the hydrocarbon was recrystallized from benzene–methanol to a melting point of 106.4–107.0°.

*Anal.** Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.89, 92.96; H, 7.00, 6.92.

Summary

A new synthesis for hydrocarbons containing the 3,4-benzphenanthrene nucleus is described. The method is based on a double ring closure of β-benzohydrylglutaric acid to yield 2,9-diketo-1,2,9,10,11,12-hexahydro-3,4-benzphenanthrene. By reduction and dehydrogenation this diketone is converted into 3,4-benzphenanthrene, whereas by reaction with methyl- or ethylmagesium bromide followed by dehydration and dehydrogenation, the diketone is converted into 2,9-dimethyl- or 2,9-diethyl-3,4-benzphenanthrene, respectively.

COLUMBUS, OHIO RECEIVED DECEMBER 23, 1937

NOTES

An Obscure Reaction of Phosphorus Trichloride

BY ROBERT D. COGHILL

Two explosions occurring in the elementary organic laboratory this past Fall have prompted me to write this note as a warning to other teachers. The accidents occurred during the preparation of acetyl chloride from phosphorus trichloride and acetic acid. In each case the student was ignoring the printed directions and attempting to distil the acetyl chloride from the phosphorous acid residue with a free flame rather than with a hot water-bath. The phosphorous acid was thus locally overheated and exploded with sparks and a yellow flame, copious white fumes (probably phosphorus pentoxide), and the odor of phosphorus or phosphine.

In attempting to find an explanation for the phenomenon it was found that phosphorus trichloride, when evaporated in an open breaker on a steam-bath, caught fire spontaneously and burned with a yellow flame, leaving a large residue of phosphorus in the beaker. When the evaporation was carried out on an electric hot-plate the material did not burn and only a small residue of phosphorus was obtained. When the phosphorus trichloride was distilled from a distilling flask in a system protected from atmospheric moisture with a calcium chloride tube, only a faint trace of phosphorus remained.

It was thus evident that the flame and the phosphorus residue result from the reaction of phosphorus trichloride and water. Mellor[1] states that when phosphorous acid is heated, phosphine is produced. The latter is then alleged to react with phosphorus trichloride to form free phosphorus and hydrogen chloride. These reactions would serve to explain both the observed reaction of phosphorus trichloride and steam, and the laboratory explosions. In the latter cases, overheating of the phosphorous acid produced phosphine in sufficient quantity to blow out the stoppers, the gas subsequently igniting spontaneously.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
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RECEIVED DECEMBER 23, 1937

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[1] J. W. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., 1928, pp. 806, 1002–1003.

2,2,3,4-Tetramethylhexane and 3,3,5-Trimethylheptane[1]

BY NATHAN L. DRAKE AND L. H. WELSH

2,2,3,4-Tetramethylhexane (I) and 3,3,5-trimethylheptane (II) have been prepared by the hydrogenation of corresponding olefins. The olefins were obtained by the action of sulfuric acid on methylisopropylcarbinol,[2] and were hydrogenated during passage in a stream of hydrogen over a copper chromite catalyst. Attempts to hydrogenate the olefins in the liquid phase using Adams platinum black catalyst were unsuccessful; a rapid initial absorption of hydrogen was observed but hydrogenation ceased after a few minutes. However, on distilling the olefins over copper chromite[3] with excess hydrogen, saturation proceeded smoothly, and after two such

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[1] From the master's thesis of L. H. Welsh, University of Maryland, 1935.

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

[3] Adkins and Connor, *ibid.*, **53**, 1092 (1931).

treatments only a slight amount of unsaturation could be detected by use of tetranitromethane. Silica gel[4] was used to remove this unsaturated material.

After passing the olefins twice over the chromite catalyst at 270°, the products were allowed to percolate through silica gel packed in a vertical tube of approximately 20 mm. diameter. One and one-half grams of gel was employed for each gram of hydrogenation product. The effluent was collected in 5-ml. portions, and each portion tested for unsaturation. By repeated treatment it was possible to obtain products which give no color with tetranitromethane. (I) and (II) thus freed of olefins were dried by refluxing them over sodium, and were then distilled from the sodium.

PROPERTIES AND ANALYSES

		I	II
Calcd. for $C_{10}H_{22}$	C, 84.39 Found	84.24 84.35	84.40 84.22
	H, 15.61 Found	15.58 15.60	15.62 15.64
$n^{25}D$		1.4202	1.4208
d^{25}		0.7511	0.7516
MR (calcd., 48.13)		47.90	47.97
B. p. (763 mm.), °C.		156.6	159.2

The absorption spectra of these substances in the near infrared is discussed in a recent publication.[5]

[4] B. J. Mair and J. D. White, *Bur. Standards J. Research*, **15**, 51 (1935), have shown that silica gel effectively removes olefins from paraffins and naphthenes.

[5] F. W. Rose, Jr., *ibid.*, **19**, 143 (1937), R. P. 1017.

CONTRIBUTION FROM THE
UNIVERSITY OF MARYLAND
COLLEGE PARK, MD.

RECEIVED NOVEMBER 1, 1937

A Study on the Parachor of Hexamethylenetetramine (Urotropine)

BY T. C. HUANG, M. Y. PENG, K. S. HU AND P. P. T. SAH

The method of Hammick and Andrew[1] for finding the parachor of a solute in a solution is particularly valuable for some substances (like urotropine) whose direct investigation in the fused state is not possible. However, these authors reported that, using water as solvent, anomalous results were obtained for the parachors of the solutes, though they gave neither examples nor data. On the other hand, Ray[2] determined the parachors of sugars in aqueous solutions and obtained normal results. Since water is the most important solvent, we have investigated the parachor of hexamethylenetetramine in aqueous solutions, and found it also to be normal.

"Urotropine," (U. S. P., 30 mesh, Heyden Chemical Corporation), was purified by recrystalling it twice from warm absolute alcohol according to Butlerow.[3] Its different concentrations in conductivity water were made up accurately. The surface tensions, γ, were measured at four different temperatures, 20, 25, 35, and 45°, by the method of capillary rise using first a cathetometer graduated to 0.05 mm. and later one graduated to 0.01 mm. The capillary, made from the stem of a broken thermometer, was calibrated against pure water and benzene at 25°, and found to have a radius of 0.1729 cm. The thermostat used was of the toluene–mercury type keeping the temperature constant within 0.1°. The density, D, of the solution at definite temperature was determined by the regular pycnometer method, correction being made for the buoyancy of the air. The parachor of the solution, P_m, and that of hexamethylenetetramine, P, were calculated according to the equations

$$P_m = M_m\gamma^{1/4}/D$$
$$M_m = (1 - x)M_0 + xM$$
$$P_m = (1 - x)P_0 + xP$$

in which M_0 and P_0 are the molecular weight and the parachor of water and M and x the molecular weight and the mole fraction of hexamethylenetetramine. The values of P_0 were calculated from the surface tensions of water, which are 72.75, 71.97, 70.38, and 68.74 dynes/cm. at 20, 25, 35, and 45°, respectively.[4] The results are summarized in the table.

PARACHOR OF HEXAMETHYLENETETRAMINE

t, °C.	x	D	γ	P_0	P_m	P	Av. P
20	0.02926	1.0422	72.19	52.67	60.38	316.1	315.5
	.03351	1.0482	72.11	52.67	61.46	314.8	
25	.02601	1.0353	71.22	52.64	59.48	315.4	314.8
	.04233	1.0557	70.77	52.64	63.71	314.2	
35	.008174	1.0070	70.07	52.51	54.64	313.1	314.9
	.02142	1.0261	69.98	52.51	58.17	316.7	
45	.01381	1.0115	68.40	52.40	56.04	315.6	315.4
	.02964	1.0324	67.97	52.40	60.19	315.1	

The average parachor of hexamethylenetetramine for four temperatures is 315.2. Evidently the result is normal though water is used as a solvent in the solution method.

DEPARTMENT OF CHEMISTRY
NATIONAL TSING HUA UNIVERSITY
CHANGSHA, HUNAN, CHINA

RECEIVED JULY 26, 1937

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[1] Hammick and Andrew, *J. Chem. Soc.*, 754 (1929).

[2] Ray, *J. Indian Chem. Soc.*, **11**, 843 (1934).

[3] Butlerow, *Ann. Chem. Pharm.*, **115**, 322 (1860).

[4] "International Critical Tables," Vol. IV, 1927, p. 447.

Thiamine, Pyrimidine and Thiazole as Bios Factors

By Alfred S. Schultz, Lawrence Atkin and Charles N. Frey

In view of our discovery of the fermentation stimulating effect of thiamine,[1,2] studies were instituted relative to thiamine as a bios factor. Thiamine is a growth-active substance for various yeasts. Amongst strains of *Sacch. cerevisiae* the response to thiamine as a bios factor differs.

Table I

Total volume in each case 30 ml. seeded with 1 mg. of moist yeast and rocked at 30° for 24 hours. Crop × 4.54 gives mg. of moist yeast. Supplements: inositol [I] 1 mg., β-alamine [IIA] 0.005 mg., bios II B 0.13 mg., thiamine 0.01 mg., thiazole 0.01 mg., aminopyrimidine 0.01 mg., bios VI 1 cc. of a concentrate.

Ingredients of bios test	Crop Type A	Crop Type B
Sugar, salts, buffer, I, IIA, IIB	30	220
Sugar plus thiamine	120	120
Sugar plus thiamine and bios VI	220	220
Sugar plus thiazole	70	220
Sugar plus aminopyrimidine	80	200
Sugar plus aminopyrimidine + thiazole	120	150

Thus type A is stimulated by thiamine and type B is inhibited by it. This is true when the growth medium contains bios I (inositol), bios IIA (beta-alanine) and bios IIB. As may be seen it is possible to add another factor (bios VI, we have named it), which has not been freed of the other bioses but which may be found in many places. This factor further stimulates type A while removing the inhibition on type B. Examples of type A cultures are Luft II, and Rasse XII. Type B cultures are represented by *Sacch. cerevisiae* Toronto and Spc. 152.

Included in the table are results obtained with components of thiamine. "Thiazole" in the table is 4-methyl-5-beta-hydroxyethylthiazole and "aminopyrimidine" is 2-methyl-5-ethoxymethyl-6-aminopyrimidine. Thus type A yeast is partly stimulated by either fraction and completely activated by a combination. Type B yeast is not affected by the thiazole and is only slightly inhibited by the aminopyrimidine. The combination, however, inhibits type B to the same extent as thiamine.

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Received December 28, 1937

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(1) Schultz, Atkin and Frey, This Journal, **59**, 948 (1937).

(2) *Idem.*, p. 2457.

On the Calculation of the Dissociation Constants of Hypohalogenous Acids from Kinetic Data

By Eugene A. Shilov

The author recently has determined the dissociation constant of hypobromous acid by electrochemical titration with glass electrode and found it to be 2.06×10^{-9} at 20°.

This value is in disagreement with that obtained by Chapin[1] by means of the kinetical method, namely, 2.5×10^{-8}, later adopted by Prutton and Maron[2] in the calculations of their measurements of the kinetics of hypobromite decomposition.

The kinetical method used first by Gallart[3] is based on the determination of the pH at which the velocity of a hypohalite decomposition is maximal. Under assumption that the kinetical equation of the reaction has the form

$$-\frac{d[\text{OX}^-]}{dt} = k[\text{HOX}]^2[\text{OX}^-] \qquad (1)$$

$(p\text{H})_{\text{max.}}$ must correspond to one-third neutralization of the hypohalogenous acid present. From this relation in combination with the equation $K = [\text{H}^+][\text{OX}^-]/[\text{HOX}]$ it follows

$$\log K = -(p\text{H})_{\text{max.}} - \log 2$$

The method involves two sources of errors: (1) experimental errors of the determination of $(p\text{H})_{\text{max.}}$; and (2) the inexactitude of the equation (1).

On examining the decomposition curves of hypochlorite in the article of Chapin[1] the probable error of determination of $(p\text{H})_{\text{max.}}$ on the curve appears to be 0.2–0.3 pH. The total experimental error of the determination is apparently much larger, as the values of different authors vary very much between themselves. Gallart[3] and Chapin[1] have obtained in the decomposition of hypochlorite $(p\text{H})_{\text{max.}} = 6.7$ and hence $K_{\text{HOCl}} = 10^{-7}$, but Markuse[4] determined $(p\text{H})_{\text{max.}}$ as >7, and hence $K_{\text{HOCl}} < 5 \times 10^{-8}$.[5]

It seems that the control of pH in the investigations of Chapin and particularly of Markuse did

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(1) Chapin, This Journal, **56**, 2211 (1934).

(2) Prutton and Maron, *ibid.*, **57**, 1653 (1935).

(3) Gallart, *Anales Soc. españ. fís. quím.*, **31**, 422 (1933), cited from Chapin.[1]

(4) Markuse, *Reconstruction Text. Ind.* (Russ.), **5**, 43 (1935).

(5) Here may be noted also the earlier investigation of Giordani [*Gazz. chim. ital.*, **54**, 844 (1924)], who calculated the constant of hydrolysis of hypochlorite from the measurements of the kinetics of sodium hypochlorite decomposition in very alkaline solutions ($p\text{H} > 13$). The value obtained by Giordani ($K_{\text{Hydr.}} = 1.12 \times 10^{-6}$ at 30°, $K_{\text{HOCl}} = 1.5 \times 10^{-8}$) is near to modern values, but perhaps only accidentally, as the method of Giordani is not exact enough.

not stay on a high level. Chapin has determined *p*H colorimetrically after the decomposition of hypochlorite by sulfite or hyposulfite; Markuse used the buffer mixtures of known composition without any further controlling.[6]

Values of K_{HOCl} of usual "static" methods of determination of dissociation constants are between 1×10^{-8} and 4×10^{-8}.[7] Particularly the method of the glass electrode gives very consistent values 3×10^{-8} to 4×10^{-8} at room temperature.

Even if equation (1) is quite correct for hypochlorites, the "static" value can today hardly be checked by the kinetical method, since the limits of the experimental errors of the latter are too large.[7a]

The results of the kinetic and static methods applied to hypobromous acid differ among themselves, as remarked above, very much (2.5×10^{-8} and 2.06×10^{-9}). The discrepancy is hardly to be explained as due to the experimental errors of the two methods.[8]

The more plausible explanation of the divergence is the invalidity of the kinetic equation (1) in the application to hypobromous acid. Indeed equation (1) is only one of many possible equations of transformation of active bromine. As Skrabal indicated,[9] a change of the law of decomposition of hypobromous acid between Φ^2 and Φ^3 takes place Φ (being summary concentration of HOBr, Br_2 and Br_3^-), if *p*H and bromide concentration varies.[10] At these conditions the calculation of the dissociation constant of hypobromous acid from $(pH)_{\text{max.}}$ is very dubious.

On the contrary the determination of the dissociation constant of hypobromous acid enables one to calculate the composition of the reacting mixture at $(pH)_{\text{max.}}$. For the value found by Chapin, *i. e.*, $(pH)_{\text{max.}} = 7.3$, we calculate from the equation

$$[\text{H}^+][\text{OBr}^-]/[\text{HOBr}] = 2.06 \times 10^{-9}$$

that

$$[\text{OBr}^-] = 0.04\ [\text{HOBr}]$$

Thus only 4% neutralization of hypobromous acid present suffices to make the velocity of decomposition maximal. It may be regarded as a demonstration that equation (1) is not valid in the region of *p*H near to 7.

Experimental

WITH J. N. GLADTCHIKOVA

The dissociation constant of hypobromous acid was determined by titration of free hypobromous acid with sodium hydroxide solution in presence of a glass electrode. The solutions of hypobromous acid were prepared by vacuum distillation of bromine water with silver phosphate. Contrary to the opinion of Pollak and Doktor,[11] shared by Liebhafsky and Makower,[12] who declared the preparation of pure hypobromous acid solution to be an insoluble problem, dilute solutions of hypobromous acid, containing practically no bromine and bromic acid, can be obtained easily by this method.

Sodium hydroxide solutions were prepared from metallic sodium and carbon dioxide-free water.

The apparatus, based on the use of an electrometer valve, was constructed by the scheme of Sokolov and Ptchelin.[13] The glass electrodes were calibrated by means of buffer solutions of which the *p*H had been determined with a hydrogen electrode.

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(6) The original article of Gallart is not available to me.

(7) From the solubility of carbon dioxide in sodium hypochlorite solutions: 3.7×10^{-8} at 25° [Sand, *Z. physik. Chem.*, **48**, 614 (1904)] from the partition of hypochlorous acid between the aqeous solution and a vapor phase: 1×10^{-8} at 25° [Soper, *J. Chem. Soc.*, **125**, 2227 (1924)]; from the electrical conductivity of hypochlorous acid solution: $\sim 10^{-8}$ at room temperature (Nernst, cited from Sand. *l. c.*); 1.9×10^{-8} at 0° [Shilov and Kaniaev, *J. Phys. Chem.* (U. S. S. R.), **5**, 654 (1934)]; by titration with glass electrode: 4×10^{-8} [Yorston, *Pulp Paper Mag. Can.*, **31**, 374 (1931)]; 3.7×10^{-8} at 18–20° [Davidson, *J. Text. Inst.*, **24**, T185 (1933)]; 3.2×10^{-8} at 15° [Britton and Dodd, *Trans. Faraday Soc.*, **29**, 537 (1933)]; 3.7×10^{-8} at 18°; the "true" constant is calculated to be 2.95×10^{-8} [Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933)]; last value excepted, all others are the apparent dissociation constants. Two values fall out from this series: (1) that of Noyes and Wilson, 6.7×10^{-10} [THIS JOURNAL, **44**, 1630 (1922)], the fallibility of which is demonstrated by Soper (*l. c.*), and (2) that of Ríus and Arnal, 1.46×10^{-7} at 25° [*Anales soc. españ. fís. quim.*, **31**, 497 (1933); *C. A.*, **27**, 4989 (1933)] obtained by means of an unproved method (electrochemical titration with chlorine electrode).

(7a) During the printing of this article the writer obtained the knowledge of a paper of A. Skrabal and A. Berger [*Monatsh.* **70**, 168 (1937)], treating the determination of the dissociation constant of hypochlorous acid from kinetic data. The results of this thoughtful and thorough investigation are in accordance with the views evolved in this note. The mean kinetic value of K_{HOCl}, obtained by Skrabal and Berger, is 5.6×10^{-8} at 25°.

(8) Our value of the dissociation constant of hypobromous acid is at present unique, but it may be confirmed to a certain degree by our determinations of the specific conductance of hypobromous acid. The observed specific conductance of 0.01 molal solution of hypobromous acid was $1.7–2.0 \times 10^{-6}$ rec. ohms at 0° (without any correction, *i. e.*, maximal). By calculating the specific conductance by means of the dilution law (under assumption that Λ_∞ is 250) one finds for our value of K_{HOBr} $\lambda = 1.1 \times 10^{-6}$, for Chapin's value $\lambda = 4.10^{-6}$.

(9) A. Skrabal, *Z. Elektrochem.*, **40**, 237 (1934).

(10) Certainly Prutton and Maron [THIS JOURNAL, **57**, 1653 (1933)] have found that ordinary reaction of decomposition of hypobromite at *p*H 6.4–7.8, *i. e.*, in the region of the maximal velocity, obeys equation (1). However, this conclusion rests on the dissociation constant of hypobromous acid calculated by Chapin by kinetical method based on equation (1). We have, therefore, a *circulus vitiosus* here.

(11) Pollak and Doktor, *Z. anorg. allgem. Chem.*, **196**, 89 (1931).

(12) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1037 (1933); Makower and Liebhafsky, *Trans. Faraday Soc.*, **29**, 597 (1933).

(13) Sokolov and Ptchelin, *J. Applied Chem.* (U. S. S. R.), **7**, 1316 (1934).

The titrations were made at room temperature in a high beaker, provided with a stirrer, in carbon dioxide-free air.

The results were calculated by the Henderson–Hasselbalch formula

$$\log K = \log \frac{x}{A - x} - p\text{H}$$

where A is the initial quantity of hypobromous acid and x is the quantity of added alkali, both in moles.

The results of one experiment are reported in Table I. In this experiment 49.84 cc. of 0.0235 molal hypobromous acid was titrated by 0.0255 molal sodium hydroxide at 20°.

TABLE I

NaOH, cc.	$x/(A-x)$	Mv.	pH	$10^9 K$
00		153.2	4.97	
1	0.0224	270.4	7.02	(2.14)
2	.0458	288.6	7.36	2.00
4	.096	306.9	7.67	2.05
6	.1511	318.4	7.87	2.04
8	.212	325.8	8.01	2.07
12	.3546	338.1	8.22	2.14
16	.5335	348.4	8.40	2.12
20	.771	358.0	8.58	2.03
25	1.193	368.0	8.75	2.13
30	1.890	379.7	8.96	2.07
34	2.866	390.0	9.14	2.11
36	3.645	395.8	9.25	2.05
				2.07

The mean value K_{HOBr} in this experiment is 2.07×10^{-9}. The titration of 0.0437 molal hypobromous acid by 0.046 molal alkali has given mean value $K_{\text{HOBr}} = 2.04 \times 10^{-9}$.

The probable mean value of all (five) experiments is $K_{\text{HOBr}} = 2.06 \times 10^{-9}$ at 20°.

The procedure was controlled by determining the dissociation constant of hypochlorous acid. The value obtained, $K_{\text{HOCl}} = 3.16 \times 10^{-8}$ at 20°, is in agreement with the values of Britton and Dodd[7] and Ingham and Morrison.[7]

INSTITUTE FOR CHEMICAL TECHNOLOGY
RESEARCH TEXTILE INSTITUTE, IVNITI
IVANOVO, U. S. S. R.
RECEIVED NOVEMBER 3, 1937

The Preparation of Benzotrifluoride

BY J. H. SIMONS AND C. J. LEWIS

Benzotrifluoride is made in yields approaching the theoretical and without the formation of tars or resins by the action of anhydrous hydrogen fluoride on benzotrichloride. Previous methods[1-3] have used antimony trifluoride, but the authors have found that the reaction in a copper vessel with hydrogen fluoride gives fewer side reactions than when antimony trifluoride is used either alone or with hydrogen fluoride.

The benzotrichloride is placed in a copper flask kept at 0° in an ice-bath. Gaseous hydrogen fluoride is admitted slowly and continuously through a copper tube that extends to the bottom of the flask, and the exit gases escape through another copper tube from the top of the flask. The reaction mixture is stirred or agitated during the course of the reaction.

The exit gases consist chiefly of hydrogen chloride with some hydrogen fluoride and small amounts of benzotrifluoride. As the reaction nears completion, the concentration of hydrogen fluoride and the desired product increase; and they should be trapped in a copper trap kept in a salt-ice bath. The exit gases can be analyzed qualitatively for hydrogen chloride and hydrogen fluoride and relative amounts estimated by the simple procedure of testing with beads of aqueous solutions of silver nitrate and calcium chloride held in nichrome wire loops. Although the reaction can be carried to 95% completion or further, the concentration of hydrogen fluoride in the exit gases rises at about 70% completion, and it is economical to stop the reaction at this point, separate the benzotrifluoride from the mixture by distillation, and return the residue (consisting chiefly of mono- and difluorides) with a new supply of benzotrichloride to the reaction flask for further conversion.

A charge of 500 g. of starting material required about seventy-two hours for the conversion. When the reaction is stopped, the temperature is allowed to rise to room temperature, and a small amount of sodium fluoride is added to remove any hydrogen fluoride present. After standing for a short time with occasional stirring, it is ready for distillation.

Yields of from 75 to 95% were obtained. Other than mechanical losses the chief cause for less than theoretical yield is the amount of the product escaping as vapor with the exit gases.

The benzotrifluoride made by this method was used to make trifluoroacetic acid by the method described by Swartz.[1] With careful technique a yield of about 50% of acid from the starting material, benzotrichloride, can be obtained.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
RECEIVED DECEMBER 10, 1937

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(1) Swartz, *Bull. acad. roy. sci. belg.*, **35**, 375 (1898).

(2) Aelony, THIS JOURNAL, **56**, 2063 (1934).

(3) Booth, Elsey and Burchfield, *ibid.*, **57**, 2066 (1935).

Crystalline Ficin

BY A. WALTI

The latex of certain fig trees has been used as an anthelmintic by the natives of Central America for a long time. It also has been known that latex of certain species of *Ficus* contains a proteolytic enzyme. Robbins[1] has shown that such a latex which was proteolytically potent also possessed the ability to digest ascarids in vitro.

We have been able to obtain the active principle in crystalline form.[2] This substance readily can be recrystallized. A convenient manner for obtaining this crystalline substance is the following: The clarified active latex was brought to *p*H 5 by the addition of a normal sodium hydroxide solution while stirring, and the clear solution was allowed to remain at approximately 5° for several weeks. Crystals formed which could be recognized readily by the golden sheen they imparted to the brown solution. Under the microscope at a magnification of 100 to 200 diameters the crystals represent beautiful hexagonal thin plates. The crystals were centrifuged off preferably at a lower temperature. They had a yellowish color. By dissolving the crystals in a dilute hydrochloric acid solution of approximately 0.02 normality, filtering through filter cell if necessary, and neutralizing to *p*H 5 with a sodium hydroxide solution, the material could be recrystallized readily. This procedure may be repeated. The white recrystallized substance possessed similar anthelmintic properties to the original latex when tested on living ascarids and hydrolyzed gelatine and benzoylglycylamide without the addition of an activator. The substance gave a positive Millon and biuret test and also its nitrogen, carbon, hydrogen and sulfur content were in agreement with the chemical nature of a protein. The enzyme could be obtained practically free from ash. On treatment of this enzyme with phenylhydrazine, inactivation occurred toward gelatine and benzoylglycylamide. On the addition of cysteine reactivation occurred. The enzyme was also inactivated by iodine and hydrogen peroxide. Ficin is a papainase and is the first proteolytic enzyme to be obtained from plant sources.[3]

RESEARCH LABORATORIES
MERCK & CO. INC.
RAHWAY, NEW JERSEY

RECEIVED DECEMBER 10, 1937

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[1] B. H. Robbins, *J. Biol. Chem.*, **87**, 251 (1930).

[2] Presented before the Biochemical Section of the American Chemical Society meeting in Pittsburgh, September 7, 1936.

[3] Recently A. K. Balls, H. Lineweaver and R. R. Thompson have obtained crystals with the properties of papain, *Science*, October, 22, 1937, p. 379.

COMMUNICATIONS TO THE EDITOR

A NEW KETONE FROM THE URINE OF PREGNANT MARES

Sir:

Recently Marker, Kamm, Crooks, Oakwood, Lawson and Wittle [THIS JOURNAL, **59**, 2297 (1937)] have reported the preparation of pregnanedione and *allo*-pregnanedione and the isolation of pregnanediol from the non-phenolic extract of mares' pregnancy urine. This material has been under examination in these laboratories during the past year and has yielded pregnanetriol [in confirmation of the earlier work of Haslewood, Marrian and Smith, *Biochem. J.*, **28**, 1316 (1934)], a water soluble semicarbazone (m. p. 253–254° (decomp.)] which has not been investigated to date and small amounts of an undescribed saturated ketone. A preliminary statement concerning the latter is considered advisable at this time although its identity has not yet been established.

Combustion figures indicate the empirical formula $C_{19}H_{26}O_3 \pm C \pm 2H$ for the new ketone. It gives a golden yellow color with the Liebermann-Burchardt reagents and a yellow to orange solution with a green fluorescence on warming with concentrated sulfuric acid. Esterifiable hydroxyl groups are absent; no product was obtained with acetic anhydride at 100°. Quantitative hydrolysis of the semicarbazone and its composition clearly establish the fact that only one oxygen atom is present in a reactive carbonyl group. The nature of combination of the remaining two oxygen atoms has not been determined.