

m. p. 130–131°. The substance is easily soluble in hot water, alcohol and acetone, less soluble in chloroform, insoluble in cold water, benzene, ether and petroleum ether.

*Anal.* After drying at 100° *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, calcd. for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>N: C, 67.00; H, 7.32; N, 7.82. Found: C, 66.78; H, 7.11; N, 7.72.

*ε*-(*p*-Aminophenyl)-caproic Acid.—Ten grams of *ε*-(*p*-nitrophenyl)-caproic acid reduced in the same manner as the nitrophenylbutyric acid yielded 7.5 g. of crude *ε*-(*p*-

nitrophenyl)-caproic acid. It was recrystallized from 80 volumes of boiling water. Long narrow microscopic platelets, m. p. 108–109°. The substance is soluble in hot water, alcohol and acetone, less soluble in chloroform and benzol, insoluble in cold water, ether and petroleum ether.

*Anal.* After drying at 100° *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, calcd. for C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>N: C, 69.52; H, 8.27; N, 6.76. Found: C, 69.46; H, 8.36; N, 6.64.

NEW YORK, N. Y.

RECEIVED DECEMBER 30, 1933

## COMMUNICATIONS TO THE EDITOR

### ANOMALOUS FRIEDEL-CRAFTS REACTIONS WITH FURANS

Sir:

The compound formed by interaction of benzene, 2-furoic acid and aluminum chloride is *α*-naphthoic acid and not 3-phenyl-2,3-dihydro-2-furoic acid [THIS JOURNAL, 49, 565 (1927)]. The formation of *α*-naphthoic acid, probably through an endoxy compound as a consequence of 1,4-addition, may be general with related types. Other catalysts and experimental conditions, with a miscellany of compounds, are being investigated.

In the reaction between 2-furfural, isopropyl chloride and aluminum chloride in carbon disulfide [*ibid.*, 55, 4197 (1933)], the isopropyl group is introduced into a *β*-position despite the availability of an *α*-position. Bromination of the corresponding acid gives a 5-bromo-*β*-isopropyl-2-furoic acid identical with that obtained by the oxidation of the bromoaldehyde obtained from 5-bromo-2-furfural, isopropyl chloride and aluminum chloride. The same acid is obtained by hydrolysis of the ester resulting by interaction of ethyl 5-bromo-2-furoate, isopropyl chloride and aluminum chloride.

DEPARTMENT OF CHEMISTRY  
IOWA STATE COLLEGE  
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HENRY GILMAN  
M. McCORKLE  
N. O. CALLOWAY

RECEIVED DECEMBER 26, 1933

### THE MUTAROTATION OF *α*-D-GLUCOSE IN DEUTERIUM WATER

Sir:

In a previous communication [THIS JOURNAL, 55, 5056 (1933)] it has been reported that the mutarotation of *α*-*d*-glucose in 60% heavy water at 18° has a velocity coefficient of 0.00290 as

compared to 0.00546 found under identical conditions in ordinary distilled water. With the production of 100% deuterium water (D<sub>2</sub>O) in this Laboratory, it became possible to determine the velocity coefficient of the mutarotation of *α*-*d*-glucose in this medium. A 0.6030-g. sample of pure *α*-*d*-glucose was dissolved in 3.3210 g. of D<sub>2</sub>O of *d*<sub>4</sub><sup>20</sup> 1.1055 and the rotation of the solution (*d*<sub>20</sub><sup>20</sup> 1.175) was read at certain intervals of time in a 2-dm. semi-micro tube with sodium light at 20°. The first reading (*α*<sub>0</sub> 38.50°) was taken seven minutes after the addition of D<sub>2</sub>O. The results obtained are shown in Table I.

TABLE I

Time, minutes	<i>α</i>	$k_1 + k_2 = \frac{1}{t} \log \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha}$
0	<i>α</i> <sub>0</sub> = 38.50	.....
15	37.05	0.00221
50	34.09	.00221
90	31.29	.00220
120	29.50	.00221
180	26.72	.00220
300	23.06	.00222
697	19.35	.00222
1440	<i>α</i> <sub>∞</sub> = 18.83	Mean 0.00221

The velocity coefficient for *α*-*d*-glucose in ordinary distilled water is given by Hudson and Dale [THIS JOURNAL, 39, 320 (1917)] as  $k_1 + k_2 = 0.00635$  at 20°, and as  $k_1 + k_2 = 0.00225$  at 10°. A comparison of these values with the mean value for  $k_1 + k_2$  in Table I shows that the velocity of the mutarotation of *α*-*d*-glucose in pure D<sub>2</sub>O at 20° is identical with that found in ordinary distilled water at 10°. In this case, therefore, the effect of the deuterium water on the velocity of the mutarotation is equivalent to a drop of 10° in the temperature. The specific rotation of the equilibrium solution in D<sub>2</sub>O is [*α*]<sub>D</sub><sup>20</sup> 18.83° ×

$3.924/2 \cdot 1.175 \cdot 0.603 = 52.14^\circ$  as compared to  $[\alpha]_D^{20} 52.06^\circ$  in distilled water [Riiber, *Ber.*, 56, 2185 (1923)]. Evidently, the replacement of the displaceable hydrogen atom of glucose by a deuterium does not change the value of the specific rotation for the wave length of sodium light. Such a conclusion does not necessarily apply for very short wave lengths.

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EUGENE PACSU

RECEIVED FEBRUARY 5, 1934

#### ANALYSIS OF THE DISPERSION CURVES OF SUBSTITUTED PROPIONIC ACIDS

Sir:

It has been observed in this Laboratory that in homologous series of optically active configura-

levorotatory in alanine and in lactic acid and that they are of reverse sign in the levo iodo and dextro azido acids. Similar reversions of the partial rotations are observed in the configurationally related 2-thio and 2-sulfopropionic acids.

The direction and the values of the partial rotations were determined through the analysis of the rotatory dispersion curves in the visible and in the ultraviolet regions by a method previously described [P. A. Levene, A. Rothen and R. E. Marker, *J. Chem. Physics*, 1, 662 (1933)]. The details of the work, the dispersion curves, and the numerical values of the partial rotation will be published in the near future.

THE ROCKEFELLER INSTITUTE  
FOR MEDICAL RESEARCH  
NEW YORK, N. Y.

P. A. LEVENE  
ALEXANDRE ROTHEN

RECEIVED FEBRUARY 2, 1934

Substance	Rotation in the visible	Groups Y COOH, CHO, CH <sub>2</sub> =CH		Groups X SH, SO <sub>3</sub> H, N <sub>3</sub> , NH <sub>2</sub> , OH, I	
		Abs. band $\lambda_y$ , Å.	Sign of $\alpha_y$	Abs. band $\lambda_x$ , Å.	Sign of $\alpha_x$
2-Thiopropionic acid	Dextro	2100	-	≈2400	+
2-Sulfopropionic acid	Dextro	2150	+	Schumann region	-
2-Azidopropionic acid	Levo	Distant U. V.	-	≈2830	+
2-Aminopropionic acid	Dextro	2100	+	Schumann region	-
1-Octene-3-ol	Dextro	Distant U. V.	+	Schumann region	-
2-Hydroxyheptanoic aldehyde	Levo	3000	+	Schumann region	-
Lactic acid	Dextro	2150	+	Schumann region	-
2-Iodopropionic acid	Dextro	≈2150	-	≈2840	+

Braces indicate configurational relationship.

tionally related substances, individual members may differ in the sign of their rotations in the visible, but the partial rotations of the significant chromophoric group and of the rest of the molecule remain of the same sign. This is also often the case in configurationally related substances similar in structure, such as substances 5, 6 and 7 of the table. Comparing the partial rotations of levo iodo and of dextro azido propionic acids, it was found that the partial rotation of the carboxyl in both cases is dextrorotatory and the partial rotations of the iodine atom and of the N<sub>3</sub>- are both levo rotatory. Hence, it may be assumed that these two substances are configurationally related (and not levo iodo- and levo azidopropionic, as assumed by Freudenberg and Kuhn). Furthermore, inasmuch as dextro azidopropionic acid is correlated to levo alanine and this, in its turn, has been correlated to levo lactic acid, it may be assumed that levo lactic acid is correlated to dextro 2-azido and hence to the levo 2-iodo acid. It will be noticed from the table that the partial rotations of the carboxyl groups are

#### THE CONSTITUTION OF OESTRIN

Sir:

The work of Butenandt, *et al.*,<sup>1</sup> which demonstrated the presence of a phenanthrene system in the skeleton of the oestrin molecule, left indefinite the position of the five-membered ring which is also known to be present. The possible positions according to Butenandt for this ring were 8:14, 14:13, or 13:12, using the customary sterol nomenclature.

It does not seem to be generally realized that Butenandt's work, when taken in conjunction with the results obtained with unimolecular films of oestrin derivatives, offers a clear proof of the fact that the five-membered ring is in the same position as in the sterols, *i. e.*, 14:13. Measurements made on models show the following minimal areas for the cross section of the possible structures.

Formula	Position of the five-membered ring	Minimal cross-sectional area, in sq. Å.
I	8:14	39
II	14:13	33
III	13:12	38

(1) Butenandt, Weidlich and Thompson, *Ber.*, 66, 601 (1933).