

group II, a total of fifteen individuals have been examined of which three were group I and twelve group II.

Of five oranges, two were group II and three group III. The only gibbon blood examined belonged to group III.

In several cases the sera were tested on the blood cells of other individuals of the same species and found to contain isoagglutinins according to the rule for human blood.

It can be concluded from the foregoing that very probably the group specific factors characteristic for human blood appeared in the phylogeny of the primates prior to the genesis of man.

When tested with the absorbed immune sera, the bloods of thirteen species of lower monkeys (catarrhinae and platyrrhinae) all yielded negative results. Nor were distinct reactions obtained when they were tested with agglutinin solutions obtained from normal human serum group III. But agglutinin solutions from normal human serum group II agglutinated all eleven bloods of five species of platyrrhinae (new world monkeys) and one lemur and failed to react on all twenty-seven bloods of seven species of catarrhinae (old world monkeys). The reactive substances demonstrable in the bloods of the lower monkeys by these tests evidently differ from those of anthropoid and human bloods because of their failure to react with the absorbed immune sera. Similar reactions also occur in lower animals, *e.g.*, rabbits (see the absorption experiments of von Dungern and Hirschfeld.<sup>9</sup> The unexpected regularity, as exhibited by the tests on old and new world monkeys, suggests that a certain serological factor may be characteristic for a whole zoological family or group, or at least for the majority of its members.

K. LANDSTEINER,  
C. PHILIP MILLER, JR.

ROCKEFELLER INSTITUTE

## THE AMERICAN CHEMICAL SOCIETY<sup>1</sup>

### ORGANIC DIVISION

*Catalytic reduction of cinnamic aldehyde to cinnamic alcohol by hydrogen and platinum black:* W. F. TULEY with ROGER ADAMS. When cinnamic aldehyde is reduced with such reagents as sodium and alcohol, iron and hydrochloric acid, or even platinum black and hydrogen, there is invariably obtained as the chief product, phenyl-propyl alcohol. Only traces of cinnamyl alcohol are ever produced, but certain amounts of phenyl propionaldehyde can usually be found. Small amounts of iron or zinc salts activate platinum black as a catalyst in aldehyde reductions. On the other hand they render the platinum

less active for the reduction of olefines. By reducing cinnamic aldehyde in the presence of platinum black and a very small amount of a mixture of zinc and iron salts, it has been possible to cause the first molecule of hydrogen to react only with the aldehyde group with the formation of cinnamyl alcohol without the production of phenyl-propyl alcohol. The product as obtained directly from the reaction mixture melts only a few degrees lower than the pure substance.

*The catalytic reduction of alpha-nitronaphthalene:* ARTHUR N. PARRETT with ALEXANDER LOWY. A study has been made of the catalytic reduction of alpha-nitronaphthalene to the amine in the liquid phase under pressures of 50 and 100 pounds of hydrogen. A small laboratory autoclave fitted for rapid stirring was used. The nitro epd. was reduced in glycol with palladium black as catalyst at temperatures from 50 to 100°. Maximum yield 98.4 per cent. Percentage reduction to amine increased with the temperature. Glycerol, water, and isopropyl alcohol were used in place of glycol. Palladium oxide, platinum oxide, and nickel were also used as catalysts. Temperature and time factors were studied with the different solvents. Molten alpha-nitronaphthalene was reduced by hydrogen and PdO in 93.9 per cent. yield against a yield of 14.3 per cent. with nickel.

*Catalytic dehydration of alcohols by aqueous hydrobromic acid:* HENRY D. HIRSCH. Four secondary and two tertiary alcohols were heated in sealed tubes at 100° with about 2 per cent. by weight of 48 per cent. hydrobromic acid. The formation of unsaturated products was followed by titration with standard bromide-bromate solution. The dehydration reaction was found to be reversible. The reaction constants for the dehydration reactions are as follows: sec-Propyl .00073, sec-Butyl .00128, sec-Amyl .00082, sec-Hexyl .00034, tert-Butyl .0045, tert-Amyl .0070.

*Ortho-cresaurin:* M. GOMBERG and L. C. ANDERSON. o-Cresol can be condensed with carbon tetrachloride or oxalic acid with the formation of ortho-cresaurin (3, 3', 3''-trimethyl aurin). The constitution of this dye has been definitely established. The free radical of the trimethyl ether derivative has been prepared in solution, and other derivatives have been synthesized. Ortho-cresaurin can be used in acidimetry, its color changing between pH 6.6 and pH 7.6. Its conversion to blue compounds analogous to aniline blue, hitherto unobtainable, has been realized.

*Mercuration of aromatic sulfonic acids:* LOUIS EHRENFELD. Aromatic sulfonic acids are mercurated with extreme ease on refluxing with aqueous mercuric acetate. Mercuric ions disappear in less than one hour. The following sulfonic acids have been mercurated: benzene-p-chlorobenzene, p-bromobenzene, p-iodobenzene, o-toluene, p-toluene, 2,5-dichlorobenzene, and 2-chloro-toluene-5-sulfonic acid. The products are usually complex mixtures soluble in bases but not reprecipitated by acid. In a few cases water soluble products may be obtained. The product from p-toluene sulfonic acid re-

<sup>1</sup> Baltimore meeting, April, 1925.

acts with iodine to form 2-iodo-toluene-4-sulfonic acid, thus proving that the mercury entered *meta* to the sulfonic acid group. Crystallization from water gives hydrated 2-hydroxymercuri-toluene-4-sulfonic acid. Over calcium chloride this loses the water of hydration, and over phosphorus pentoxide it forms the inner salt.

*New syntheses in the benzothiazole group:* MARSTON TAYLOR BOGERT and A. STULL. When *o*-aminophenyl mercaptan or its zinc salt is condensed with aldehydes, the products in all cases examined are the 2-substituted benzothiazoles identical with those obtained when the corresponding acyl halides are used instead of the aldehydes, and no thiazolines are formed. This is in agreement with the work of Hofmann and at variance with that of Claasz. Both bis (*o*-aminophenyl) disulfide and its zinc salt have been carried through many interesting condensations with aldehydes and esters of bibasic acids, and the products so obtained then used as initial materials for other syntheses.

*Some new derivatives of 2-phenyl-benzothiazole:* M. T. BOGERT and H. B. CORBITT. The crystalline product obtained by Hofmann when he treated 2-phenyl-benzothiazole with phosphorus pentachloride has been shown to be the 6-chloro derivative. New nitro, amino, sulfo, and other derivatives have been prepared and investigated, as a further contribution to the chemistry of this group.

*On the constitution of some thiazole derivatives:* F. B. DAINS. When ethylene bromide reacts with a di-substituted thiourea, a thiazolidine is formed in which the more positive group of the thiourea is at (2) and the less positive at (3) of the new thiazolidine. When the sodium salt of a mono-substituted thiazolidone is allowed to react with a methyl halide, the methyl group attaches itself to the Ph.N and not to nitrogen (3) as suggested by Beckerts and Frerich.

*Some derivatives of ethylselenomercaptan:* E. H. SHAW, JR. and E. EMMET REID. Ethylselenomercaptan reacts with ketones in the presence of dry hydrogen chloride to form mercaptols of the type  $R_2C(SeC_2H_5)_2$ . These break down on oxidation to form ethylseleninic acid. Sodium ethylselenomercaptide gives the typical reaction for mercaptans with 1,5-butylsulfone anthraquinone sodium sulfonate, the  $-SeC_2H_5$  group being substituted for the  $-SO_3Na$  group, with the formation of selenium anthraquinone derivatives. Diseleno ethers result from the action of sodium ethylselenomercaptide with mustard gas, its sulfoxide and its sulfone. An analytical method for determining Se in organic compounds has been developed, making use of the Parr bomb.

*Nitridation:* F. Y. CHUCK. Just as the aquo nitric acid,  $HNO_3$ , is an oxidizing agent, so the ammonio nitric acid,  $H-N \equiv N \equiv N$ , is a nitridizing agent. In water solution this acid converts sulfur to sulfuric acid, ethyl alcohol to acetic acid and methyl amine, benzyl alcohol to benzaldehyde, benzoic acid and aniline. In liquid ammonia solution it nitridizes methyl amine to guanidine, hexamethylene tetramine to formamidine, hydrobenzamide to lophine and benzonitrile, benzyl amine to benzamidine.

Using  $NH_2Cl$ ,  $NH_2Br$ , or  $NH_2I$  in liquid ammonia as nitridizing agent, sulfur and hydrogen sulfide were nitridized to ammonio sulfurous and thiosulfuric acids,  $S_4N_4$  to a compound which seemed to be  $N \equiv S \equiv N$ , the anammonide of ammonio sulfuric acid.

*Hyponitrites:* ALFRED W. SCOTT. Sodium hyponitrite has been made from ethyl nitrite with hydroxylamine and sodium ethylate. The commercially available nitrites of amyl and *n*-butyl have been substituted for the ethyl nitrite. The reaction has been studied with reference to concentrations, time, and temperature. The best yield of sodium hyponitrite obtained was 13 per cent.

*A synthesis of 5-iodo-isatin:* A. J. HILL and MARION PFUND. It has been shown by Schulz and one of us that the condensation products of isatin with either diketopiperazine or hydantoin may be used for the preparation of oxindole acetic acid. 5-Iodo-isatin has now been synthesized with a view to preparing iodo-oxindolacetic acid. 5-Iodo-isatin may be prepared by allowing a mixture of isatin, 5 per cent. sodium hydroxide, and iodine to stand 6 days in diffused light. The iodo-isatin may be prepared in two forms, red and yellow. The yellow may be changed to the red by heating alone, or with acids, or with organic solvents. Sublimation of the red form gives the yellow.

*Mechanism of the oxidation of thymine. Thymine glycol:* OSKAR BAUDISCH and DAVID DAVIDSON. In order to test the assumption that thymine glycol is an intermediate product in the oxidation of thymine, this glycol has been synthesized and some of its chemical properties studied. Thymine glycol in alkaline solution is quantitatively hydrolyzed to urea, acetol, and carbon dioxide. Thymine glycol upon oxidation and subsequent hydrolysis gives pyruvic acid. These reactions of thymine glycol are in agreement with the original hypotheses, since oxidation of thymine, followed by hydrolysis of the oxidation products, yields urea, acetol, and pyruvic acid.

*Pyrimidine indigoids:* DAVID DAVIDSON and OSKAR BAUDISCH. The oxidation of isobarbituric acid proceeds in two ways, giving isodialuric acid, and a new type of colored derivative. Apparently there is a strong analogy between isobarbituric acid and indoxyl by reason of the grouping  $-NHCH_2CO-$ . The formation of the new type of colored substance from isobarbituric acid is then analogous to the production of indigo from indoxyl. Consequently the name Pyrimidine Indigoids is suggested for this new class of substances. 5-Amino-uracil gives a similar oxidation product.

*A synthesis of keto-tetrahydroquinoxaline and some of its derivatives:* A. J. HILL and T. K. CLEVELAND. Keto-tetrahydroquinoxaline has been prepared by the reduction of either *o*-nitrophenylglycine or its ethyl ester, the amino compound undergoing immediate ring closure. 2,2'-Diethyl keto-tetrahydroquinoxaline is formed by the interaction of the ethyl ester of diethyl bromoacetic acid and *o*-phenylene diamine. The methylene group of keto-tetrahydroquinoxaline will condense with isatin, 5-bromo-isatin, 5,7-dibromo-isatin, and 5-iodo-isatin. The beta-isatin derivatives are yellow or light brown, and the

alpha analogues in each case of a deeper shade, but not blue, despite the close structural relationship to indigo.

*The discovery of a new pyrimidine base in the nucleic acid of tubercle bacilli:* ROBERT D. COGHILL and TREAT B. JOHNSON. Only three pyrimidines have hitherto been found among the nitrogen compounds formed by hydrolysis of animal and plant nucleic acids, namely: Uracil, Thymine, and Cytosine. We are now able to announce the occurrence of a fourth pyrimidine compound among the hydrolytic products of a bacterial nucleic acid, namely, 5-methyleytosine. This pyrimidine has been identified in the phosphotungstic acid fraction associated with cytosine after acid hydrolysis of tuberculinic acid, which we have separated from tubercle bacilli. This pyrimidine was synthesized by Wheeler and Johnson in 1904.

*The constitution of diazo-imides and of aliphatic diazo compounds:* HENRY GILMAN, C. E. ADAMS and H. H. PARKER. The products of reaction of diazo-imides ( $RN_2$ ) and of aliphatic diazo compounds ( $R_2CN_2$ ) with Grignard reagents can be interpreted most satisfactorily on the basis of straight chain structures. (Ber. 40, 2390, 1907; Monatsh. 34, 1631, 1913.) However, because of the possibility of a tautomeric hydrogen atom, the structures of the straight chain nitrogen compounds are uncertain. By the use of reliable reagents for "anchoring" the  $-MgX$  group in the intermediate compound it is shown that the Grignard reagent adds to the terminal nitrogen atom. Apparently diazo-imides and aliphatic diazo compounds can have the structures,  $C_6H_5-N=N-N=$ ,  $(C_6H_5)_2C=N-N=$ . These formulas find confirmation in the results of unpublished work on the reaction of Grignard compounds with azo compounds, and with compounds having terminal cumulated unsaturated groups. Structures after the octet theory will be considered.

*The structure of compounds containing unsaturation between nitrogen atoms:* CHARLES D. HURD. Compounds containing two nitrogen atoms connected by a double or a triple bond reveal an unusual inertness at the point of apparent unsaturation. In contrast to the fact that a multiple linkage is usually regarded as a point of weakness, in this case it appears to be a point of strength. The reactions of such nitrogen compounds are considered under the following headings: Additive reactions, reduction, attempted syntheses of N-N linkages, hydrolyses, rearrangements, and thermal decompositions. G. N. Lewis has recently discussed the non-reactivity of molecular nitrogen and ascribes its stability to the following structure,  $:N:::N:$ . If we accept the assumption that a sextet of electrons provides a very stable configuration, it is possible to explain the inertness of multiply linked nitrogen compounds with similar electronic arrangements.

*The Beckmann rearrangement involving optically active radicals:* LAUDER W. JONES and EVERETT S. WALLIS. Acid azides and hydroxamic acid derivatives undergoing the Beckmann rearrangement are assumed, according to Stieglitz and Jones, to decompose giving isocyanates.

Jones and Hurd have further shown that the relative ease of rearrangement seems to depend upon the tendency of the radical R in the intermediate univalent nitrogen derivative to exist as a free radical. d-Benzylmethylacethydroxamic acid and d-benzylmethylacetazide, compounds of the above type in which R is an optically active radical have been prepared. The azide has been studied in particular. By its rearrangement an optically active isocyanate was obtained, from which an active amine and an active monosubstituted urea were made. A discussion of these results is to be given.

*Hydroxyethyl-hydroxylamines:* L. W. JONES and G. R. BURNS. This paper deals with the preparation and properties of the compounds formed by the action of ethylene oxide on hydroxylamine and ethyl-hydroxylamine. o-Ethyl-hydroxylamine gives o-ethyl-N,N-dihydroxyethyl-hydroxylamine, and its dihydroxyethyl ether. O,N-Diethylhydroxylamine gives O,N-diethyl-N-hydroxyethyl-hydroxylamine. Free hydroxylamine gives N,N-dihydroxyethyl-hydroxylamine and trihydroxyethylamine oxide. These can be reduced to the corresponding amines. Trihydroxyethylamine oxide when heated with sodium hydroxide solution decomposes into dihydroxyethylamine. When heated with hydrochloric acid it decomposes largely into trihydroxyethylamine.

*Natural occurrence of aconitic acid and its isomers:* O. A. BEATH. Normal aconitic acid is reported as occurring in aconites, larkspurs, beet and cane sugar residues, and other plant sources. The free acid from diverse sources has been isolated and identified in our laboratories. In most cases the stable form has been found to be not the normal acid melting at  $191^\circ$ , but rather the labile type melting at  $172-3^\circ$ . Our work is the first establishing the occurrence of this form in plants.

*The chemical composition of rosin:* L. B. SEBRELL and D. N. SHAW. That abietic acid or other similar acids may be obtained from rosin has long been known. However, there is much conflicting data in the literature as to whether the free acid exists in rosin or whether its acidic nature is due to the presence of the acid anhydride. We have been able to show that rosin heated in carbon dioxide free of excess oxygen undergoes no change. However, the presence of a little oxygen in the carbon dioxide causes the formation of an oxyacid which readily loses water. Rosin, therefore, must consist essentially of free abietic acid.

*A discussion of the work of the international committee on organic nomenclature:* Led by AUSTIN M. PATTERSON, American member of the committee.

*A new acidic substance isolated from the products of oxidation of 2,3,5,6-tetramethyl-d-glucose by alkaline hydrogen peroxide solution:* W. LEE LEWIS and E. L. GUSTUS. Nef and his students have studied the products of oxidation of various sugars by means of Fehling's solution, air and hydrogen peroxide, and have advanced certain theoretical considerations to account for the formation of the various polyhydroxy acids obtained. A

study of the oxidation of the methylated sugars should give direct evidence on the correctness of these theories. Due to the stabilizing effect of methylation 2,3,5,6-tetramethyl glucose should give only a 1,2-ene-diol and the corresponding oxidation products. Oxidation by alkaline hydrogen peroxide at 45°, followed by acidification with hydrochloric acid and removal of volatile acids by vacuum distillations at 60–80°, gave a salty residue which was freed from organic matter by extraction with absolute ethyl alcohol. Vacuum evaporation of the alcoholic extract gave a gum from which crystals separated. This substance was purified and found to be 2,5-dimethyl-d-arabono-lactone, a new substance. The carbon dioxide and formic acid formed during the oxidation correspond to the theory for three carbons per mole of methylated glucose.

*The action of alkalis on d-glucose:* WM. L. EVANS and RACHEL H. EDGAR. The action of aqueous potassium hydroxide of known normality on d-glucose at 25° and 50° has been studied for the purpose of learning what relationship, if any, exists between the yield of lactic acid and the concentration of the base used. The results are briefly these: (a) The yield of lactic acid increases both with the concentration of the base and with the temperature; (b) the yield of formic acid reaches a maximum at 1.0 N base; (c) pyruvic aldehyde formation reaches a maximum at approximately 0.1 N base at 25°.

*Tetramethyl-d-fructose, gamma form:* W. LEE LEWIS, M. L. WOLFROM and R. D. GREENE. A study of the behavior of the methylated monosaccharides with dilute alkalis is being undertaken to throw light upon the Lobry de Bruyn reaction and saccharinic acid formation. Due to the well-known stabilizing effect of methylation, tetramethyl glucose should give no related methylated levulose in the Lobry de Bruyn reaction. Correspondingly, the methylated levulose should give neither the related methylated mannose nor glucose. Methylation of d-fructose in slightly acid solution gave the methylated gamma form of the sugar. Since this work was completed a note has been published by Haworth in which he indicates the same result. (*J. Chem. Soc.*, 125, 2468, Dec., 1924.)

*Fluorescence and hydrogen-ion concentration:* L. J. DESHA. Measurements of the relative intensities of the total fluorescent light emitted under illumination by ultra violet light from a quartz mercury lamp have been made with quinine, various naphthols, naphthylamines and sulfonic acids in concentrations of  $M \times 10^{-2}$  to  $M \times 10^{-4}$  in buffer solutions which had been checked by the hydrogen electrode. The curves of intensity of fluorescence against pH closely resemble the dissociation curves of indicators. The region of maximum change is usually confined to about 2 pH units. Neutral salt effects have been observed and the influence of different ions determined. The well known inhibition of halide ions on the fluorescence of quinine has been observed in other cases as well.

*Gossypol:* ALVIN S. WHEELER and E. D. JENNINGS.

Although gossypol is said to be the substance which renders cotton seed meal poisonous, very little is known about it. Consequently an investigation of this substance has been undertaken. Cotton seed meal, nearly free from hulls, yields less than one per cent. of gossypol. It is a bright yellow substance which forms a red jelly at 180–190° and seems to form a compound with alcohol.

*A qualitative color test for the Grignard reagent:* HENRY GILMAN and F. SCHULZE. All Grignard reagents, so far tested, give a deep blue color when treated with a saturated benzene solution of Michler's ketone, then with a few drops of water, and finally with a 0.2 per cent. solution of iodine in glacial acetic acid. If metallic magnesium is present, the solution should be filtered prior to the addition of the iodine solution. Because the test is only given when the  $-MgX$  group is attached to carbon, it is of considerable value in showing when all the  $RMgX$  compound has been used up. The test is shown by the corresponding calcium and barium compounds and with sodium alkyls and aryls. With ethyl magnesium iodide a positive test is obtained when the concentration is as low as 0.076 molar. The mechanism of the reaction will be considered.

*The active agent in aqueous bromination. (Lantern):* A. W. FRANCIS. Bromination of organic compounds in aqueous solution has often been ascribed to the action of hypobromous acid on the organic compound. Evidence has been found, however, against this theory. Solutions of hypobromous acid always give grayish or dark brown bromination products with aniline and other amino compounds, evidently because of oxidation; while bromine water gives colorless products. Furthermore, bromination of m-nitrophenol is about 1,000 times as rapid with bromine water as with hypobromous acid, prepared from bromine water and silver sulfate. The active agent in both solutions is suggested to be nascent bromine. This is consistent with all the evidence offered for hypobromous acid as the active agent. It is also supported by the fact that gold leaf dissolves readily in bromine water, but is unattacked by hypobromous acid, and only slowly by non-aqueous solutions of bromine.

*The partial bromination of some derivatives of aniline. (Lantern):* A. W. FRANCIS. The addition of insufficient amounts of bromide-bromate solution to an acid solution of aniline precipitates tribromoaniline in amounts less than the amount of bromine added. These precipitates correspond to a smooth curve which is a function of the relative velocity constants of bromination. m-Amino compounds, which are likewise tribrominated, give exactly the same curve, showing that the other substituent affects the rate of bromination in each position to the same extent. o- and p-Amino compounds are only dibrominated and have two other curves, respectively, which are the same for members of each class.

*Further studies of the absorption spectra of aliphatic ethers in the ultra-violet. (Lantern):* ARTHUR J. YANEY, CECIL E. BOORD and ALPHEUS W. SMITH. The aliphatic ethers show absorption bands in the ultra-violet region very similar to those of benzene. Those ethers having a

normal chain of six carbon atoms have their absorption bands in identically the same position as the bands for benzene which they resemble in a remarkable way. As the molecular weight is increased the absorption pattern moves towards the longer wave length and the bands become more closely grouped. Branching of the chains seems to distort the absorption pattern so that the individual bands can no longer be distinguished. Ethers of the same molecular weight apparently have the same central frequency, but the symmetry of the absorption pattern varies directly with the symmetry of the molecule.

*The relation of reaction velocity to rate of stirring in various systems:* F. C. HUBER and E. EMMET REID. Three classes of reactions have been observed: (1) Those practically independent of the rate of stirring, (2) those in which the reaction rate changes with the stirring only above a certain speed and (3) those in which the reaction velocity is a linear function of the rate of stirring. In the first class are the saponification of ethyl benzoate and olive oil by sodium hydroxide, and the reaction of benzyl chloride with sodium carbonate or acetate. In the third class are the ethylation of benzene by ethylene and aluminum chloride, the condensation of carbon monoxide with toluene and aluminum and cuprous chloride, and the reduction of nitrobenzene by iron and acid, the solution of iron in acid, and the oxidation of sodium arsenite by gaseous oxygen. In the hydrogenation of cottonseed oil and of "solvenol" the relation is linear only above a certain speed.

*N-Acyl derivatives of 3-Amino-4-hydroxy-phenylarsonic acid:* GEORGE W. RAIZISS and BARRETT C. FISHER. This acid is important because of its close relation to arsphenamine. We have succeeded in forming a number of its acyl derivatives by means of the anhydrides of the lower members of the fatty acid group. A series of these new arsonic acids and their alkali salts have been obtained in chemically pure form as colorless crystalline substances.

*A new method for preparing furane:* W. COURTNEY WILSON. The preparation of furane from furoic acid (pyromucic acid) has been a difficult operation because carried out in sealed tubes. It has been possible to avoid this difficulty by merely heating the furoic acid at about 220° and removing the furane vapors at least six inches above the level of the acid. Yields of 65 per cent. are obtained. The method has been developed on a small plant scale.

*The oxidation of indene by mercuric acetate:* RALPH L. BROWN. Mercuric acetate either adds to olefines or oxidizes them to glycols. Indene reacts with mercuric acetate in dilute acetic acid at 25° to form a 25 per cent. yield of cis-hydrindene-1, 2-diol (m.p. 107-8°) and a slight amount of the trans isomer (m.p. 159-60°). The rest of the indene is converted into resinous material. About .9 mol of mercurous acetate is precipitated for each mol of indene used.

*The discoloration of alcoholic potassium hydroxide:* WM. F. WEBER. A 0.5 N solution of KOH in absolute alcohol turns yellow quicker than a similar solution in 95 per cent. alcohol. This coloration can not be prevented

but can be delayed by preliminary removal of aldehydes and by storing in glass vessels in the presence of an inactive gas. Methods of treatment are discussed.

*The preparation of ethyl crotonate:* C. J. BROCKMAN. The reaction between alpha-bromobutyric ester and dimethylaniline has been studied. As high as 41 per cent. yields of ethyl crotonate have been obtained in this reaction.

*Reduction of crotonaldehyde. (By title):* HAROLD HIBBERT and C. P. BURT. Reduction of crotonaldehyde with various metallic couples gives mixtures of butyraldehyde, butyl alcohol, crotyl alcohol and dipropenyl glycol. The statement of Charon that no butyl alcohol is formed by means of the zinc-copper couple is incorrect, as the two alcohols, butyl and crotyl, are formed in approximately equal amounts. The relative proportions of the products varies markedly with the couple used. The largest yield of crotyl alcohol is obtained with Zn-Cu, while that of dipropenyl glycol reaches a maximum with Hg-Zn.

*The electro reduction of acrolein:* R. R. READ and R. M. FREER. One of the principal products of the electro reduction of crotonaldehyde is dimethyl cyclopentene aldehyde. That this is not an isolated instance is shown by the present research on the electro reduction of acrolein, the product being cyclopentene aldehyde. Divinyl glycol treated under similar conditions remains unchanged.

*The relation between melting points and directive influence in the benzene ring. (By title):* A. W. FRANCIS and JOHN JOHNSTON. In most of the limited number of cases for which data are available, the *meta* isomer has the lowest entropy of fusion when the two groups are *like* in directive influence, and the *highest* when they are *unlike*. In about 80 per cent. of the commoner systems, the *meta* isomer has the lowest melting point, when the groups are *like*, and the *ortho* isomer when the groups are *unlike*.

*Hydrofluoric acid compounds of organic bases:* J. F. T. BERLINER and RAYMOND M. HANN. Hydrofluorides of organic bases have not been studied. A series of hydrofluorides of aromatic aliphatic primary, secondary and tertiary amines, diamines, and amino acids have now been prepared and studied. In every case analyses show that four moles of HF combine with each -NH<sub>2</sub> group present. Wide variations in conditions fail to cause changes in the composition of these compounds. Most of them sublime unchanged. Some compounds, such as mono-methyl aniline, which do not usually give crystalline compounds with mineral acids, yield crystalline hydrofluorides.

*Preparation and application of benzoyl hydroperoxide:* HAROLD HIBBERT and C. P. BURT. The conditions for high yield and purity have been determined, and the conditions relating to its application to unsaturated compounds such as styrene, etc., have been ascertained.

*The nitration of p-cymene:* ALVIN S. WHEELER and C. R. HARRIS. Dinitrocymenes may be obtained by nitrating p-cymene or mono-nitrocymene. Purification is best accomplished by crystallization from a 5:1 mixture of

petrol ether and carbon tetrachloride, in which the chief by-product, 2, 4-dinitrotoluene, is less soluble. The dinitrocymene obtained is probably the 2, 6-isomer. This compound and its derivatives are being studied.

*The mercuration of naphthoic acids. (Preliminary paper):* A. L. FOX. Of the common methods for preparing alpha-naphthoic acid the most satisfactory has been found to be the fusion of the sulfonate with cyanide to form the nitrile which is then hydrolysed by a mixture of glacial acetic acid, water and sulfuric acid. The yield of pure acid calculated on the basis of sulfonate used is 25 per cent. The acid reacts unusually readily with mercuric acetate giving poly-mercured products which are now being studied. A number of substituted naphthoic acids has been prepared. It is found that the ease of mercuration varies over wide limits. As in so many cases, ease of mercuration appears to run parallel to ease of bromination.

*Further studies of chloroethers:* F. E. CLARK, C. E. GARLAND, J. W. FARREN and H. R. FIFE. Further studies have been made of compounds of the types  $R-O-CH_2Cl$  and  $R'CO_2CH_2OR$ . Methods of preparation have been improved and extended to include chloromethyl ethers of secondary as well as primary alcohols. The ethers and corresponding esters have been made from isopropyl and secondary butyl alcohol.

*Condensation of the isomeric tolyl-2-thio-4-ketothiazolidines (rhodanic acids) with substituted vanillins:* RAYMOND M. HANN. The condensation products of the three tolyl compounds with vanillin, 5-chloro-, 5-bromo-, 5-iodo- and 5-nitro-vanillin are yellow to deep brown dyes, but are not fast to light.

*The condensation of rhodanic acids with isatin:* RAYMOND M. HANN. Isatin has been condensed with phenyl-, o-, m- and p-tolyl-, "pseudocumidyl-," o-, m- and p-anisidyl-, 4-m and 2-p xylydyl- and alpha- and beta-naphthyl-rhodanic acids to give the corresponding 3-aryl-rhodanal-5, 3'-oxindoles.

*Derivatives of arsanilic acid and amino-arsanilic acid. (Second paper):* W. LEE LEWIS and P. L. CRAMER. Arsenated quinoxalines have been prepared from amino-arsanilic acid and glyoxal, lactosone and maltosone. Arsenated Schiff's bases have been prepared from glucose, mannose, galactose, laevulose, arabinose and xylose. The rotations are inverted by the introduction of the arsenated ring. The two arsonic acids have been condensed with a number of sulfone chlorides. Ethylene oxide and related compounds have been condensed with the two arsonic acids.

*A method for measuring the separate ionization constants of poly-acids and -bases:* O. E. MAY and S. F. ACREE. We have begun the actual measurement of H-ion concentrations of solutions of dibasic acids titrated with alkali varying from zero to more than two equivalents, at the same time measuring the free organic acid by partition with a solvent like  $CCl_4$ . With these data and values for the equivalent conductances of the acid anion equal to about one half those for the dibasic anion, we

have calculated ionization constants for fifteen dibasic organic acids.

*Quantitative studies of the mechanism of oxidation of phenolphthalein to phenolphthalein:* RAYMOND M. HANN and S. F. ACREE. The electrometric titration curve for the two phenolic groups in phenolphthalein lies between pH 6 and 11. Only in this region is it found easy to study the oxidation by ferricyanides. The exact mechanism of the oxidation is being studied by means of electromotive force measurements and spectrophotometric data. Substituted phenolphthalins are also being studied to determine the effect of the substituent groups and of the change in the ionization constants of the phenolic groups on the reaction.

*Spectrophotometric studies of the ionization constants, end points and fading of phthalein and sulfonphthalein indicators:* K. S. MARKLEY, J. F. T. BERLINER and S. F. ACREE. At about pH 11 the end point of the titration curve for phenolphthalein is reached and the fading begins to be perceptible. A cell is described for the study of these phenomena at constant temperatures while spectrophotometric measurements are being made. The absorption curves for a number of indicators have been measured.

*Sodium acid phthalate as an acidimetric and electrometric standard:* N. E. KNIGHT and S. F. ACREE. Sodium acid phthalate is found to be a satisfactory standard. It is easily purified and obtained in stable form. It titrates sharply as an acid salt. A tenth molar solution has pH 3.96. The pH values determined at various dilutions give a value for  $K_2$  for phthalic acid of  $6 \times 10^{-6}$  which checks with other determinations.

*Elimination of contact potential between organic buffer solutions with potassium chloride and ammonium chloride:* C. N. MURRAY and S. F. ACREE. Loomis and Acree found that 4.1 N potassium chloride nearly completely eliminates the contact potential between solutions containing HCl, KCl and organic buffers, in conformity with the theory of Planck that concentrated solutions with ions of equal mobilities should be most effective in this respect. We have studied the effectiveness of potassium chloride and ammonium chloride in solutions from 0.1 N upward. Nearly identical results are obtained. The use of rubidium bromide and potassium and ammonium perchlorates in this field will be investigated.

*The use of organic buffers in colloid and H-ion studies in analytical chemistry:* G. L. ROBERTS and S. F. ACREE. Buffer mixtures containing acetates, formates, phthalates, phenolsulfonates, borates and phosphates have been used to regulate the H-ion concentrations and the adsorbed ions in solutions of Al, Fe, Co, Ni, Cr, Mn and other metals in which the microscopic and cataphoresis studies of these colloidal precipitates have been made. Important analytical applications are indicated.

FRANK C. WHITMORE,  
Secretary

NORTHWESTERN UNIVERSITY,  
EVANSTON, ILLINOIS