The product so prepared melted at 231–233°. It was insoluble in ether, chloroform, ethyl acetate and benzene. It crystallized from hot 95% ethyl alcohol in beautiful lemon yellow needles having a final melting point of 288.5°.

Anal. Qualitative: C, H, N, +; S, Cl, –. Calcd. for $C_{12}H_{11}O_3N$: C, 66.35; H, 5.07. Found: C, 66.32; H, 5.00.

The yield of the product melting at 231–233°, as shown in three separate runs, averaged slightly below 20%. The yield of the product melting at 288.5° was approximately 12% of the theoretical. This low yield was believed to be due to the retention of much of the product in the precipitated chromium hydroxide, which was difficult to filter out, and almost impossible to wash.

Summary.—Optochin has been oxidized with chromic oxide in an acid solution. The analysis of the product, and its method of preparation, indicated that it was 6-ethoxyquinoline-carboxylic acid-4.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY   RECEIVED MAY 23, 1932
SCHOOL OF MEDICINE   PUBLISHED AUGUST 5, 1932
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

COMMUNICATIONS TO THE EDITOR

THE POTENTIAL OF THE Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s) CELL, SHOWING THE EFFECT OF FLOWING THE ELECTROLYTE OVER ONE ELECTRODE ONLY

Sir:

Carmody, in a recent note [THIS JOURNAL, **52,** 210 (1932)], states that when the electrloyte is flowing over a Ag(s), AgCl(s) electrode, there is a difference of 0.006 volt positive to a Ag(s), AgCl(s) electrode at equilibrium with the cell solution [p. 191]. This note was written because the value obtained for the Pb, Pb^{++} potential by Randall and Cann [THIS JOURNAL, **52,** 589 (1930)] was 0.1203 v. whereas Carmody [THIS JOURNAL **51,** 2905 (1929)] had obtained the value 0.1263 v. The difference in values was attributed by Carmody to the fact that Randall and Cann had allowed the electrolyte to flow over the Ag(s)–AgCl(s) electrode.

Because of this apparent discrepancy the authors investigated the cell Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s), using an H-cell, set up according to Fig. 1, keeping the electrolyte on one side stationary, and allowing it on the other side to be in motion, entering the cell at I and leaving it at II. The Ag(s)–AgCl(s) electrodes were prepared in precisely the same way as had been done previously by Randall and Cann, care being taken to free them from adsorbed gas. The electrodes were white because they were protected from all light. Every operation was performed in containers painted black on the outside. Two cells were made, one containing 0.025 *M* KCl and the other 0.05 *M* KCl. All measurements were made with a Type K potentiometer, using an oil-bath regulated at 25°.

Analysis of the results reveals the following facts. First, readings were always taken with the electrolyte on both sides of the cell stationary. In each case a period of at least twenty-four hours was allowed for this equilibrium to be obtained. After the flow of the electrolyte was started, a period of about twenty minutes was allowed to elapse before any readings were taken, in order to permit the cell to come to equilibrium under the new conditions. When the electrolyte was flowing, the potentials were always negative to those obtained when the electrolyte was stationary.

More than forty readings were taken on Cell A and about fifteen on Cell B. With Cell A the readings varied from the lowest values of -0.00023 v. to the highest of -0.00162 v. With Cell B the lowest reading was -0.00072 v. and the highest -0.00190 v. The average of the differences from the mean in Cell A was 0.00038, and the average deviation of the average differences was 0.000078. The average of the differences from the mean in Cell B was 0.00031 and the average deviation of the average differences was 0.0001.

It might seem that the greater the rate of flow the more negative the difference becomes. A large variety of different rates of flow was examined, but apparently no definite relationship exists between rate of flow and difference of potential. Also, readings of the barometer were invariably taken, but the variations in this value, a maximum of eight millimeters, appeared to have no effect. The average difference in potential due to the flowing of the electrolyte in Cell A was -0.00074 v., and that in Cell B was -0.00100 v.

Fig. 1.

These results indicate that Carmody is correct in his contention that there is a drop of potential when electrolyte is flowing over the Ag(s), AgCl(s) electrode. But the value obtained by us, using potassium chloride as the electrolyte, is much less than that suggested by Carmody, who used hydrochloric acid as the electrolyte. Our values of -0.00074 and
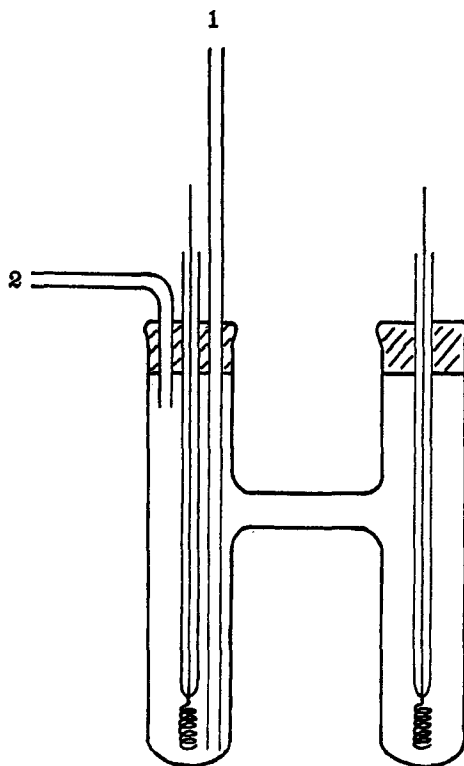
−0.00100 are not sufficient to account for the discrepancy between the values of 0.1203 v. for the Pb, Pb^{++} electrode as obtained by Randall and Cann and the value of 0.1263 v. as obtained by Carmody.

DEPARTMENT OF CHEMISTRY   JESSIE Y. CANN
SMITH COLLEGE   ELIZABETH LA RUE
NORTHAMPTON, MASSACHUSETTS
RECEIVED JUNE 17, 1932
PUBLISHED AUGUST 5, 1932

THE CONSTITUTION OF BORNYL ANILINE

Sir:

In a recent publication, P. Lipp and G. Stutzinger [*Ber.*, **65**, 241 (1932)] presented evidence purporting to establish the identity of the so-called "bornyl aniline" of Ullmann and Schmidt [*ibid.*, **43**, 3202 (1910)] with the secondary amine obtained by the condensation of aniline with camphene in the presence of aniline hydrochloride and also with the amine resulting from the reduction of camphor anil with hydrogen and platinum. These findings have duplicated in part investigations well under way in this Laboratory. on which a preliminary report was presented by the authors at the recent Fall Meeting of the American Chemical Society at Buffalo, N. Y., under the title "The Fixation of Aniline by Hydrocarbons of the Terpene Series." The results of our experiments confirm the statement of L. and S. as to the identity of the camphene-aniline condensate with "bornyl aniline," but appear to be at variance with regard to the amine obtained from camphor anil by reduction. We performed the reduction of the anil with sodium and aniline as the reducing medium, obtaining a secondary amine whose acetyl derivative melted at 112–113° while L. and S. report 123° as the melting point of their product. The behavior of these amines, and also one obtained by the condensation of aniline with α-pinene in the presence of aniline hydrochloride are under investigation in this Laboratory in a further attempt to establish their structures by exhaustive methylation. The bornyl aniline of Ullmann and Schmidt and also that obtained from camphene have been found to yield camphene nearly quantatively, while those obtained from α-pinene and reduced camphor anil exhibit behavior on exhaustive methylation which is similar to that of bornyl amine.

We expect to publish a complete account of this investigation in the near future.

DEPARTMENT OF CHEMISTRY   JOHN J. RITTER
WASHINGTON SQUARE COLLEGE   HENRY O. MOTTERN
NEW YORK UNIVERSITY
NEW YORK, N. Y.
RECEIVED JUNE 18, 1932
PUBLISHED AUGUST 5, 1932

THE HEAT CAPACITY OF SOME HYDROGEN HALIDES AT HIGH TEMPERATURES AS CALCULATED FROM RAMAN SPECTRA

Sir:

The existing data on the heat capacity of the hydrogen halides in gaseous form are very meager and are on the whole unsatisfactory as Eastman [*Bur. Mines, Tech. Paper* 445 (1929)] has pointed out in his critical summary of the specific heats of gases. Experimental evidence on HBr, HI and HF is entirely lacking, while such data as are available for HCl leave something to be desired. Since the heat capacities of N_2 and HCl are practically identical in so far as one can tell from the fragmentary evidence on the latter, and since the energy of the lower levels in the molecules of HCl, HBr and HI is not very different from that of the corresponding level in N_2, Eastman assigned to the three halide gases the heat capacity of N_2, which is known with reasonable accuracy. This assumption, which admittedly introduces some error, was nevertheless the best one that could be made under the circumstances.

Since the methods heretofore employed in making heat capacity measurements at high temperatures have involved a difficult technique and have led in a great many cases to questionable results, it seems not unlikely that for a polar molecule calculations based on the well-known Planck–Einstein specific heat equation may in the end be more satisfactory than direct observations, in spite of the fact that such factors as the increases in potential energy due to stretching of the molecule are neglected.

Reliable values of the fundamental frequency of vibration of HCl, HBr and HI have recently been derived by Salant and Sandow [*Phys. Rev.*, **37**, 373 (1931)] from Raman spectra. Using their results (HCl, $\Delta^1/\lambda = 2886$ cm.$^{-1}$, HBr, $\Delta^1/\lambda = 2558$ cm.$^{-1}$, HI, $\Delta^1/\lambda = 2233$ cm.$^{-1}$) it is possible to calculate the heat capacity of these gases with an accuracy apparently somewhat greater than that of the values selected by Eastman, which are probably the best of the existing data.

Such a calculation has been made and the results, expressed as C_p ($C_p = C_v + R$), are shown in the accompanying table. The single set of

TABLE I

HEAT CAPACITY OF HYDROGEN HALIDES

Temp., °K.	C_p HCl as calcd.	C_p HBr calcd.	C_p HI calcd.	C_p Eastman's best value
600	7.07	7.13	7.26	7.17
800	7.28	7.44	7.58	7.33
1000	7.54	7.71	7.86	7.50
1200	7.78	7.94	8.10	7.67
1400	7.98	8.12	8.28	7.86
1600	8.14	8.28	8.42	8.06
1800	8.28	8.40	8.53	8.27
2000	8.38	8.48	8.59	8.49

values chosen by Eastman as representing the heat capacity of all three halide gases has been included for comparison.

It will be seen that the agreement between Eastman's selected figures and the calculated values for HCl is satisfactory, the maximum deviation being approximately 1.5%. It is perhaps worth noting that above 2000° Eastman's values run higher than the calculated ones and that this is the same direction in which Eastman's values deviate from the best of the experimental observations.

For HBr and HI differences as great as 5% exist between the results of the calculations and the data of Eastman. Unfortunately there appear to be no experimental observations on which to check the calculations but in view of the agreement found with HCl it seems probable that the calculated values are not much in error and almost certainly give a closer description of the true heat capacity of these gases than is obtained by assigning the same figure to all.

THE RESEARCH LABORATORY   J. B. AUSTIN
UNITED STATES STEEL CORP.
KEARNY, N. J.
RECEIVED JUNE 22, 1932
PUBLISHED AUGUST 5, 1932

THE CHLORINATION OF NEOPENTANE

Sir:

All recorded methods of making neopentane failed to give appreciable yields except that of Lwow [*Z. Chem.*, 520 (1870)] involving dimethyl zinc and a tertiary butyl halide. The iodide, bromide and chloride gave 42, 46 and 51% yields, respectively. The hydrocarbon froze and boiled at approximately -20 and $+10°$, respectively.

The chlorination of neopentane was very easy. At room temperature in diffused light the color of chlorine disappeared in fifteen minutes. The chloride boiled at 24° (80 mm.) and froze at $-20°$. The analysis for chlorine was 1.5% low for an amyl chloride. Tertiary amyl chloride showed b. p. 23.5° (8 mm.) and m. p. $-73°$. A small amount of a dihalide, b. p. 35° (8 mm.), was also obtained. The monochloride when shaken with cold water for thirty minutes showed the presence of 6% of tertiary halide (Michael). The amount of tertiary halide was increased only slightly, if at all, by heating the chloride at 140° for one and one-half hours. All known methods of converting a halide to a Grignard reagent failed. These facts indicate that the halide obtained is neopentyl chloride.

Neopentane is being prepared in larger amounts to make possible a more thorough study of its chlorination in relation to the mechanism of rearrangements. The limited amount of tertiary amyl chloride formed and the surprising stability of the neopentyl chloride carry implications of great

significance in this field [Whitmore, THIS JOURNAL, **54,** 3274 (1932); Whitmore and Rothrock, *ibid.*, **54,** 3431 (1932)].

DEPARTMENT OF CHEMISTRY   GEO. H. FLEMING
PENNSYLVANIA STATE COLLEGE   FRANK C. WHITMORE
STATE COLLEGE, PENNSYLVANIA
RECEIVED JUNE 27, 1932
PUBLISHED AUGUST 5, 1932

DEHYDRATION OF DIETHYLCARBINOL

Sir:

By dehydrating diethylcarbinol in a flow reactor at 40 lb. pressure and at 365–410° with a phosphoric acid catalyst on silica gel we have obtained a mixture of olefins of b. p. 65–70° which on ozonolysis gives formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde. The first two were identified by the resorcinol–sulfuric acid test and as acetaldehyde–ammonia, respectively. The last two were converted to the 2,4-dinitrophenylhydrazones, which were identified by melting point and mixed melting point determinations. Small amounts of impure 2,4-dinitrophenylhydrazones probably corresponding to methyl ethyl ketone and diethyl ketone were also obtained. These results show that the dehydration of diethylcarbinol gives both the normal and rearranged products. This study is to be continued on a larger scale in an endeavor to determine quantitatively the various modes of dehydration.

DEPARTMENT OF CHEMISTRY   F. A. KARNATZ
PENNSYLVANIA STATE COLLEGE   FRANK C. WHITMORE
STATE COLLEGE, PENNSYLVANIA
RECEIVED JUNE 27, 1932
PUBLISHED AUGUST 5, 1932

THE REACTION OF ACID IODIDES WITH ETHERS

Sir:

In a recent paper by Meerwein and Maier-Hüser [*J. prakt. Chem.*, **134,** 51 (1932)] on the cleavage of ethers by acid halides and anhydrides in the presence of catalysts, these workers have called attention to the isolated observation of Kishner [*J. Russ. Phys.-Chem. Soc.*, **41,** 651–659 (1909); *Chem. Zentr.*, II, 1132 (1909)] that benzoyl iodide is capable of splitting primary aliphatic ethers at 100° without the presence of a catalyst, giving alkyl iodides and benzoates. This work has not previously received the further study which its suggestive character would indicate.

With the hope that aliphatic acid iodides might prove more reactive, permitting the cleavage of ethers at ordinary temperatures, we have investigated the behavior of acetyl iodide and the chloro substituted acetyl iodides with a number of aliphatic ethers, thio ethers and oxides. This

study has shown that the cleavage reaction between acid iodides and ethers proceeds in all probability through a preliminary formation of an oxonium compound between the ether and the acid iodide.

Secondary ethers have been found to be much more readily cleaved into alkyl iodides and esters than are primary ethers. The substitution of chlorine in the α-position in aliphatic acid iodides has been found to diminish their ability to cleave ethers. The tendency of acetyl iodide, chloroacetyl iodide and dichloroacetyl iodide to split primary ethers was found to be diminished by increasing substitution of chlorine. Trichloroacetyl iodide showed no tendency to cleave either primary or secondary ethers at ordinary temperatures even in the presence of zinc iodide as a catalyst, though evidence of the formation of an oxonium compound was obtained. Similarly, substitution of chlorine in the α-position in aliphatic ethers greatly increased their resistance to cleavage by acid iodides.

SCHOOL OF CHEMISTRY AND PHYSICS   EDWIN L. GUSTUS
PENNSYLVANIA STATE COLLEGE   PHILIP G. STEVENS
STATE COLLEGE, PENNSYLVANIA
RECEIVED JULY 11, 1932
PUBLISHED AUGUST 5, 1932

IS THE NUTRILITE FOR "GEBRÜDE MAYER" YEAST OF UNIVERSAL BIOLOGICAL IMPORTANCE?

Sir:

We have obtained a considerable body of evidence that a single unknown hydroxy acid with molecular weight about 200 is the responsible agent for a remarkable growth stimulation of "Gebrüde Mayer" yeast.[1] Furthermore, what appears to be this same acid has been found universally in a great variety of living tissues.

The tissues extracted include (1) rice polish (Spermatophyta), (2) Aspergillus niger (Fungi), (3) Spirogyra and Oscillatoria, mixed (Algae), (4) Bacillus subtilis (Schizophyta), (5) Planarian worms (Plathylminthes), (6) Earthworms (Annulata), (7) Oysters (Mollusca), (8) Sea urchin eggs (Echinodermata), (9) Crabs eggs (Arthropoda), (10) Beef liver (Chordata), (11) Milk (Chordata). Not only was a growth stimulating substance present in every extract but on fractional electrolysis in an eight-compartment cell the activity in each case migrated under our experimental conditions to a cell with PH value of about 4 and was usually completely removed from cells having a PH of 5 or more.

[1] The criticism of Richards [*J. Biol. Chem.*, **96**, 416 (1932)] that our results may have been due to inorganic materials is not valid inasmuch as the article cited [THIS JOURNAL, **53**, 4171 (1931)] states that the activity was lost on ignition (p. 4176). Yeast nutrition like mammalian nutrition is undoubtedly affected by traces of elements of less frequent occurrence, but the effect of unknown organic materials is of entirely different order of magnitude and operates over an incomparably larger range.

The diffusion constant of the active substance (using rice polish and beef liver as sources) indicates that its molecular weight is about 200. The acid (rice polish was the source) has no primary or secondary amino group (nitrous acid anhydride treatment). It has been esterified with both methyl and ethyl alcohols. The esters are not basic (fractional electrolysis), hence the acid is not amphoteric. The presence of several hydroxy groups is indicated by (1) complete destruction of the active substance by treatment with dimethyl sulfate in the cold, (2) complete non-volatility of the methyl ester at a pressure of 10^{-3} mm., (3) solubility of the esters in water and comparatively slight solubility in ether. The activity is not destroyed by hydrogenation following the methods of Roger Adams *et al.*, indicating that the substance is not olefinic and contains no aldehyde nor ketone group nor aromatic nucleus.

The possibility of the universal occurrence of a single acid substance of the character we have indicated opens up some very interesting questions. There is fragmentary evidence that the same acid may function in the growth stimulation of certain bacteria, molds and mushrooms and that it is one of the substances involved in the growth stimulation of other yeasts such as Wildiers' and No. 578 (American Type Culture Collection). The presence of this acidic substance in soils and composts suggests the possibility that it may function in the stimulation of the growth of green plants. It is synthesized by the mold Aspergillus niger, and seems to be more widely and evenly distributed in tissues than any known vitamin.

Because of their rather far reaching interest we wish at present to emphasize the tentative character of our conclusions [THIS JOURNAL, **53**, 4171 (1931)].

CHEMICAL LABORATORY   ROGER J. WILLIAMS
UNIVERSITY OF OREGON   CARL M. LYMAN
EUGENE, OREGON   GEORGE H. GOODYEAR
                                             JOHN H. TRUESDAIL
RECEIVED JULY 1, 1932
PUBLISHED AUGUST 5, 1932

NEW BOOKS

Quantitative Chemical Analysis. An Intermediate Textbook. By FRANK CLOWES and J. BERNARD COLEMAN. Revised by D. STOCKDALE and J. DEXTER. Thirteenth edition. P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa., 1931. xiv + 605 pp. Illustrated. 14.5 × 23 cm.

Analytical Factors and their Logarithms. By EARLE RADCLIFFE CALEY, M.Sc., Ph.D., Assistant Professor of Chemistry in Princeton University. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. v + 112 pp. 13 × 20 cm. Price, $2.00.

The first of these volumes, originally published forty-one years ago as a laboratory textbook, is now a rather complete manual on the art of quantitative analysis. The book is divided into eight parts: (I) (65 pages) general processes; (II) (58 pages) simple gravimetric estimations; (III)