°.

terio acid were identical in melting point, and fractional crystallization (Table II) failed to indicate the presence of more than one form. The two samples of dideuterio acid, on treatment with acetyl chloride, gave two identical specimens of succinic-*α-d,α′-d* anhydride (Table II).

As previously pointed out,[1b] carbon analyses of deuterium compounds may indicate semi-quantitatively the presence of deuterium, while hydrogen isotope analyses are generally of little value. The carbon analyses (Table II) are sufficiently different from the anhydride analogs to show clearly that deuterium was not entirely replaced during any of the previous treatments, and the density determinations (Table II) indicate that if any replacement at all occurred it was not appreciable in amount.

All of the evidence derived from the above-mentioned experimental results points, in a negative sense, to the symmetry of the carbon RR′CHD. It was thought to be of additional and equal interest to compare the degree of optical activity of several deuterium and hydrogen analogs. This was made possible by studying the rotations of the brucine, quinine, strychnine and cinchonine salts of both succinic-*α-d,α′-d* acid and succinic acid. The rotations of the hydrogen and deuterium salts (Table III) were observed under as nearly identical conditions as possible. Within the limits of experimental accuracy, these rotations were identical.

Granted that the one form of succinic-*α-d,α′-d* acid obtained from the above-mentioned reductions might have been the *meso* modification, it

TABLE III

ROTATIONS[a] OF ALKALOIDAL SALTS OF DEUTERIO-SUCCINIC AND SUCCINIC ACIDS

Alkaloidal salt	Weight[b]	Solvent	α^{20}_{D}[c]	$[\alpha]^{20}_{D}$
Succinic acid (brucine)	0.1971	Water	−0.50	− 25.4 ± 0.5
Succinic-*α-d,α'-d* acid (brucine)	.1964	Water	− .50	− 25.5 ± .5
Succinic acid (quinine)	.1003	95% Alcohol	−1.66	−165.5 ± .5
Succinic-*α-d,α'-d* acid (quinine)	.1007	95% Alcohol	−1.66	−164.9 ± .5
Succinic-*α-d*$_2$,*α'-d*$_2$ acid[1b] (quinine)	.1004	95% Alcohol	−1.66	−165.3 ± .5
Succinic acid (strychnine)	.2033	Water	−0.52	− 25.6 ± .3
Succinic-*α-d,α'-d* acid	.2033	Water	− .51	− 25.3 ± .3

[a] All readings were taken at 20 ± 0.1° to prevent variations in ionization. [b] This weight was made up to 10.00 cc. [c] l = 1 dec.

was nevertheless desirable to attempt the resolution of this acid. The cinchonine salt was selected for this purpose as cinchonine has been used successfully to resolve tartaric acid.[7] The fractionation gave four crops of dideuterio salt, identical in crystalline form, melting point, and rotation. None of these fractions gave any evidence of mutarotation.

Experimental

Diethyl Fumarate.—This ester was prepared according to the method described in "Organic Syntheses,"[8] and was purified by two distillations at atmospheric pressure followed by a final distillation *in vacuo*. The fraction used in the reduction experiments below had the following physical constants: b. p. 218–218.5° (corr.) at 740 mm. or 109–110° at 16 mm.; n^{20}_{D} 1.4410.

Diethyl Maleate.—The product from esterification of maleic acid with absolute alcohol by the same procedure had, after careful fractionation, the following physical constants: b. p. 225° (corr.) at 740 mm. or 115–116° at 16 mm.; n^{20}_{D} 1.4415. These constants check those described in the literature.

Diethyl Succinate-*α-d,α'-d* (from Diethyl Fumarate).—The apparatus employed for the reduction was identical to that previously described.[1b] Two separate reduction experiments were carried out, the same conditions prevailing in each. Each reduction tube was charged with 4.00 g. of diethyl fumarate, 0.05 g. of platinum catalyst, and 7 cc. of dry ethyl acetate (acetic acid free). An excess of practically 100% deuterium was available. The reduction was complete at the end of eight hours and no additional absorption took place in an additional three hours. At the end of this time the reaction mixture was filtered from the catalyst and the ethyl acetate solvent distilled off below 60° at slightly reduced pressure. The residue was distilled *in vacuo* at two different pressures, the latter being carefully controlled by a constant pressure regulator. The boiling point (Table I) was constant and gave no indication of the presence of isomers. The yield of purified diethyl succinate-*α-d,α'-d* from 4.00 g. of diethyl fumarate was 3.4–3.7 g. (83–91%). This product was free from any unsaturated material as shown by an alkaline permanganate test.

Diethyl Succinate-*α-d,α'-d* (from Diethyl Maleate).—Complete reduction of diethyl maleate carried out in a similar manner was attained in six hours, and no additional absorption of deuterium took place in two more hours. The boiling point of the product was constant, gave no indication of the presence of isomers, and was identical with the boiling point of the product obtained from diethyl fumarate (Table I) (yield 88%). This product gave no indication of unsaturation as shown by alkaline permanganate.

Diethyl Succinate.—This ester was prepared by the reduction of either diethyl fumarate or diethyl maleate with hydrogen. The same conditions were used as in the reduction experiments with deuterium. The constants check those recorded in the literature (Table I).

Succinic-*α-d,α'-d* Acid (Origin: Diethyl Fumarate).—The hydrolysis of diethyl succinate-*α-d,α'-d* (origin: fumarate; d^{20}_{4} 1.0533) was accomplished by boiling 10 g. of the ester for five to six hours with 100 cc. of water containing three drops of concentrated nitric acid. After the hydrolysis was complete, the clear solution was cooled and the nitric acid was neutralized by adding the calculated quantity of sodium carbonate. The solution was then evaporated to dryness *in vacuo* at 40–50° to give 6.6 g. of crude acid. The latter was fractionally crystallized in the following manner. The entire amount of crude succinic-*α-d,α'-d* acid was dissolved in 90 cc. of hot water, filtered, and the resultant solution allowed to evaporate slowly. The evaporation was carried out in stages; a crop of crystals was separated after each 20% decrease in volume. These crops were purified by further crystallization.

In no case was the presence of isomers indicated during the fractionation of the acid, as the solubilities and melting points were essentially identical in all fractions. Succinic-*α-d,α'-d* acid crystallized in colorless needles which appeared to be identical to those obtained from the reduction of diethyl maleate and identical to succinic acid itself. The melting point of the deuterio acid was about 0.5° lower than that of succinic acid (Table II).

Succinic-*α-d,α'-d* Acid (Origin: Diethyl Maleate).—Diethyl succinate-*α-d,α'-d* (d^{20}_{4} 1.0543) obtained by the reduction of diethyl maleate was hydrolyzed in exactly the same manner as used in the hydrolysis above. The latter was fractionally crystallized by the procedure outlined for the dideuterio acid from diethyl fumarate. The melting points and solubilities were identical for the various fractions and also identical with the values of the acid from diethyl maleate reduced with deuterium (Table II).

Succinic Acid.—A pure specimen of succinic acid was prepared in the same way as the above by the saponifica-

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(7) Pasteur, *Ann. chim. phys.*, **38**, 469 (1853).

(8) "Organic Syntheses," Vol. X, 1930, p. 48.

tion of diethyl succinate. Both the diethyl succinate resulting from the reduction of diethyl fumarate and diethyl maleate were used in preparing succinic acid. The acid so obtained was recrystallized from water, which method gave a product with the same melting point as that obtained by sublimation. It was found that at low pressure (1 mm. at 145°) sublimation could be conveniently used to recover deuteriosuccinic acid (or succinic acid) from otherwise unworkable residues. Samples purified in this way had the same melting point as crystallized material.

Succinic-*α-d,α'-d* Anhydride.—The purified deuterio acid (2.36 g.; origin, diethyl fumarate) was refluxed for three hours with acetyl chloride (4.7 g.). At the end of this time, the clear solution was allowed to cool spontaneously whereby colorless prisms of succinic-*α-d,α'-d* anhydride were deposited. After further cooling in ice-water, the product was separated by filtration, washed with cold, absolute ether, and vacuum dried over soda-lime to remove traces of acid chloride. The crude succinic-*α-d,α'-d* anhydride (yield 91%) was fractionally crystallized from freshly distilled acetic anhydride. Only a single form was indicated, m. p. 119.3–119.6°.

Succinic-*α-d, α'-d* acid (origin: diethyl maleate) was converted in the same way as the above into the anhydride. The succinic-*α-d,α'-d* anhydride was identical with the product from diethyl fumarate, m. p. 119.3–119.6°. The density of both this and the sample above was determined by the procedure previously described.[1b] The values from these density determinations (Table II) indicate that under the conditions used in the previous hydrolyses there was no appreciable amount of deuterium lost by exchange with hydrogen.

Succinic Anhydride.—This anhydride was prepared in the same way as the dideuterio compound.

ALKALOIDAL SALTS OF SUCCINIC-*α-d,α'-d* ACID

A Comparison of the Rotations of Deuterium and Hydrogen Analogs

Brucine Salt of Succinic-*α-d,α'-d* Acid.—To a solution of 0.1800 g. of succinic-*α-d,α'-d* acid in 20 cc. of hot absolute alcohol was added 0.6994 g. of *l*-brucine (hydrate). The solution was boiled for several minutes after all of the alkaloid had dissolved, was filtered while hot, and set aside to crystallize. The first crop of colorless clusters amounted to 0.55 g. and the second, 0.12 g. Both crops melted at 216–218° (dec.) and the melting point was not changed by further recrystallization from absolute alcohol. Rotations of various fractions were identical.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{23}H_{26}O_4N_2$: N, 6.16. Found: N, 6.04.

Brucine Salt of Succinic Acid.—This salt was prepared in the same manner as above for the deuterium analog. On recrystallization from absolute alcohol it formed colorless prism clusters melting at 216–218° (dec.).

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot 2C_{23}H_{26}O_4N_2$: N, 6.17. Found: N, 6.06.

Quinine Salt of Succinic-*α-d,α'-d* Acid.—To a solution of 0.150 g. of succinic-*α-d,α'-d* acid in 30 cc. of hot water was added 0.405 g. of *l*-quinine. The alkaloid went into solution immediately, and on allowing the solution to cool, colorless, soft needles of the salt separated. The first crop amounted to 0.32 g. and the second, 0.1 g. Both crops melted with shrinking at 175°, becoming entirely liquid at 201°. As indicated by the melting point, the salt was evidently hydrated.[9] The melting point was not altered by further recrystallization from water, but when the sample was dried *in vacuo* at 100° for twenty-four hours it melted without shrinking at 198–201°. All fractions were identical in properties.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot C_{20}H_{24}O_2N_2 \cdot H_2O$: N, 6.06. Found: N, 6.21.

Quinine Salt of Succinic-*α-d₂,α'-d₂* Acid.—This salt was prepared from the tetradeuterio acid[1b] by the same method used for the dideuterio compound. It crystallized from water in the same form and was dried in the same way as the analogs; m. p. 198–201°.

Anal. (micro-Dumas). Calcd. for $C_4H_2D_4O_4 \cdot C_{20}H_{24}O_2N_2 \cdot H_2O$: N, 6.03. Found: N, 6.06.

Quinine Salt of Succinic Acid.—This salt was prepared in the manner used above for the analogs. It crystallized from water in colorless, fluffy needles which, after drying *in vacuo* at 100°, melted at 198–201° (dec.).

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot C_{20}H_{24}O_2N_2 \cdot H_2O$: N, 6.08. Found: N, 6.11.

Strychnine Salt of Succinic-*α-d,α'-d* Acid.—An amount of 0.2400 g. of succinic-*α-d,α'-d* acid was dissolved in 20 cc. of hot absolute alcohol, followed by the addition of 0.668 g. of *l*-strychnine. The mixture was allowed to evaporate above 35° and two fractions separated. These were identical. After drying *in vacuo* at 100°, the crystals softened at 190° and melted at 210°. By the usual procedure of crystallization, strychnine crystallized and had to be separated mechanically from the salt.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.11. Found: N, 7.29.

Strychnine Salt of Succinic Acid.—This was prepared as described for the deuterium analog. The colorless spurs[10] which crystallized from absolute alcohol were dried *in vacuo* at 100°. They softened at 190° and melted at 210°.

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.13. Found: N, 7.19.

Attempted Resolution of Succinic-*α-d,α'-d* Acid

Cinchonine Salt of Succinic-*α-d,α'-d* Acid.—To a solution of 0.3600 g. of succinic-*α-d,α'-d* acid in 10 cc. of hot water was added 0.883 g. of *d*-cinchonine. The mixture was refluxed for several minutes to give a clear solution. As the salt crystallized only with great difficulty from an unseeded aqueous solution, crystalline salt was prepared from dioxane as a solvent, allowing the dioxane to evaporate very slowly. These crystals were later used to seed the water solution which was preferred to dioxane as a fractionating solvent. After two days of standing, large colorless prisms had separated. Several fractions were obtained as follows: (1) 0.26 g.; (2) 0.19 g.; (3) 0.27 g. and (4) 0.13 g., totalling 0.85 g. (68.5%). All of these fractions were obviously hydrated[11] as they effloresced on exposure to the air. The above weights of the various

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[9] Lindet, *Bull. soc. chim.*, [3] **15**, 1160 (1896).

[10] Crespi, *Gazz. chim. ital.*, **13**, 176 (1883).

[11] Hesse, *Ann.*, **176**, 232 (1874).

fractions were taken after drying the samples for a day in a vacuum desiccator over sulfuric acid. After this treatment, all of the crops melted over the range, 130–160°. The rotations were first read at 0°, then at 20°, and finally again at 0° in order to observe any possible mutarotation. All fractions exhibited, within the limits of experimental error, the following identical rotations: $[\alpha]^{0}\text{D}$ +158 ± 1 (c = 1.000, l = 1 dec., $\alpha^{0}\text{D}$ +1.58); $[\alpha]^{20}\text{D}$ + 152 ± 1 (c = 1.000, l = 1 dec., $\alpha^{20}\text{D}$ +1.52). There was no indication of mutarotation in any of the fractions.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{19}H_{22}ON_2$: N, 7.90. Found: N, 7.80.

Cinchonine Salt of Succinic Acid.—This salt, used as a comparison standard, was prepared in the manner described above for the deuterium analog. The dried sample melted over a range of 130–160°. As in the above instance all rotations were taken on solutions of the same concentration and at temperatures controlled to within 0.1°. The latter precautions were taken to prevent ionization. The following rotations were observed for this hydrogen analog: $[\alpha]^{0}\text{D}$ +159 ± 1 (c = 1.008, l = 1 dec., $\alpha^{0}\text{D}$ + 1.60); $[\alpha]^{20}\text{D}$ + 153 ± 1 (c = 1.008, l = 1 dec., $\alpha^{0}\text{D}$ +1.54).

Summary

1. Diethyl succinate-α-d,α'-d was prepared from both diethyl maleate and diethyl fumarate by reduction with deuterium. The presence of more than one compound was not indicated.

2. Succinic-α-d,α'-d acid from diethyl succinate-α-d,α'-d from either diethyl maleate or fumarate appeared to be a homogeneous substance. It melted 0.5° lower than succinic acid. Its alkaloidal salts exhibited the same rotation as the corresponding salts of succinic acid. No separation of diastereoisomeric salts was possible.

3. Succinic-α-d,α'-d anhydride melted at the same point as succinic anhydride.

4. The densities of diethyl succinate-α-d,α'-d and of succinic-α-d,α'-d anhydride indicated no appreciable replacement of deuterium by hydrogen during the various reactions. The values were slightly lower than those calculated from the densities of the hydrogen analogs on the basis of the assumption that the molecular volume of hydrogen and deuterium is identical.

URBANA, ILLINOIS RECEIVED JUNE 4, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Deuterium Compounds of the Type RR′CHD: Camphane-2,3-d_2

BY MARLIN T. LEFFLER[1] AND ROGER ADAMS

A recent article by Biilmann, Jensen and Knuth[2] described the preparation and subsequent study of the optical properties of camphane-2-d. Although camphane, due to its symmetry, is optically inactive, camphane-2-d was found to have an observed rotation of αD + 0.08° (c = 10.00 of ether, l = 2 dec.). This was presented as direct evidence in favor of the asymmetry of the molecule RR′CHD. As pointed out by the above authors, the preparation of the hydrogen and deuterium analogs of camphane by the hydrolysis of bornylmagnesium chloride with water and deuterium oxide, respectively, is accompanied by the formation of several other optically active products. The latter must necessarily be removed completely by repeated crystallizations before any comparison can be drawn between the optical properties of camphane and camphane-2-d. The difficulty with which camphane derivatives are purified renders any process of purification questionable as to its thoroughness. No attempt was made by Biilmann to characterize the camphane or camphane-d used for comparative rotation studies either by analysis, density or other physical constants with the exception of melting points, which are not significant. Since the results of these investigators are not in complete accord with the present and previous[1,3] researches concerning this problem of asymmetry, it seems advisable to make the herein described report at this time before the investigation is satisfactorily finished. In addition, it is worth mentioning that the first mentioned authors found that the sample of active camphane-2-d was converted into an inactive product, presumably camphane, by treatment with hydrogen in the presence of platinum and carbon at room temperature. It is rather odd that cleavage by hydrogen of an ordinary carbon–deuterium bond would occur with

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[1] For the previous article in this field see Leffler and Adams, THIS JOURNAL, **58**, 1551 (1936).

A description of this investigation herewith reported was included in an address in connection with the Willard Gibbs Medal award to the senior author, May 23, 1936.

[2] Biilmann, Jensen and Knuth, *Ber.*, **69**, 1031 (1936).

[3] Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).