These results indicate that the ratio of Al_2Br_6 to C_6H_6 is 1 :6 and that the complex contains some hydrogen bromide.

When the oil was shaken with petroleum ether it decreased in volume. The residual oil gave on analysis the ratios Al 1, Br 2.9, C_6H_6 0.63. It appeared that the product contained Al_2Br_6 and C_6H_6 in the ratio 1:1.

The vessel containing a sample of the original oil was evacuated at 12 mm. Crystals soon appeared. This behavior is different from that of the complexes formed from the other hydrocarbons which gave no crystals but left a product containing the bromide and the hydrocarbon. The crystals appeared to be aluminum bromide. When 18.2 g. of the complex was held under diminished pressure, in about three hours the residue weighed 8.8 g., which is very close to the weight of the aluminum bromide in the complex.

In a second experiment the complex was held at 12 mm. for four hours and then at 0.002 mm. The loss at the latter pressure was 0.01 g. The residue was slightly impure aluminum bromide. The sum of the percentages of aluminum and bromine was 94.4%.

Summary

1. The ethyldimethylbenzene prepared by the Friedel and Crafts reaction from ethyl bromide and *m*-xylene has been restudied and evidence given that the hydrocarbon has the symmetrical structure.

2. The preparation and properties of complexes of certain aromatic hydrocarbons and aluminum bromide or aluminum chloride are described.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 10, 1940

NOTES

Reaction between a Highly-Substituted Bromopyridine and Lithium

BY C. F. H. ALLEN AND G. F. FRAME

In view of the increasing interest in organometallic heterocyclic compounds[1] it seems advisable to record that lithium reacts slowly with the highly-substituted 2-bromo-3,4,6-triphenylpyridine. The resulting suspension does not seem to react with carbon dioxide, aldehydes, or ketones. Upon decomposition by acids, a 20–25% yield of 2,4,5-triphenylpyridine can be secured by distilling in a high vacuum. No conditions were found under which the highly-substituted 2,3,5-triphenyl-4-bromofuran would react with lithium. Neither of these substances reacts with magnesium.[2]

In the usual apparatus, swept by nitrogen, a mixture of 50 cc. of dry ether, 0.5 g. of lithium, and 13.8 g. of 2-bromo-3,4,6-triphenylpyridine was refluxed with stirring for four hours. A slow reaction was noted and the solution became a deep reddish-brown. After standing for several days practically all the metal had disappeared. The ether layer, which separated after adding iced hydrochloric acid, was removed, washed, dried, and the solvent evaporated. After efforts to induce crystallization had failed, the thick oil (1.2 g.) was distilled at 1.2–2 microns; a black tarry residue remained. The clear distillate (1.8 g.) crystallized when rubbed with alcohol. 2,4,5-Triphenylpyridine crystallizes in glistening, slightly iridescent rods, m. p. 112°, readily soluble in alcohol, ether and benzene.

Anal. Calcd. for $C_{23}H_{17}N$: N, 4.6. Found: N, 4.5.

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.
RECEIVED FEBRUARY 20, 1940

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[1] Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940).

[2] Allen and Rosener, *ibid.*, **49**, 2113 (1927).

The Carbonation of Organoalkali Compounds

BY HENRY GILMAN AND H. A. PACEVITZ

The kind and ratio of products obtained by carbonation of organometallic compounds are influenced markedly by the rate and temperature of carbonation. With organolithium compounds,[1] in particular, low temperature together with a large excess of carbon dioxide (conditions realized by pouring RM compounds jet-wise on crushed solid carbon dioxide) give predominantly the acid and little of the ketone or tertiary alcohol. Furthermore, carbonation by solid carbon dioxide depresses markedly the formation of malonic acids from benzylmetallic types. This is strikingly illustrated in studies submitted recently[2] with compounds like benzylsodium, benzylpotassium and 3,5-dimethylbenzylpotassium. These RM compounds when carbonated by solid carbon dioxide give almost exclusively the corresponding carboxylic acids; however, carbonation by gaseous

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[1] Gilman and Van Ess, THIS JOURNAL, **55**, 1258 (1933). See, also, Gilman and Parker, *ibid.*, **46**, 2816 (1924).

[2] Gilman, Pacevitz and Baine, *ibid.*, **62**, June (1940).

carbon dioxide gives, in addition to the expected carboxylic acids, significant quantities of the malonic acids. The malonic acids probably owe their formation largely to a secondary metalation reaction of the active methylene group by the unused RM compound present in slow carbonation. The typical transformations may be illustrated by the studies of Ivanoff and Spassoff[3] with benzylmagnesium chloride.

$$C_6H_5CH_2MgCl + CO_2 \longrightarrow C_6H_5CH_2CO_2MgCl$$

$$C_6H_5CH_2CO_2MgCl + C_6H_5CH_2MgCl \longrightarrow [C_6H_5CHCO_2MgCl][MgCl] + C_6H_5CH_3$$

$$[C_6H_5CHCO_2MgCl][MgCl] + CO_2 \xrightarrow{[H_2O]} C_6H_5CH(CO_2H)_2$$

Our carbonation experiments with benzylalkali types[2] raise a question concerning benzylidene-dialkali compounds like $C_6H_5CHM_2$. If such compounds are formed in one way or another incidental to the several procedures[2] for the preparation of benzylalkali compounds, then it is possible, but somewhat unlikely, that they are not carbonated by solid carbon dioxide. We are at present of the opinion that they are either not formed or are formed to a subordinate extent, incidental to the preparation of benzylalkali types.

Of more immediate interest are the aliphatic types, $RCHM_2$, like amylidene-disodium.[4] From the experiments now reported, we find that the organosodium compound or compounds formed by interaction of *n*-amyl chloride and sodium give largely caproic acid with very little *n*-butylmalonic acid when carbonation is effected by solid carbon dioxide; and a mixture of caproic acid with large amounts of *n*-butylmalonic acid when gaseous carbon dioxide is used. Additional experiments may provide an answer to the question as to whether secondary metalations or other transformations, some of which have been reported,[4] are responsible for the reactions of compounds of benzylidene-dimetallic and amylidene-dimetallic types.

Experimental Part

In a typical experiment, a solution of 16.5 g. (0.155 mole) of freshly distilled *n*-amyl chloride (b. p., 107–108°) in 15 cc. of petroleum ether (b. p. 85–100°) was added dropwise over a one-hour period to 8.75 g. (0.38 g. atom) of sodium sand in 75 cc. of petroleum ether. The mixture was stirred at room temperature for four hours, after which it was carbonated by pouring jet-wise on solid carbon dioxide, the addition being completed within ten seconds. The products obtained (by isolation and weighing) were 6.9 g. or 38.5% of caproic acid and less than 1% of impure *n*-butylmalonic acid. In a check experiment on this carbonation by solid carbon dioxide the yield of *n*-caproic acid was 7.3 g. or 40.8%; and the yield of impure *n*-butylmalonic acid was again less than 1%. In a parallel experiment in which carbonation was effected by admitting gaseous carbon dioxide to the surface of the reaction mixture over a five-hour period at 27–28° and with stirring, the yield of *n*-caproic acid was 2.72 g. or 15.2%; and the yield of *n*-butylmalonic acid was 2.1 g. or 16.9%.

Again using the same quantities of reagents, two parallel experiments were carried out by first stirring at 27–28° for one hour and then at 42° for two hours. Rapid carbonation (solid carbon dioxide, ten seconds) yielded 6.52 g. or 36.4% of *n*-caproic acid, and less than 1% of impure *n*-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, five hours) yielded 3.53 g. or 19.5% of *n*-caproic acid, and 1.83 g. or 14.8% of *n*-butylmalonic acid.

Acting on the suggestion that low boiling petroleum ether might give different results, parallel experiments were carried out with purified petroleum ether distilling over the range 28–38°. Rapid carbonation (solid carbon dioxide, five to ten seconds) yielded 51.5% of caproic acid and less than 2% of *n*-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, four hours) yielded 17.3% of caproic acid and 31.4% of *n*-butylmalonic acid.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED FEBRUARY 27, 1940

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[3] Ivanoff and Spassoff, *Bull. soc. chim.*, **49**, 19 (1931). See, also, Morton, Fallwell and Palmer, THIS JOURNAL, **60**, 1426 (1938), for the carbonation of benzylsodium.

[4] Morton and Richardson, *ibid.*, **62**, 129 (1940). Earlier references are to be had from this most recent article.

Agaric Acid and the Donnan Theory of Membrane Equilibrium

BY R. J. HARTMAN, E. W. KANNING AND J. E. WEBER[1]

The electromotive force of the following cell was measured at 25°.

Calomel electrode	Satd. KCl	Outside solution: dilute HCl	"Parlodion" membrane	Inside solution: agaric acid, 1.25%; $Ca(OH)_2$ or HCl, in varying quantities	Satd. KCl	Calomel electrode

The agaric acid was prepared by electrodialyzing "Noble Difco" agar agar for twenty-four hours under a potential of 110 volts according to the procedure of Hoffman and Gortner.[2] The procedure followed in making the electromotive force measurements was essentially the same as that used by Loeb.[3] After about twenty-four hours a true membrane equilibrium was established as

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[1] This paper is constructed from a dissertation presented by Joseph Elliott Weber to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Hoffman and Gortner, *J. Biol. Chem.*, **65**, 371 (1925).

[3] J. Loeb, "Proteins and the Theory of Colloidal Behavior," Chapter XI, McGraw-Hill Book Co., New York, N. Y., 1924, p. 177.

TABLE I

MEMBRANE AND HYDROGEN ELECTRODE POTENTIALS FOR THE SYSTEM, AGARIC ACID/HYDROCHLORIC ACID

N $Ca(OH)_2$ in 50 ml. of agaric acid solution, ml.	Milliequivalents HCl in 50 ml. of agaric acid solution	Original *p*H	Final *p*H outside	Final *p*H inside	*p*H Out − *p*H In	H_2 elect. potential, mv.	Measured potential, mv.
50.0	..	3.95	4.00	3.93	0.07	4.1	3.85
25.0	..	3.64	3.73	3.64	.09	5.3	5.24
10.0	..	3.28	3.38	3.28	.10	5.9	6.00
6.0	..	3.13	3.26	3.14	.12	7.1	6.85
4.0	..	3.06	3.20	3.06	.14	8.3	8.59
3.0	..	3.02	3.19	3.03	.16	9.5	8.92
2.0	..	2.97	3.00	2.91	.09	5.3	4.82
1.0	..	2.70	2.71	2.68	.03	1.8	2.09
0.5	..	2.66	2.69	2.67	.02	1.2	1.16
..	0.0	2.48	2.48	2.47	.01	0.6	0.92
..	0.5	1.79	1.80	1.78	.02	1.2	.88
..	1.0	1.42	1.47	1.41	.06	3.6	1.19
..	2.0	1.20	1.23	1.20	.03	1.8	1.59
..	3.0	1.09	1.10	1.04	.06	3.6	2.85
..	4.0	1.01	1.02	0.94	.08	4.7	4.85
..	5.0	0.98	0.99	.91	.08	4.7	4.15
..	6.0	.94	.95	.90	.05	3.0	2.99
..	10.0	.72	.73	.71	.02	1.2	1.05
..	12.0	.71	.72	.70	.02	1.2	1.07

is shown in Table I where the observed P. D. (Measured Potential) is found to be in reasonably good agreement with the hydrogen electrode potential calculated from the *p*H values of the two solutions (measured at the end of the experiment). The membrane potential thus obtained arises from the unequal distribution of H^+ and Cl^- on opposite sides of the membrane. Tests of the hydrogen chloride solution revealed that neither Ca^{++} nor agarate ions passed through the membrane in detectable quantities.

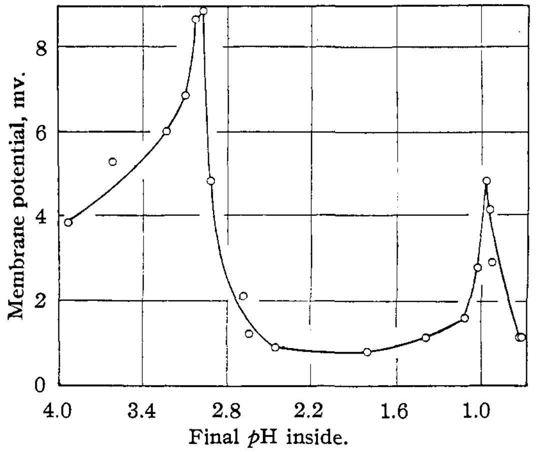

Fig. 1.—Relationship between *p*H and membrane potential.

When the final *p*H inside is plotted against the measured membrane potential, two maxima are found at *p*H values of approximately 3.0 and 1.0 (see Fig. 1). The second maximum is attributed to the hydrolytic decomposition of the agar. Since the membrane potential of such systems is a colligative property depending upon the number of discrete discontinuities of the dissolved constituent present, it is to be expected that the membrane potential will vary as a function of the concentration of the osmotically active particles. Agaric acid, a polyuronide, yields uronic acid units and reducing sugars.[4] Therefore, a second equilibrium is to be expected at *p*H values of approximately 1.0 where the agar complex is known to hydrolyze into simpler units.

(4) A. G. Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Oxford University Press, Oxford, England, 1937.

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, IND.

RECEIVED DECEMBER 4, 1939

Melting Points of the *p*-Bromoanilides of Solid Fatty Acids[1]

BY DAVID F. HOUSTON

The melting points of the *p*-bromoanilides of certain solid fatty acids recently prepared in this Laboratory differ greatly from those in the literature.[1a] Several of our results agree with those previously ascribed to higher homologs. A graph of our values has the general form of the melting-point curves of aliphatic series; that of

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(1) Not subject to copyright.

(1a) P. W. Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).

TABLE I

ANALYSES AND MELTING POINTS OF THE *p*-BROMOANILIDES OF SOLID FATTY ACIDS

p-Bromoanilide	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Bromine Calcd.	Bromine Found	Melting point in °C. Lit.[c]	Melting point in °C. Found
Capric	58.92	59.03[a]	7.37	7.54[a]	24.6	24.7[b]	102	101.9
Lauric	61.02	61.02	7.94	7.93	22.6	22.5	104	106.7
Myristic	62.81	62.94	8.41	8.26	20.9	21.2	107	110.2
Palmitic	64.38	64.33	8.81	8.74	19.5	19.2	110(114)[d]	113.2
Stearic	65.72	65.63[a]	9.16	9.38[a]	18.3	18.4[b]	114	115.2

[a] Analyses by W. T. Haskins, National Institute of Health; all others by C. J. Rodden, National Bureau of Standards. [b] Pregl method. Other bromine analyses by Zacherl and Krainick method. [c] Robertson's values[1a] except *d*. [d] Acree and LaForge (*J. Org. Chem.*, **2**, 308 (1937)). A sample of their material showed a melting point of 113.1° when determined by the writer by means of the Francis and Collins method.

the literature values has an opposite convexity. Hence it has seemed wise to publish our results.

The reagent quality acids were first recrystallized from concentrated sulfuric acid[2] until no further discoloration of the solvent occurred, and they were then repeatedly recrystallized interchangeably from acetone, benzene, and glacial acetic acid until no further change in melting point occurred. The acids were converted into their acid chlorides with thionyl chloride.

The *p*-bromoaniline was prepared (a) by the reduction of *p*-nitrobromobenzene (m. p. 126.3°), (b) by hydrolysis of *p*-bromoacetanilide (m. p. 168.6°) according to Vecchiotti,[3] and (c) by recrystallization of a commercial product from chloroform and then from aqueous alcohol to remove colored matter[4] and tribromoaniline, respectively. The three preparations of *p*-bromoaniline thus obtained had melting points between 63.5 and 64.0°, and gave products with palmitic acid which had identical melting points.

The chlorides were treated with a benzene solution of *p*-bromoaniline according to the procedure of Kuehn and McElvain,[5] with the single modification of first crystallizing the product directly from the benzene solution instead of evaporating the benzene. In the case of the long chain acids, this affords a more rapid purification.

The melting points were determined with a partial-immersion thermometer (calibrated at this Bureau) by the improved capillary-tube method of Francis and Collins.[6] This procedure, which maintains an extremely slow rate of temperature rise at the melting point, gives values that are somewhat lower than those usually obtained by capillary-tube methods (see footnote *d* of table). The results are, however, in better agreement with those obtained by equilibrium measurements on larger amounts of material.

NATIONAL BUREAU OF STANDARDS
U. S. DEPARTMENT OF COMMERCE
WASHINGTON, D. C.

RECEIVED JANUARY 20, 1940

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(2) F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. London*, **A158**, 706 (1937).

(3) L. Vecchiotti, *Gazz. chim. ital.*, **58**, 231 (1928).

(4) W. M. D. Bryant, THIS JOURNAL, **60**, 2748 (1938).

(5) M. Kuehn and S. M. McElvain, *ibid.*, **53**, 1173 (1931).

(6) F. Francis and F. J. E. Collins, *J. Chem. Soc.*, 137 (1936).

The Separation of Hydroxy from Non-hydroxy Fat Acids by Means of a Dibasic Acid Anhydride[1]

BY FLOYD E. KURTZ[2] AND P. S. SCHAFFER[2]

The methods used for separating hydroxy from non-hydroxy fat acids have been based for the most part on differences in physical properties of the acids or of the derivatives formed with the carboxyl group. When the fat acid mixture contains acids in which these differences are small, it becomes difficult to secure a separation by such methods. This is particularly true if one of the similar acids is present as a minor constituent while the other is present in a high concentration.

In the method proposed here, the mixed esters are heated with a dibasic acid anhydride, the reaction mixture is dissolved in petroleum ether, and the derivative formed with the hydroxy esters is extracted with alkali. Since this method consists in the separation of an alcoholic from a non-alcoholic compound rather than upon the separation of two acids, its efficiency is not affected by a similarity in the physical properties of the acids.

Of the most readily available dibasic acid anhydrides, phthalic anhydride was considered unsuitable because of the difficulty of freeing the recovered fat acids from phthalic acid. Maleic anhydride was thoroughly investigated. It formed derivatives with methyl ricinoleate and with 12-hydroxymethylstearate which could be extracted readily from petroleum ether solutions, less readily from ether solutions, by means of dilute potassium hydroxide. Since ricinoleic acid and 12-hydroxystearic acid represent two hydroxy acids with quite different physical properties, it is considered likely that similar results could be ob-

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(1) The part relating to maleic anhydride was presented before the Division of Biological Chemistry at the 97th meeting of the American Chemical Society, April 3-7, 1939, at Baltimore, Maryland. (Not subject to copyright.)

(2) Division of Dairy Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.

TABLE I

SEPARATION OF RICINOLEIC ACID FROM A NON-HYDROXY ACID

Experimental conditions: Heated with		Equiv.	Time, hr.	Temp., °C.	Ricinoleic acid, %: Concn. in starting mat.	In hydroxy acid fraction: Concn. sepd.	Orig. recov.
Maleic anhydride		6	18	120	5	47	63
		6	18	120	10	86	70
		1.5	6	100	50	95	84
Succinic anhydride with solvent	AmOAc	10	18	120	10	68	70
	Dioxane	10	18	120	10	73	47
	Pyridine	10	7	130	10	93	78
	Pyridine	10	18	130	10	92	86

tained with a large variety of hydroxy fat acids. Maleic anhydride is sufficiently soluble in esters, so that the reaction mixture can be made homogeneous by the addition of only a small proportion of dioxane and often without any solvent. Pyridine is not suitable as a solvent because of the formation of large amounts of a tarry precipitate. A disadvantage in the use of maleic anhydride was found in an unexpected side reaction which takes place to a certain extent between methyl oleate and maleic anhydride to form a saturated compound. Succinic anhydride does not have this disadvantage but because of its lower solubility in the higher esters a solvent is necessary. With dioxane low yields are obtained. With pyridine better yields are obtained, but on prolonged heating considerable quantities (though much less than with maleic anhydride and pyridine) of a tarry precipitate are formed. It is recommended that when the separation involves only saturated acids, maleic anhydride be used, and that when unsaturated acids are present, succinic anhydride be used.

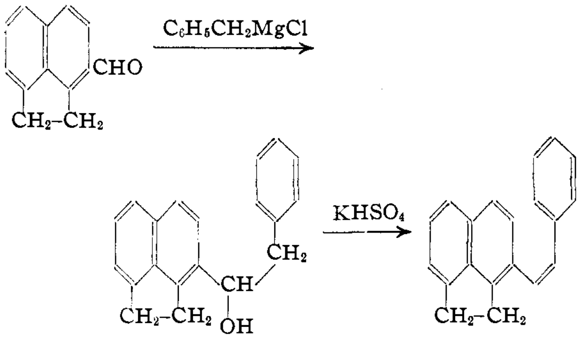
Table I summarizes the results of some typical experiments. It is obvious from the data that, in most cases, more than one application of the separation would be necessary to secure the one type of acid free from the other. In the case of the castor oil acids, which contain about 85% of hydroxy acids, it was found that by two applications of the separation the hydroxy acids were obtained practically free from non-hydroxy acids.

BUREAU OF DAIRY INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
RECEIVED DECEMBER 4, 1939

1-(β-Styryl)-acenaphthene

BY E. B. HERSHBERG[1] AND LLOYD M. JOSHEL[2]

The hydrocarbon mentioned in the title seemed of interest because in the *cis* form it constitutes an "opened" model of the carcinogenic cholanthrene from which it differs merely by the absence of one linkage connecting the benzenoid rings. The substance was synthesized by condensing 1-acenaphthaldehyde[3] with benzylmagnesium chloride and dehydrating the resulting carbinol. The hydrocarbon is crystalline and shows fluorescence in ultraviolet light.



Experimental Part[4]

1-Acenaphthylbenzylcarbinol.—A solution of 3.7 g. of 1-acenaphthaldehyde in benzene was added to the Grignard reagent from 3.5 cc. of benzyl chloride and 0.8 g. of magnesium in ether and after refluxing for one and one-half hours the mixture was decomposed with ammonium chloride and the solvents removed with steam. The product was taken up in ether and after washing and drying was obtained from ether–ligroin as needles, m. p. 107–109.5°, sufficiently pure for the next step; yield 4.9 g. (88%). A sample recrystallized for analysis from ether–ligroin (Norit) formed colorless needles, m. p. 109–110°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 87.55; H, 6.61. Found: C, 87.62; H, 6.82.

1-(β-Styryl)-acenaphthene.—A mixture of 1.5 g. of the carbinol and about 0.1 g. of fused potassium bisulfate was heated at 200° until the evolution of water had ceased (ten minutes) and the product was then vacuum distilled and crystallized from absolute alcohol. The yield of twice crystallized hydrocarbon, m. p. 91.5–93°, was 1.0 g. (71%), but further recrystallizations were required to give material of the constant m. p. 93.2–94.0° (0.6 g.), possibly because

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(1) Research Fellow on grants from the National Cancer Institute and the Eli Lilly Company.

(2) Fellow of the Finney-Howell Research Foundation.

(3) Fieser and Hershberg, THIS JOURNAL, **62**, 49 (1940).

(4) All melting points are corrected. Microanalyses by Lyon Southworth.

of the presence of *cis–trans* isomers. The substance exhibits a very strong blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.49.

A **dipicrate** was obtained from alcohol and crystallized as very dark red needles, m. p. 141.5–143°, dec.

Anal. Calcd. for $C_{20}H_{16}{\cdot}2C_6H_3O_7N_3$: N, 11.76. Found: N, 11.61.

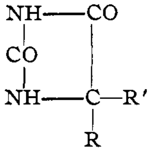
CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
RECEIVED MARCH 27, 1940

Some New 5,5-Disubstituted Hydantoins

BY DAVID MARSH AND C. L. LAZZELL

It appears desirable to record data obtained on some six new 5,5-disubstituted hydantoins which have been prepared in this Laboratory following Bucherer's[1] method incidental to some other investigations. These substances were all recrystallized from 50% alcohol and were dried for five days at 85°. Except for the di-(*p*-dimethylaminophenyl) analog, which was yellow and soluble in benzene, they were all white crystalline solids, readily soluble in such organic solvents as acetone and 95% alcohol, but only moderately soluble in water.

TABLE I



—R	—R′	M. p. °C. (cor.)	Yield, %	Molecular weight Calcd.	Molecular weight Found	% Nitrogen Calcd.	% Nitrogen Found
Methyl	Cyclohexyl	204–205	48	199.31	200	14.1	14.1
Methyl	Styryl	217 d.	12	216.26	214	13.07	13.1
p-Dimethylaminophenyl	*p*-Dimethylaminophenyl	136–137	3	338.50	344	16.63	16.6
Methyl	2-Methylpropenyl	209–210	18	168.26	168	16.73	16.8
Methyl	*p*-Aminophenyl	100–101	36	205.33	202	20.57	21.0
Methyl	2-Methyl-2-hydroxypropyl	180–181	10	186.27	188	15.12	15.0

The yields obtained were rather low, but since it was only desired to obtain a pure sample of each hydantoin, no effort was made to improve them.

[1] Bucherer and Lieb, *J. prakt. Chem.*, [2] **141**, 5 (1934).

DEPARTMENT OF CHEMISTRY
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA
RECEIVED FEBRUARY 5, 1940

The Addition of Hydrogen Bromide to Methyl Methacrylate

BY CHARLES C. PRICE AND EUGENE C. COYNER

It has been found that methyl methacrylate adds hydrogen bromide to form methyl *β*-bromoisobutyrate exclusively. Only the *β*-bromo ester was produced even in pentane solution with peroxide catalysis, the conditions most favorable for reversing the mode of addition of hydrogen bromide to a double bond.[1]

This is in agreement with similar experiments with acrylic and crotonic acids and ethyl crotonate reported by Walling, Kharasch and Mayo and by Grimshaw, Guy and Smith[2] since the initiation of this investigation.

Since only the boiling points of the two possible addition products have been recorded, the two isomeric methyl bromoisobutyrates have been carefully characterized.

Methyl *β*-Bromoisobutyrate.—When redistilled methyl methacrylate[3] (10 g.) in hexane or carbon tetrachloride solution (50–100 cc.) was treated with hydrogen bromide at 0 or 25° in the presence of 1% of hydroquinone, benzoyl peroxide or "Lucidol"[4] or while exposed to direct sunlight in a quartz flask, nearly quantitative yields of methyl *β*-bromoisobutyrate were obtained; b. p. 67° (17 mm.),[5] $n^{20}{}_D$ 1.4551; $d^{20}{}_4$ 1.426; $M^{20}{}_D$ (calcd.) 34.71; $M^{20}{}_D$ (found) 34.47.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found[6]: Br, 44.38.

No other product could be detected; even the first few drops of distillate had properties in agreement with those above. When methanol was used as a solvent no addition occurred at room temperature.

The hydrogen bromide was generated by dropping bromine into tetralin; it was bubbled through tetralin to free it from bromine vapor.

Methyl *α*-Bromoisobutyrate.—For comparison, the *α*-bromo ester was prepared by the Hell–Volhard–Zelinsky method. Bromine (102.5 g.) was added to 29.5 g. of

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[1] Walling, Kharasch and Mayo, THIS JOURNAL, **61**, 1711 (1939).

[2] Walling, Kharasch and Mayo, *ibid.*, **61**, 2693 (1939); Grimshaw, Guy and Smith, *J. Chem. Soc.*, 68 (1940).

[3] E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[4] Lucidol Corporation, Buffalo, New York.

[5] Vocke (*Z. physiol. Chem.*, **191**, 83 (1930)) reported the boiling point as 65–67° (12 mm.).

[6] Method described by Rauscher, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 296 (1937).

isobutyric acid and 5 g. of red phosphorus at 70–80°. The excess bromine was removed by evaporation under diminished pressure and the residue cooled in ice while 20 cc. of methanol was added. On fractional distillation, 14.4 g. (25%) of methyl α-bromoisobutyrate was obtained; b. p. 52° (19 mm.),[7] n^{20}_{D} 1.4410; d^{20}_{4} 1.331; M^{20}_{D} (calcd.), 34.71; M^{20}_{D} (found), 35.01.

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.15. Found[6]: Br, 43.14.

The physical properties of this ester changed appreciably on standing for a few hours since hydrogen bromide is evolved with extreme ease. This accounts for the low bromine content of the product. The physical properties recorded above were observed immediately after distillation.

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[7] Wheeler and Barnes, *Am. Chem. J.*, **24**, 79 (1900).

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RECEIVED MARCH 20, 1940

The Identity of Obaculactone, Evodin and Dictamnolactone with Limonin[1]

BY MILTON S. SCHECHTER AND H. L. HALLER

Several investigators[2,3] have isolated from the extractives of the bark of the amur cork tree (*Phellodendron amurense* Rupr.) a colorless, crystalline, optically active compound, which melts with decomposition at 292–293° and possesses the properties of a dilactone. The compound was named "obaculactone" by Fujita and Wada,[2] who were the first to describe it. On the basis of combustion analyses and molecular weight determinations they assigned the formula $C_{15}H_{16}O_6$ to obaculactone, but subsequent studies have shown this formula to be in error. The molecular formula $C_{26}H_{30}O_8$ is now generally accepted as correctly representing the composition of the compound.

In 1934 Fujita, Kaku and Kutani[4] showed that obaculactone is identical with evodin and with dictamnolactone. Evodin was first isolated by Keimatsu[5] in 1902 from the benzene extractives of the fruit of *Evodia rutaecarpa* Hook. f. and Thoms., and subsequently by several investigators from the fruits of other species of *Evodia*. Dictamnolactone was first described by Thoms and his co-workers[6] who obtained it from the extractives of white dittany (*Dictamnus albus* L.). The latter workers surmised that evodin and dictamnolactone were identical but were unable to make a direct comparison. The identity of the three compounds was established[4] by mixture melting point determinations and specific rotations in neutral and alkaline solution. In acetone all three compounds are levorotatory; $[\alpha]_D$ about $-123°$. In ethanolic potassium hydroxide solution they are dextrorotatory; $[\alpha]_D$ about $+30°$.

None of the early formulas assigned to the lactone were correct. In 1933 Chen and Chen[7] proposed the formula $C_{26}H_{30}O_8$. Mayeda[8] confirmed this and suggested that some of the previous difficulties in the determination of the molecular formula may have been due to the fact that the lactone crystallizes from acetic acid with one mole of acetic acid of crystallization. The lactone melts with decomposition, and melting points ranging from 280 to 293° have been reported for obaculactone, evodin and dictamnolactone by the several investigators.

A recent communication by Higby[9] describes the isolation of limonin from the pulp and seeds of the Valencia orange. This colorless, crystalline compound was first obtained by Bernay[10] in 1841 from the seeds of several varieties of citrus. Limonin has been shown to be an optically active dilactone, and combustion analyses and molecular weight determinations indicate it to possess the formula $C_{26}H_{30}O_8$. Koller and Czerny[11] have reported that limonin melts with decomposition at 280° (uncor.), whereas Higby found 292° (cor.). Citrolimonin, which is considered by Feist and Schulte,[12] by Koller and Czerny, and by Higby as being identical with limonin, is reported to melt with decomposition at 304° (Kofler micro melting point apparatus) by the first-mentioned workers.

In the course of our studies on the insecticidal properties of the fruit of the amur cork tree, the results of which will be reported elsewhere, obaculactone has been obtained from the ether and the acetone extracts of the fruit. The compound, when recrystallized by solution in acetone followed by the addition of ethanol, melted with decomposition at 299–300° (cor.).[13] When recrystallized from glacial acetic acid, it melted with decomposition at 297–298° (cor.). An aqueous

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[1] Not subject to copyright.

[2] Fujita and Wada, *J. Pharm. Soc. Japan*, **51**, 506 (1931), (in German 52).

[3] Kaku, Cho and Orita, *ibid.*, **52**, 593 (1932), (in German 73).

[4] Fujita, Kaku and Kutani, *ibid.*, **55**, 67 (1935).

[5] Keimatsu, *ibid.*, No. **248**, 979 (1902).

[6] Thoms, *Ber. deut. pharm. Ges.*, **33**, 68 (1923).

[7] Chen and Chen, *J. Am. Pharm. Assoc.*, **22**, 716 (1933).

[8] Mayeda, *J. Pharm. Soc. Japan*, **55**, 90 (1935).

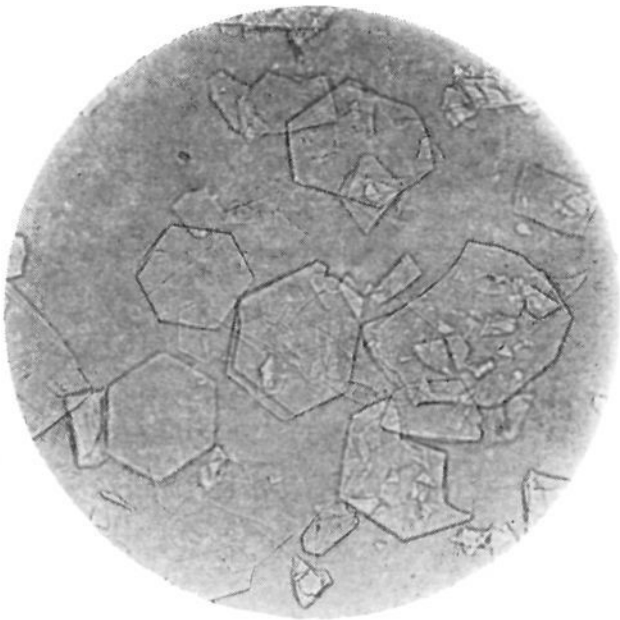
[9] Higby, THIS JOURNAL, **60**, 3013 (1938).

[10] Bernay, *Ann.*, **40**, 317 (1841).

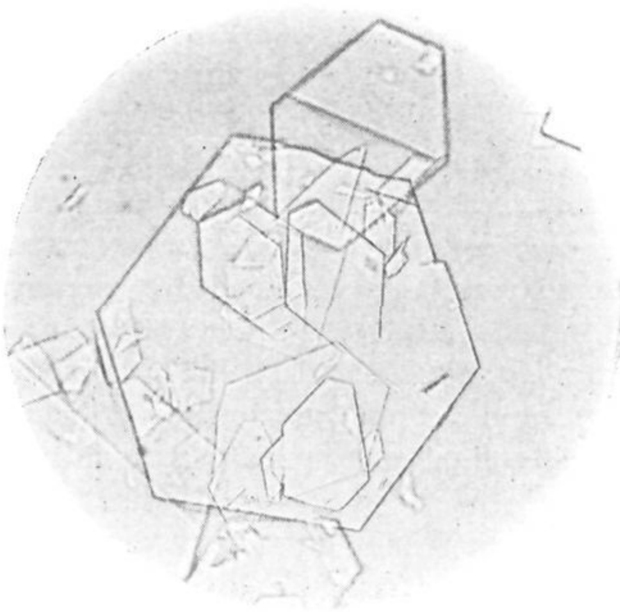
[11] Koller and Czerny, *Monatsh.*, **67**, 248 (1936); **70**, 26 (1937).

[12] Feist and Schulte, *Ber.*, **69**, 1322 (1936).

[13] All the melting point determinations reported were made in open melting point capillaries, using a total immersion thermometer calibrated by the National Bureau of Standards, Washington, D. C.



Obaculactone (× 77).



Limonin (× 193).

Fig. 1.

ethanol solution of the lactone has an intensely bitter taste. It is insecticidally inert.

Some of the chemical properties recorded for obaculactone have been confirmed by us. It is a dilactone, dissolves in concentrated sulfuric acid with the formation of an intense red brown color, and does not absorb bromine in chloroform solution. It does not possess alkoxyl groups, or reactive carbonyl or hydroxyl groups. Contrary to the statement of Fujita and Wada,[2] it has been found that obaculactone absorbs hydrogen slowly on catalytic hydrogenation with the formation of a mixture of products. A study of these products will form the subject of a future communication.

Obaculactone recrystallized from a mixture of ethanol and acetone and then dried in an Abderhalden drier at 100° gave the following analytical data:

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.43; mol. wt., 470. Found: C, 66.39, 66.20; H, 6.52, 6.50; mol. wt. (Rast), 445; equiv. wt. (sodium hydroxide titration), 240. *Optical rotation:* 0.0888 g. in 10 cc. of acetone at 20.5° rotated $-2.29°$; $l = 2.0$ dm.; $[\alpha]^{20.5}\text{D}$ $-129°$. 0.0844 g. in 5 cc. of 0.5 N ethanolic potassium hydroxide and 5 cc. of water at 20.5° rotated $+0.55°$; $l = 2.0$ dm.; $[\alpha]^{20.5}\text{D}$ $+32.6°$.

The melting point, the rotation in neutral solution, the behavior toward alkali, and the identity of the molecular formula of obaculactone and limonin led us to believe that the two were the same. Through the courtesy of Dr. M. B. Matlack, Food Research Division, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture, we obtained a sample of limonin isolated by him from orange seed. When recrystallized from ethanol or from glacial acetic acid the compound melted with decomposition at 297–298° (cor.). A mixture of equal parts of limonin and obaculactone also melted with decomposition at 297–298° (cor.).

The optical rotations of limonin in acetone solution and in 0.25 N aqueous ethanol potassium hydroxide solution were practically identical with the values obtained for obaculactone in these solvents.

Obaculactone and limonin recrystallized from ethanol consisted of colorless, micaceous, six-sided plates and were found to be identical microscopically.[14] Refractive indices (determined by immersion in oily liquids): $n_\alpha = 1.563$; $n_\beta =$ indet.; $n_\gamma = 1.582$; both ± 0.002. In parallel polarized light (crossed nicols) the birefringence is moderate, usually first-order grays being shown. There appears to be no definite elongation. In convergent polarized light (crossed nicols) the plates were found to extinguish sharply, indicating that the plane of the optic axes is approximately parallel to the broad face of the plates so that interference figures could not be expected. Therefore, the refractive indices were determined by a variation of the statistical method, plates showing maximum double refraction for obtaining n_α and n_γ being selected.

The foregoing results indicate clearly that obaculactone and limonin are identical.

Since obaculactone, evodin, dictamnolactone, limonin, and citrolimonin are the same compound, it would appear desirable to retain one name and discard the others. As the compound was first

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[14] We are indebted to George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture, for the photomicrographs and for the optical crystallographic data reported here.

obtained by Bernay, who designated it "limonin," we suggest that this name be retained.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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WASHINGTON, D. C.

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Mechanism of Nuclear Isomer Separation Process

BY G. T. SEABORG, G. FRIEDLAENDER AND J. W. KENNEDY

It has been shown that the energy released during the radioactive transition from an upper to a lower isomeric state of an atomic nucleus can be used to effect a chemical separation of two genetically related nuclear isomers and this discovery has provided a powerful method for the study of nuclear isomerism.[1,2,3,4] These so-called *isomeric transitions* have been the source of activation energy for many interesting chemical reactions and offer a unique method for a study of chemical activation.[1–6] We wish to report briefly some experiments which we have performed for the purpose of elucidating the mechanism of the chemical separation process.

The small amount of recoil energy, about 5.6 kcal. per mole,[7] acquired in the majority of the cases by the Br^{80} atom as the result of the emission of an internal conversion electron during an isomeric transition in a Br^{80} nucleus, seemed to be too small to account for the bond rupture and activation experiments (sometimes 100% efficient[1]) observed with bromine compounds. We have performed experiments with the isomeric transitions[3] in radioactive Te^{127} and Te^{129}, where the recoil energies are again very small. Internal conversion electrons are emitted in these cases and the recoil energies[3] of the tellurium atoms are 9.2 and 6.6 kcal. per mole for Te^{127} and Te^{129} respectively. We made a quantitative study of the change of telluric acid to tellurous acid which occurs when the radioactive Te^{127} or Te^{129} nucleus in the telluric acid undergoes a transition from its upper to its lower isomeric state. The experiments show, for both Te^{127} and Te^{129}, that the isomeric transitions effect reduction of telluric to tellurous acid with approximately 100% yield in aqueous solution at room temperature or even when frozen to the temperature of liquid air.

These experiments suggest, in view of the very small recoil energies involved, that the bond rupture and activation occurs, not as a result of the recoil energy, but as a consequence of the high state of electronic excitation which results from the vacancy in the K- or L-shell created by the emission of the internal conversion electron. A direct test of this view could be obtained by determining whether or not bond rupture could be initiated by an isomeric transition in which the transition gamma-ray undergoes very little internal conversion. Just such a case[8] is radioactive Zn^{69}, where the transition gamma-rays are largely *unconverted* and are of such an energy as to impart 40 kcal. of energy to the recoiling zinc atoms. We compared the effectiveness of the Zn^{69} transition in producing bond rupture with that of Te^{127} and Te^{129} under comparable conditions, namely, with the zinc and tellurium in the form of their gaseous diethyl compounds at 110°. The separation of the radioactivity corresponding to the lower isomeric state, as shown by its presence on the walls of the containing vessel (where fragments of the ruptured molecules collected), made it evident that again the isomeric transitions in Te^{127} and Te^{129} had been effective in producing an isomer separation process, while in the case of the zinc diethyl no separation was observed. The tellurium isomers were separated either in the presence or absence of electrically charged plates while the zinc isomers were not separable in any case. It is difficult to see how the isomer separations observed in tellurium compounds can be attributed to the recoil energy involved, since the recoil energy in the case of zinc is roughly five times greater and yet produces no separation in a similar molecule with similar bond energies.

These results lead to the not unexpected[6] conclusion that the state of high electronic excitation which exists after the loss of an internal conversion electron is responsible for the accompanying isomer separation process. For example, the tellurium atom is excited after K-shell conversion to the extent of 32 Kev. (740,000 kcal. per mole) or after L-shell conversion to 4.9 Kev. (110,000 kcal. per mole). During the electronic rearrangement which follows, the molecule should have ample opportunity to dissociate by reaching

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(1) E. Segrè, R. S. Halford and G. T. Seaborg, *Phys. Rev.*, **55**, 321 (1939).

(2) D. C. DeVault and W. F. Libby, *ibid.*, **55**, 322 (1939).

(3) G. T. Seaborg, J. J. Livingood and J. W. Kennedy, *ibid.*, **57**, 363 (1940).

(4) A. Langsdorf, Jr., and E. Segrè, *ibid.*, **57**, 105 (1940).

(5) L. J. LeRoux, C. S. Lu and S. Sugden, *Nature*, **143**, 517 (1939).

(6) J. E. Willard, THIS JOURNAL, **62**, 256 (1940).

(7) G. E. Valley and R. L. McCreary, *Phys. Rev.*, **56**, 863 (1939).

(8) J. W. Kennedy, G. T. Seaborg and E. Segrè, *ibid.*, **56**, 1095 (1939).

either a repulsive state or an attractive state with sufficient vibrational energy (due to the operation of the Franck–Condon principle).

In some cases activation of a chemical reaction by an isomeric transition may follow from the formation of an undissociated molecular residue which, either before or after it regains an electron, is itself in a sufficiently reactive state. The irradiation of solutions by X-rays, wherein the same type of molecular excitation is produced, has also led to the observation of chemical decomposition and activation processes.[9]

[9] See H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938), for bibliography.

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Reaction of Sulfur with Mercuric Acetate in Glacial Acetic Acid

BY RICHARD E. VOLLRATH

When sulfur is heated with mercuric acetate in glacial acetic acid, no mercuric sulfide is formed but instead mercurous acetate. Quantitative experiments in which the reduction product was estimated as mercurous chloride and the oxidation product as barium sulfate indicate that the chief process taking place corresponds to

$$6Hg(C_2H_3O_2)_2 + S \longrightarrow 6HgC_2H_3O_2 + 6HC_2H_3O_2 + H_2SO_4$$

By carrying on the reaction in a sealed tube at 135°, over 90% of the mercury can be recovered as mercurous acetate. No more than a trace of mercuric sulfide was obtained after prolonged heating.

Prolonged heating of the mixture gives some mercurated acetic acid or related compound, as indicated by the fact that addition of sodium iodide no longer gives a precipitate of red mercuric iodide but instead a pale yellow iodide having the characteristics of an organic mercury compound. Further work is being done on this phase of the problem.

DEPARTMENT OF PHYSICS
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA
RECEIVED JANUARY 27, 1940

NEW BOOKS

Statistical Method from the Viewpoint of Quality Control. By WALTER A. SHEWHART, Ph.D., Member of the Technical Staff, Bell Telephone Laboratories, New York, with the editorial assistance of W. EDWARDS DEMING, Ph.D., Senior Mathematician, The Department of Agriculture, Washington. The Graduate School, The Department of Agriculture, Washington, 1939. ix + 155 pp. Illustrated. 16.5 × 24.5 cm.

Based on four lectures delivered in March, 1938, this book is a critique of statistical quality control, for readers who already have some acquaintance with the elements of statistical theory, and are more interested in applying than in developing it. Chemists and physicists will be interested in the analysis of the data on basic physical and chemical constants, in the light of which the incompatibilities pointed out by R. T. Birge may be evidence that statistical sins, even in high places, do not go forever unpunished. "When a scientist makes a mistake in the use of statistical theory, it becomes a part of 'scientific law'; but when an industrial statistician makes such a mistake, woe unto him for he is sure to be found out and get into trouble." The discussion of the specification of accuracy and precision will be a disappointment to readers who are looking for easy answers, "...neither the physical nor the numerical aspect of an operation by itself can be taken as a complete description of the operation." The table of contents by sections goes far toward atoning for the lack of an index, and the typography reflects credit on the Lancaster Press.

ELLIOT Q. ADAMS

Theoretical Qualitative Analysis. By J. H. REEDY, Associate Professor of Analytical Chemistry, University of Illinois. McGraw-Hill Book Co., Inc., 330 West 42d St., New York, N. Y., 1938. ix + 451 pp. 34 figs. 14.5 × 21 cm. Price, $3.00.

Most present-day Qualitative Analysis texts consist of companion sections on the theory of the processes of precipitation and separation, and on the characteristic reactions of the various ions, with the detailed analytical procedures. The author has followed this plan, presenting first some 150 pages of theory dealing with solutions, colloids, mechanics of precipitation, analytical operations, equilibrium, mass law, ionization and its applications, sulfide behavior, amphoterism, complex ions, hydrolysis, cell potentials, and the handling and balancing of equations. This list is a comprehensive and ambitious one for the space allotted; the treatment of each item is matter-