

strains studied. This is appreciably lower than that reported (p_H 6.6-6.8) for two strains by Fred,³ but agrees very closely with the senior writer's findings regarding the maximum hydrogen-ion concentration tolerated by these organisms in soils (p_H 5.9-6.0).⁴

As the hydrogen-ion concentration of the medium decreased, growth increased until p_H 6.1 to 6.4 was reached. Here growth appeared to be quite as vigorous as at lower concentrations.

No fixation of nitrogen took place in a hydrogen-ion concentration greater than p_H 5.9, while fixation in concentrations of p_H 6.3 to 6.5 was as great as in lower concentrations. The optimum reaction for the fixation of nitrogen appeared to be very closely associated with the optimum reaction for growth.

The total quantity of acid produced by the various cultures was insignificant. The culture medium employed required only about 0.05 cc N/1 acid per 100 cc to produce a change of 0.1 p_H in reaction. Even with this low buffer index only slight changes in the hydrogen-ion concentration of the medium were produced by the growth of any strain of the organism. This would indicate the production of inappreciable quantities of either acid or basic metabolic by-products by these organisms.

P. L. GAINNEY

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PRELIMINARY NOTES ON VAUXITE AND PARAUAUXITE

AMONG the mineral specimens collected on the Vaux-Academy Andean expedition of 1921 are two that have proved to be new. As the crystallographic work on these will take some time, the following brief notes are therefore presented:

VAUXITE

Color: Sky-blue to Venetian-blue (Ridgway); streak white. Luster vitreous. Transparent. Form: Aggregates of small crystals

³ E. B. Fred: *Jour. Agr. Res.*, Vol. 14, pp. 317-336.

⁴ P. L. Gainney: *Jour. Agr. Res.*, Vol. 14, pp. 265-271.

tabular parallel to b (010). Hardness 3.5. Specific gravity = 2.45.

Composition: $4 \text{ FeO} \cdot 2 \text{ Al}_2\text{O}_3 \cdot 3 \text{ P}_2\text{O}_5 \cdot 24 \text{ H}_2\text{O} + 3 \text{ H}_2\text{O}$.

Crystal system: Triclinic.

Optical properties: Optically +; $\alpha = 1.551$; $\beta = 1.555$; $\gamma = 1.562$; all $\pm .003$; $\gamma - \alpha = .001$; $2V = 32^\circ$; Bx_{ac} emerges on sections parallel to b (010). Dispersion considerable $\rho > \nu$. Strongly pleochroic, colorless to blue.

Occurrence: On wavellite from the tin mines of Llallagua, Bolivia.

Name: In honor of the well-known amateur mineralogist, Mr. George Vaux, Jr., of Bryn Mawr, Pennsylvania.

PARAUAUXITE

Colorless; streak white. Luster vitreous to pearly. Transparent. Form: Small prismatic crystals. Hardness 3. Specific gravity: 2.30.

Composition: $\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O} + 5\text{H}_2\text{O}$.

Crystal form: Triclinic. Cleavage, perfect parallel to b (010).

Optical properties: Optically +; $\alpha = 1.554$; $\beta = 1.558$; $\gamma = 1.573$; all $\pm .003$; $\gamma - \alpha = .019$; $2V$ (calculated) 35° . Sections parallel to b (010) show the emergence of an optic axis.

Occurrence: On wavellite from Llallagua, Bolivia.

SAMUEL G. GORDON

ACADEMY OF NATURAL
SCIENCES OF PHILADELPHIA,
APRIL 15, 1922

THE AMERICAN CHEMICAL SOCIETY

(Continued)

SECTION OF CHEMICAL EDUCATION

Edgar F. Smith, *chairman*

Neil E. Gordon, *secretary*

First year college chemistry: WILLIAM MCPHERSON.

A first course in general chemistry: WILHELM SEGERBLOM. A brief comparison is made of fourteen of the more modern texts in chemistry suitable for secondary schools. The results of a recent text-book survey made by the New England Association of Chemistry Teachers are given. The usual custom of starting beginners in chem-

istry on gases and gas laws is criticized. The belief that the ordinary student can get more tangible results by starting with more tangible substances is put forth. A scheme of experimentation, which was tried out at Exeter some years ago, and which starts the student on some common metals and leads up through a series of ninety experiments to a little chemical investigation of an unknown substance without the use of a conception of atoms, molecules and symbols, is described. The scheme was satisfactory from the point of view of teaching chemistry but had its limitations for those who must primarily prepare students for the college entrance examinations. A possible revision of the College Entrance Examination Board syllabus is suggested.

First year chemistry for women: MINNIE B. FISHER. Women students who take chemistry as a cultural subject, or as a prerequisite to home economics courses, should be taught in separate groups. They lack background for scientific work, will devote little time to pure science and need very careful laboratory direction and supervision. Conference periods should be arranged to clear up difficult points. The utmost accuracy in observation and recording of facts should be insisted on. Greatest cultural value is to instill into students greater respect for truth. Greater proportion of time should be devoted to study of chemical history, theory and non-metallic elements.

Metric system: EUGENE C. BINGHAM. Metric education has been too largely neglected in the elementary schools, so we need not only to instruct our students in its use, but also in the desirability of an extension of the use of the metric system. Particularly we should give an object lesson to students by buying apparatus and chemicals and selling it in metric quantities.

Methods for presenting first year chemistry: F. P. VENABLE.

The project method of teaching chemistry: NEIL E. GORDON. A project method has been worked out in the first year chemistry where the laboratory work and the text work have been very closely correlated. What the student can find out and has time to find out is not presented in the text. Blank spaces are left for inserting this material by the student, and hence the book is not complete until the student has done his part. The method has been found very efficient in training the student's power to think, ability to reason and arousing his curiosity.

Studying chemical engineering by the unit-

operation method: DR. W. K. LEWIS and PROFESSOR R. T. HASLAM. A brief description of the School of Chemical Engineering Practice of the Massachusetts Institute of Technology and the methods employed in teaching chemical engineering by means of experimental work on full-scale operating equipment is given. The field of chemical engineering is divided into "unit-operations," the more important of which are flow of fluids, flow of heat, evaporation, distillation, drying, filtration, combustion, extraction, electrolysis, etc., and these unit-operations are studied quantitatively, particular attention being paid to the efficiency of the operation, how this efficiency can be improved or the losses decreased, and how the equipment can be changed to get increased production. The students in this school design, carry out and work up the results of these investigations by themselves under suitable guidance from members of the institute faculty resident at the plant, who devote their time wholly to work in the practice school. A description of the quantitative tests carried out in the study of these unit-operations is given, showing the wide scope and the fundamental character of these plant investigations.

Standardization of courses in quantitative analysis for students in chemical engineering: JOHN L. DANIEL. A study of the courses given to chemical engineering students in sixty-nine institutions shows that the time given to quantitative analysis laboratory varies from 72 hours as a minimum to 714 as a maximum. The time given to recitation work in quantitative varies from none to 270 hours. There is no suggestion of any agreement among these schools as to the proper time to give to quantitative. Teachers of this subject should confer with a view to standardizing the course so that sufficient time would be given to it to accomplish its aim and purposes and to avoid devoting an excessive amount of time to it as this crowds desirable courses out of the curriculum.

Discussion of committee's report on chemical engineering education: R. H. MCKEE.

Content of chemistry courses: L. J. DESHA. With a fixed limit to the time available for instruction in chemistry and an ever-widening science, the problem of what to omit becomes fundamental. Courses have grown by simple addition of the newer developments to the traditional content, without sufficient attention to consolidation. As a result, the student's knowledge consists chiefly of isolated facts but poorly knit to-

gether by laws and theories. Reorganization should start with a clear-cut decision as to just what we are going to try to teach in the four years available, the careful selection of the subject matter best suited to this end and the equally careful omission of extraneous facts.

Importance and time given for courses in economics and industrial management in chemical engineering training: C. S. WILLIAMSON, JR.

Distribution of time between "pure" and "applied" science: GRAHAM EDGAR.

Recent progress at Columbia University: MARSTON TAYLOR BOGERT. Certain new advanced courses in chemistry are now available for those interested. Statistics are given relating to the present student body in the department of chemistry.

Some laboratory helpers: J. N. SWAN. The planning of a chemical building is a fine piece of research work. Many problems present themselves for solution. Attention is here called to just two items as representing different fundamental ideas to be kept in mind in planning for two different things in the same laboratory. In the matter of locks for desks in the freshman laboratory the fundamental idea is to save time. Getting into a desk is wholly a matter of routine; hence a time saver is worth while. Therefore compare the time involved with different locks and, as a secondary matter, expense and trouble to the institution. In the matter of reagent bottles it has got into the minds of some that time saving is the fundamental principle. Not so, they are teachers. The time of students spent in looking at reagent bottles is well spent; therefore the bottles should be where they can be seen. The fundamental principle is to have excellent reagent bottles where they hold the attention of the student. A comparison is then made of varieties of locks and of reagent bottles.

A chart of the synthetic intermediates: CHAS. W. CUNO. A chart of the various commercial intermediates prepared from the distillates of coal tar, their type syntheses, the relation of these intermediates to one another, and their relationship to the common dyes of commerce. Three objects are in view: (1) to give the student in organic chemistry a bird's-eye view of this immense field; (2) to aid the manufacturer and commercial chemist in understanding and covering his field; (3) to show the research chemist possible gaps in present syntheses.

Training for agricultural chemistry: W. F. HAND.

Unified chemistry courses: JACK P. MONTGOMERY.

Standard tests in science, especially chemistry: H. A. WEBB. Standard tests have become adopted as a definite method in educational practice. A standard test may be defined as a method of measuring quantitatively a pupil's intelligence or his achievements in a certain branch of study. Various workers in the field of science as early as 1917 began to publish proposed standard tests in different scientific branches. The different types of tests and methods suggested up to the present time were illustrated. It is proposed by some that a type of quick, rapidly taken test be substituted for the conventional two or three hour examination which is so frequently used. The results obtained with such tests were discussed, and the advantages and disadvantages set forth. The use of standard tests in science has not been widely adopted, for none of them are standardized in the ordinarily accepted sense of the word, the whole matter being in a very experimental stage.

Science or athletics? E. G. MAHIN. The steady increase in extra-curricular activities in our colleges is believed to be largely responsible for the much discussed decline in our standards of scientific education. It is believed also that the abnormal development of commercialized intercollegiate athletics is the greatest obstacle to restriction of such activities to sane and reasonable limits. In this paper it is argued that our standards can not be materially improved until the colleges divorce themselves from commercialized athletics, and that this necessarily involves elimination of the high salaried professional coach and correction of the disproportion now existing in expenditures for athletics and for educational purposes.

SECTION OF HISTORY OF CHEMISTRY

C. A. Browne, *chairman*

Lyman C. Newell, *Secretary*

Dr. Thomas Cooper—A pioneer American chemist: EDGAR F. SMITH.

The chemical and scientific achievements of Father Athanasius Kircher, S. J.: GEORGE A. COYLE.

A book and a battery (Section of Sir Humphry Davy's battery and a volume of the complete works of Davy): J. N. SWAN.

An early type of chemical slide rule: JOHN A. GUNTON. An improved scale of chemical equivalents, dating from 1828, is described. It was designed by Beck and Henry of Albany as an im-

provement on a scale invented by Wollaston in 1814 and differs from the original in having a greater number of elements listed and also in the fact that hydrogen is taken as the radix or unit. Altogether 36 elements and 144 compounds are listed on which computations may be based. The calculation is carried out by means of sliding portion, as in the ordinary slide rule, the slider being subdivided into divisions representing the logarithmic ratios of the numbers from 8 to 330. The "equivalent weights" as given and the nomenclature are interesting from the historical standpoint.

Reminiscences of Italian chemists: WILLIAM MCPHERSON.

A few sources of information upon early chemistry and chemical industries in America: C. A. BROWNE.

Some facts relating to early chemists and chemical industries in Alabama: B. B. ROSS.

Some early southern chemists and their work: EUGENE A. SMITH.

Not much time was taken in the discussion of the papers, as the program was long without discussion. There were more than one hundred present during at least part of the time the section was in session, which was probably the largest attendance of any section at the meeting.

Quite a number of autograph letters, pamphlets, pictures and books were shown and some pieces of apparatus.

DIVISION OF ORGANIC CHEMISTRY

H. T. Clarke, *chairman*

Frank C. Whitmore, *secretary*

The preparation of methylmercuric acetate and methylmercuric hydroxide: M. C. SNEED and J. LOUIS MAYNARD. During the course of an investigation of the thermal decomposition of mercurous acetate in an atmosphere of nitrogen, the formation of a small quantity of an organic derivative of mercury was noted. This product was assumed to be methyl mercuric acetate, despite the fact that its properties did not agree with those described by Otto. Doubt was cast on the purity of his salt prepared by the action of acetic acid on mercury dimethyl at 120°. Jones and Werner have shown that, at higher temperatures, a more complicated reaction takes place with no evidence of the formation of the desired salt. The true methylmercuric acetate has been prepared by four reactions, each of a different type, none of which admits the possibility of the decomposition of the desired organomercuric salt.

These methods were: (1) Action of mercuric acetate with mercury dimethyl; (2) Action of methylmercuric iodide and silver acetate; (3) Neutralization of methylmercuric hydroxide with acetic acid; (4) Action of methylmercuric hydroxide with ethyl acetate. The same organomercuric salt was formed in each of the above reactions. It was identical with the mercury derivative produced in the decomposition of mercurous acetate. The hitherto unprepared methylmercuric hydroxide required in methods 3 and 4 was obtained as a white crystalline solid by the action of moist silver oxide on methylmercuric iodide.

An electrolytic method for the preparation of mercury dimethyl: HENRY C. HOWARD, JR., and J. LOUIS MAYNARD. Although mercury dimethyl has been obtained by Kraus by the electrolysis of aqueous solutions of methylmercuric salts, the low conductivity of such solutions renders the process unsuitable as a means of preparation of the dialkyl. However, it has been found that the addition of pyridine in approximately equimolecular quantities increases the conductivity to such an extent that electrolysis becomes a satisfactory method of preparation. In the course of this investigation the conductivities of solutions of methylmercuric hydroxide and several of its salts were determined. It is interesting to note that these measurements show methyl mercuric hydroxide to be an extremely weak base. This is contrary to the statements in the literature.

The asymmetry of diazodiethylglutamate: WILLIAM A. NOYES and H. M. CHILES. While Noyes and Marvel did not succeed in obtaining optically active diazo esters in which the asymmetry was due to the carbon atom to which the diazo group is attached, Levene and Mikesha have reported the preparation of such a compound from *l*-diethyl aspartate. We have obtained an active diazo ester, $\text{EtO}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CN}_2-\text{CO}_2\text{Et}$, from *d*-diethyl glutamate by the Curtius method. The carefully purified ester is a yellow oil which boils 92-93° under a pressure of 0.1 mm. Other optically active substances which might have been present were carefully removed and the composition was established by analysis. The specific rotation at 20° for the D line is +1.68°. The specific rotation in a 10 per cent. ether solution is +4.03°. The diazo ester, in solution in ether, gives the *d*-hydroxy ester on shaking with NH_4SO_4 . Saponification of the hydroxy ester gives the sodium salt of a hydroxy acid which is also dextro-rotatory. It is difficult to reconcile the optical

activity of this diazo compound with the Lewis-Langmuir theory of the combination of atoms in "non-polar" compounds.

Further observations on the nitration of halogenated phenols: L. CHAS. RAIFORD and LIANG YI HO. Previous work by Raiford and Heyl has shown that the method of nitration of brominated phenols first used by Zincke is suitable for the bromine and iodine compounds, but that the nitro radical fails to replace chlorine; and that, further, both dibrominated and tribrominated derivatives of ortho and meta cresols may be expected to give isomeric nitro derivatives. The small yield (10-12 per cent.) of the para isomeride, 3-bromo-5-nitro-o-cresol, obtained when dibromo-o-cresol was nitrated in this way raised the question as to whether the position taken by the nitro radical depends more upon the relative position of the halogen atom or upon its character. To get data on this point, 3-chloro-5-bromo-o-cresol and its isomer, 3-bromo-5-chloro-o-cresol, were nitrated. In each case the bromine was displaced, giving the isomeric compounds, 3-chloro-5-nitro-o-cresol and 3-nitro-5-chloro-o-cresol.

New organic selenium compounds: MARSTON TAYLOR BOGERT and Y. G. CHEN. By the action of hydrogen selenide upon acyl anthranilic nitriles, selenoquinazolones have been prepared and studied. Derivatives of 2-phenyl benzselenazole also have been investigated and show some interesting properties.

The synthesis of a thiazole analog of cinchophen (atphan): MARSTON TAYLOR BOGERT and E. ABRAHAMSON. 2-phenyl benzothiazole is nitrated, giving the 6-nitro derivative, which is reduced to the amine, and the latter is then changed to the corresponding carboxyl compound through the diazo reaction. Various derivatives and collateral compounds were prepared. The position of the nitro group was proved by decomposition of the amine and by its conversion to the benzobis thiazole.

Hydrocyanic acid: an ammono carbonous acid and an ammono formaldehyde: EDWARD C. FRANKLIN. From a purely formal point of view HNC represents hydrocyanic acid as an ammono carbonous acid, while the nitrile formula represents it simultaneously as an ammono formaldehyde and as formic ammonid. Sodium ammono carbonite may be nitrized to an ammono carbonate by a considerable number of methods, as, for example, by the action of sodium ammono nitrate and of cyanogen as represented by the equations, $\text{NaNc} + \text{NaNa} = \text{NCNNa}_2 + \text{N}_2$ and

$\text{NaNc} + \text{C}_2\text{N}_2 = \text{NaN}(\text{CN})_2 + \text{C}$. As an ammono aldehyde, hydrocyanic acid undergoes polymerization and condensation, forms addition compounds with bisulfites, ammonia, water and alcohol, reacts with hydroxylamine, hydrazine and phenylhydrazine, and is reducible to an ammono alcohol.

A study of the optimum condition for the formation of the Grignard reagent: HENRY GILMAN and CHAS. H. MEYERS. Two satisfactory methods for the estimation of the Grignard reagent are being used. One involves titration with standard acid and the other the measurement of gas evolved when the reagent is decomposed by water. The study concerns those ordinary factors affecting the yield: rate of addition of RX , concentration of reagents, kind of magnesium, cooling during formation, refluxing after formation, stirring, kind of air protection (calcium chloride, soda lime, etc.), catalysts, etc. This preliminary report is on ethyl magnesium iodide.

The reaction between thionyl aniline and the Grignard reagent: HENRY GILMAN and HARRY L. MORRIS. In connection with a series of studies on the mode of reaction of the Grignard reagent with compounds having more than one reactive grouping, thionyl aniline ($\text{C}_6\text{H}_5\text{N}=\text{S}=\text{O}$) has been treated with several RMgX compounds. Phenyl magnesium bromide gives a good yield of the anilide of benzenesulfonic acid. Excess of the Grignard reagent gives the same compound. Up to the present no success has attended attempts to determine the mechanism of the reaction—the $-\text{MgX}$ may have added either to the nitrogen or to the oxygen.

Arsenated heterocyclic compounds prepared from 3,4-diaminophenyl arsonic acid (amino arsanilic acid): W. LEE LEWIS and R. S. BLY. The great reactivity of the ortho-diamines with a great variety of substances yielding quinoxalines, azimides, piazthioles, imidazoles, etc., suggested the easily available amino arsanilic acid as a fruitful starting point for new organic arsenicals. 3,4-diaminophenyl arsonic acid is made by nitrating oxalyl p-arsanilic acid and reducing the nitro compound with ferrous chloride and ammonia. Thus far this compound has been condensed with benzil, oxalic acid, pyruvic acid, maltosone yielding the following: 2,3-diphenyl-quinoxaline-6-arsonic acid, 2,3-diketoquinoxaline-6-arsonic acid, 2-methyl-3-hydroxy-quinoxaline-6-arsonic acid, and 3-(glucosido-erythrityl)-quinoxaline-6-arsonic acid.

Derivatives of the beta-chloro-vinyl arsines: W. LEE LEWIS and H. W. STIEGLER. The chloro-

vinyl arsines were prepared by the action of acetylene upon arsenic chloride in the presence of aluminum chloride and were separated by fractionation under reduced pressure. The following derivatives were prepared: Beta-chloro-vinyl arsenious oxide, beta-chloro-vinyl arsonic acid, beta-chloro-vinyl di-iodo arsine, beta-chloro-vinyl bi-bromo arsine, hydrated bis-beta-chloro-vinyl arsenic acid, bis-beta-chloro-vinyl arsenious sulfide and bis-beta-chloro-vinyl arsenious oxide.

Chemical and crystallographic notes on the acid phthalates: FRANCIS D. DODGE. The use of potassium acid phthalate as ultimate standard in alkalimetry was suggested by the writer in 1915. This salt and the corresponding salts of sodium, ammonium, lithium and magnesium have since been more carefully examined. Acid salts of the formula, $2\text{MHC}_8\text{H}_4\text{O}_4 \cdot \text{C}_8\text{H}_6\text{O}_4$ ($\text{M} = \text{K}, \text{NH}$), were also observed. The acid phthalates crystallize remarkably well, and invited further study. The potassium, sodium, ammonium and lithium salts have been measured. The potassium and ammonium salts are isomorphous, and also show an interesting isomorphism with the corresponding salts of ortho-sulfo-benzoic acid. The rubidium and cesium salts were also prepared, and appear to belong to the same isomorphous group. In optical properties, the crystals of the potassium and lithium acid phthalates proved interesting, as they exhibit crossed axial plane dispersion toward the violet end of the spectrum. The same variety of dispersion is also very well shown by the mixed crystals of potassium and rubidium acid phthalates.

The occurrence of formic acid in essential oils: FRANCIS D. DODGE. A crystalline sediment which had been deposited in a zinc lined container of oil of geranium was found to be zinc formate, and its occurrence was explained by the presence of formic acid in the oil. This acid, in combination with the alcoholic compounds as esters, is apparently a normal constituent of the oil, the amount of ester, calculated as geraniol formate, ranging from 9 to 13 per cent. A method was devised for the determination of the acid in oils, and a number of the latter were examined. The relatively large amount of formic ester found in oil of geranium seems to be characteristic, and the determination may be of service in the technical valuation of the oil.

Catalytic reduction of the $\text{C}=\text{N}$ complex: DEWITT NEIGHBORS, S. M. CLARK, J. E. MILLER, A. L. FOSTER and J. R. BAILEY. Lochte and Bailey have recently applied the catalytic method employing colloidal platinum to the reduction of

dimethylketazine, $\text{Me}_2\text{C}=\text{N}-\text{N}=\text{CMe}_2$. This reaction has been successfully applied to the reduction of acetone semicarbazone to i-propylsemicarbazide, of menthone semicarbazone to menthylsemicarbazide, of camphor semicarbazone to bornylsemicarbazide, and of acetaldehydephenylhydrazones to phenyl hydrazoethyl. The investigation of i-propylsemicarbazide has been completed. Among the salts prepared are the hydrochloride and the oxalate. Other derivatives made are the nitroso and benzoyl compounds. The latter with caustic soda yields the corresponding i-propylphenylhydroxytriazole. With 80 per cent. H_2SO_4 i-propylsemicarbazide hydrolyzes to i-propylhydrazine, previously obtained by Lochte in the reduction of acetone hydrazone. Oxidation of the semicarbazide with permanganate in either acid or alkaline solution gives 2-carbonamidoazopropane, $\text{NH}_2-\text{CO}-\text{N}=\text{N}-\text{CHMe}_2$, along with acetone semicarbazone. The azo compound readily undergoes rearrangement to the hydrazone.

The preparation of mono- and parabromacetaldehyde and their application to synthetic work in cellulose chemistry: HAROLD HIBBERT and HAROLD S. HILL. These substances have been prepared in a state of purity and have been applied to the synthesis of a variety of substances closely related to the polysaccharides.

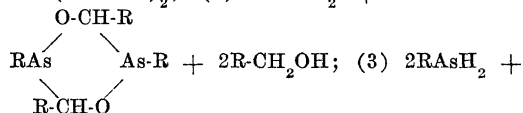
The electrolytic reduction of crotonaldehyde: HAROLD HIBBERT and ROLAND R. READ. Using a lead cathode, the principal product is an unsaturated cyclic aldehyde, apparently 4-aldehyde-2,3-dimethyl-2,3-dihydro-R-pentene (cyclopentadiene). The authors discuss the mechanism of this reduction and see in it valuable evidence for Nef's vinyl alcohol theory of the aldol condensation.

Preparation and properties of 1-mercaptobenzothiazole and its derivatives: L. B. SEBRELL and C. E. BOORD. The preparation of this substance from thiocarbonyl and sulfur, from aniline, carbon disulfide and sulfur, and from both the zinc and ammonium salts of phenyldithiocarbamic acid and sulfur were carefully studied and compared as to yield, purity of product, etc. This work was extended to the methyl derivatives of 1-mercaptobenzothiazole, heretofore unknown, and their preparation and properties described.

Absorption spectra of phenylazophenol and its derivatives in the visible region: C. S. ADAMS and C. E. BOORD. The absorption spectra of azobenzene, phenylazophenol, and the substitution products of phenylazophenol were studied in both alcoholic and alkaline solutions. The shift in the absorption band due to position isomerism, variation in the dye concentration, changes in the

solvent, changes in the nature and concentration of the alkalis used were carefully noted and the results recorded as extinction curves. The work includes the methyl, chloro, bromo, iodo, nitro and hydroxy derivatives.

The condensation of primary aromatic arsines with aldehydes: C. S. PALMER and ROGER ADAMS. It has been found that primary aromatic arsines react with aldehydes in three ways, depending on the condition. These may be illustrated by the equations: (1) $\text{RAsH}_2 + 2\text{H-CH} = \text{RAs(CHOHR)}_2$; (2) $2\text{RAsH}_2 + 4\text{R-CHO} =$



$2\text{R-CHO} = \text{R-As=As-R} + 2\text{R-CH}_2\text{OH}$. The first reaction proceeds by treating the arsine with the aldehyde at room temperature with a little concentrated hydrochloric acid as a catalyst. The products are high-boiling oils, or in the aromatic series, solids. They are stable to water, alkalis, and cold dilute acids; they oxidize readily to give the aryl arsonic acids and aldehyde; they react with many other reagents as though they consisted of a mixture of the aldehyde and the arsine; they form addition products with chloroplatinic acid. The second reaction proceeds by treating the arsines and aldehydes with anhydrous hydrogen chloride, or by treating the compounds obtained by reaction (1) with hydrogen chloride, acetyl chloride, or acetic anhydride. Alcohol is evolved and 1,4,3,6-dioxidiarsines are produced having the structure given above in equation (2). These products do not form when aromatic aldehydes are used. The third reaction proceeds by heating the arsine with the aldehyde at a high temperature with or without hydrochloric acid or at a low temperature without hydrochloric acid.

Organomercury compounds formed from salicylaldehyde and its nitro derivatives: EDMUND BURRUS MIDDLETON with FRANK C. WHITMORE. Salicylaldehyde, since it is not readily oxidized and contains a phenolic hydroxyl, can be mercurated with mercuric acetate. The principal product is 3,5-diacetoxymercuri-salicylaldehyde. Using an excess of the aldehyde in water solution gives a mono-acetoxymercuri-salicylaldehyde, although the chief product is still the dimercurated compound. 3-nitro- and 5-nitro-salicylaldehyde react with mercuric acetate in alcohol to give mono-mercurated products. The sodium salts of these compounds are highly colored and soluble. Oxidation changes the mercurated aldehydes to

the corresponding acids. The mercurated aldehydes have been condensed with the following amines: aniline, p-toluidine, anthranilic acid and p-aminobenzoic acid. The mercurated salicylaldehydes are decomposed by aqueous inorganic iodides giving inorganic mercury compounds, alkali and the unmercurated aldehydes.

Organomercury compounds formed from benzenesulfonic and benzyisulfonic acids: FRANK C. WHITMORE and LOUIS EHRENFELD. Benzenesulfonic acid in aqueous solution dissolves mercuric oxide readily. Evaporation of the resulting solution does not give the expected mercuric salt. All the mercury is then attached to carbon, the product apparently being a mixture of at least two organic mercury compounds. Benzyisulfonic acid dissolves mercuric oxide and changes to an organic mercury compound even on gentle warming. The product contains only one substance. The position of the mercury is to be determined. The remarkable ease of mercuration of these sulfonic acids is without parallel among aromatic compounds which contain no "activating group" such as $-\text{OH}$ or $-\text{NH}_2$. Preliminary report.

Mass action in the preparation of compounds of urea with acids and salts: JACK P. MONTGOMERY.

Mononitro derivatives of the benzoic acid esters of the trihalogen tertiary butyl alcohols. T. B. ALDRICH and JULIA E. BLANNER. Through the interaction of o-, m-, and p-nitrobenzoyl chlorides and trichloro tertiary butyl alcohol and tribromo tertiary butyl alcohol, the six possible esters have been prepared. Nitration of the benzoic ester of trichloro tertiary butyl alcohol gives a nitro ester which is identical with the product obtained from m-nitrobenzoyl chloride. The nitro esters crystallize from alcohol in the form of colorless plates or needles. They are insoluble in water, but readily soluble in organic solvents; are not readily saponified; are practically odorless and tasteless; and can be reduced to amino compounds. They are not as active physiologically as the alcohols from which they are prepared. Possibly this is due to their insolubility.

Some reaction products of malonic ester and cyclohexane derivatives: E. C. KENDALL and A. E. OSTERBERG. Cyclohexane ethoxyglycol was prepared from ortho-chloro-cyclohexanol and sodium ethylate in alcohol. This substance heated with malonic ester replaces one or both ethyl groups according to conditions. The disubstituted product heated with malonic ester gives the monosubstituted compound. Ortho-amino-cyclohexanol reacts

with malonic ester with either one or both groups. The amino group is first substituted. The methylene hydrogen atoms of the malonic residue in this compound are easily replaced by chlorine. Sodium ethylate and alcohol react with this to form "dichloroacetyl of ortho-amino-cyclohexanol." The reaction product between amino-cyclohexanol and malonic ester in which both groups react with the ester at a high temperature reacts in such a manner that two molecules combine with an acetal linkage.

The alkylation of aniline: A. B. BROWN and E. EMMET REID. Mixtures of aniline vapor with methyl, ethyl, propyl and butyl alcohols have been passed over special silica gel at from 300 to 450°. This substance is an efficient catalyst for this reaction, though its activity falls off with time. In all cases the product is chiefly the monoalkyl derivative. The optimum temperature is from 365 to 395°. At the start 43 to 51 per cent. of alkyl anilines are produced with one equivalent of the alcohol and 68 to 70 per cent. with two equivalents, except in the case of butyl alcohol, where an excess is of little advantage.

The amination of alcohols: A. B. BROWN and E. EMMET REID. An extensive study has been made of the conversion of methyl, ethyl, propyl and butyl alcohols into the corresponding amines by passing their vapors mixed with ammonia over various catalysts at different temperatures up to 500°. The optimum temperatures and percentages of the primary, secondary and tertiary amines formed have been determined for the different catalysts. The best catalyst so far found is a specially prepared silica gel.

The alkylation of benzene: T. M. BERRY and E. EMMET REID. Continuing the work of Milligan and Reid, a more thorough study has been made of the alkylation of benzene by ethylene and propylene in the presence of aluminum chloride. The proportion of the alkylated benzenes in the two layers has been specifically investigated. It has been found that the higher alkylated benzenes, except the hexa-, are concentrated in the lower layer, which also contains almost all of the aluminum chloride. The absorption of propylene is relatively slow but continues till the tetra- product, at least, is formed.

Ditolyl ketene: HENRY GILMAN and CHESTER E. ADAMS. Several unsuccessful attempts have been made by others to synthesize this ketene. Azitolil, prepared by the oxidation of monohydrazil tolil, loses nitrogen when heated in benzene at 75 to 80° C., rearranging to the desired ketene. In addition to its general interest as a

new type it is being used in connection with another study.

The effect of an "iso" grouping on the melting and boiling points of organic compounds belonging to various classes: F. B. FLICK, H. M. CRAWFORD, R. HOYLE and H. GILMAN. In connection with some work on the structure of tetra-tolyl ethylene, a substance with an apparently "abnormal" melting point, a regularity in the boiling points of ethylenic hydrocarbons having an "iso" group was observed. The study extended to other classes of compounds having an "iso" grouping revealed certain regularities, some of which might have been forecasted.

Physiological action and chemical constitution: the replacement of the benzoyl by related acyl groups: HENRY GILMAN and RUSSELL M. PICKENS. A number of organic acids, aromatic and aliphatic, are related in different ways to benzoic acid. The physiological behavior (the present study concerns local anesthetics) of derivatives of these acids is being compared. The diethylamino-ethyl and the benzyl esters of pyromucic, feryl acrylic and alpha-thienic acids are described.

Arsenated benzanilide and its derivatives: W. LEE LEWIS and C. S. HAMILTON. Dichloro-p-arsinobenzoyl chloride was prepared according to the method of Lewis and Cheetham and condensed with various amines. With aniline there resulted p-arsinobenzanilide which, on reduction, gave p-arseno-benzanilide. Similarly there were made p-arseno-benzanthranilide and -anisidine and the arseno derivative of the latter. Further derivatives prepared are the following: p-arsinobenzoyl-p-phenetidine, its arseno derivative, diiodo-p-arsino-benzoyl-p-phenetidine, p-arseno-benzoyl-p-xylylide, p-arseno-benzoyl-alpha-naphthylamide, and p-arsonosobenzoyl-arsanilide.

Arsenated benzophenone and its derivatives: W. LEE LEWIS and H. C. CHEETHAM. A previous paper by the authors dealt with the condensation of di-chloro-p-arsinobenzoyl chloride with aromatic hydrocarbons and phenyl ethers in the presence of anhydrous aluminum chloride. In the present paper the work has been extended to include the preparation of the following: acetophenone-p-arsonic acid, o-carboxyphenyl arsonic acid, dichloro-o-arsinobenzoyl chloride, 4-methylbenzophenone-2'-arsonic acid, 4-ethoxybenzophenone-2'-arsonic acid, 4,4'-dibenzoyl-arsenobenzene, 4-methoxybenzophenone-2'-arsonic acid, 4-methoxybenzophenone-2'-arsenous acid, 4-ethoxybenzophenone-2'-dibromo-arsine, 4-methoxybenzophenone-2'-dichloro-arsine, 4-methoxybenzophenone-2'-diiodo-arsine, 4-ethoxybenzophenone-2'-di-

iodo-arsine, 4-methoxy-benzophenone-4'-dibromo-arsine, 4-methoxy-benzophenone-4'-diiodo-arsine, and 4-methoxy-benzophenone-4'-arsinic (acid)-acetic acid.

Application of the chloroethers for the preparation of some new derivatives of diethyl malonate and barbituric acid: ARTHUR J. HILL and DEWITT T. KEACH. The present investigations are preliminary to an extended study of the hypnotic effects produced by the introduction of various ether rests in the 5 position in barbituric acid (the methylene grouping). To this end chloromethyl ethyl ether and chloromethyl methyl ether have been combined with the sodium salts of diethyl malonate and ethyl diethyl malonate, suspended in anhydrous ether. The following esters have been thereby obtained: Di (ethoxymethyl) diethyl malonate, ethyl-ethoxymethyl diethyl malonate, and ethyl-methoxymethyl diethyl malonate. These derivatives of malonic ester interact smoothly with urea in the presence of alcoholic sodium ethylate, giving respectively: 5,5-di (ethoxymethyl) barbituric acid, 5,5-ethyl-ethoxymethyl barbituric acid, and 5,5-ethyl-methoxymethyl barbituric acid.

DIVISION OF RUBBER CHEMISTRY

C. W. Bedford, *chairman*

Arnold H. Smith, *secretary*

The internal mixer as a factory unit: R. P. DINSMORE. The study of the internal type of rubber mixer in factory production has revealed two defects. The ratio of cooling surface to volume of stock is so much less in such a mixer than on a mill and the working is so much more rapid that the temperature of the batch rises rapidly, and in most tire stocks it is impractical to add sulphur before the batch is taken out of the mixer. Also, these mixers require considerable batching-out equipment in order to sheet out the finished stock thin enough so that it will cool in a reasonably short time. The time for batching-out does not vary greatly, and it is difficult to balance mixing equipment with batching-out equipment. The advantages to be gained from the internal mixer are lower mixing costs, greater freedom from the dust nuisance and lighter work for the operator.

The thermal properties of various pigments and of rubber: IRA WILLIAMS. The thermal conductivity and diffusivity of rubber is determined by two separate methods. A method for the determination of the conductivity of pigments is given and the values have been determined for the most common pigments used in rubber compounding. A method is shown by which the thermal conductivity

and diffusivity of any rubber compound may be calculated from an analysis of the stock.

Physical properties of rubber compounded with light magnesium carbonate: H. W. GREIDER. The physical properties of rubber compounded with light magnesium carbonate have been studied, including tensile strength, elongation, hardness, resilient energy capacity and permanent set. This material was shown to behave in rubber as a reinforcing or toughening pigment, the maximum effect being given by nine volumes of the filler to 100 volumes of rubber. The principal disadvantage of magnesium carbonate in rubber was found to be the high permanent set imparted to the vulcanized product, attributable to the definite crystalline character of the particles. The reinforcing effect of magnesium carbonate at nine volumes per hundred of rubber was compared with equal proportions of other reinforcing pigments, including zinc oxide, gas black, fine china clay and colloidal barium sulfate. Gas black was shown to be the only filler showing a reinforcing effect greater than that given by light magnesium carbonate.

The relation between chemical and physical state-of-cure of rubber vulcanized in the presence of certain organic accelerators: NORMAN A. SHEPARD and STANLEY KRALL. Hexamethylenetetramine, aldehyde ammonia, p-nitrosodimethylaniline and thiocarbanilide, respectively, have been introduced in such quantities into a mixing consisting of 48 parts of first latex crêpe, 48 parts of zinc oxide and 3 parts of sulfur, that equivalent physical states of cure (as gauged by the stress-strain relations) were obtained in each case when vulcanized for 60 minutes at 287° F. The coefficients of vulcanization of these cures show that there is no uniform relationship between the physical and chemical states of cure in these stocks, even though the time and temperature of curing are constant. The equivalent quantities used in this work indicate that, in the type of stock here examined, one part of hexamethylenetetramine is equivalent in accelerating power to one and one half parts of aldehyde ammonia, three parts of thiocarbanilide and one half part of p-nitrosodimethylaniline, respectively.

Physical testing graphs: W. B. WIEGAND.

Rubber Division methods for rubber analysis: Report of committee and discussion.

Organic accelerators. Symposium. Specification standards and testing, including both chemical and physical tests in compounds.

CHARLES S. PARSONS,
Secretary.