doublet $2s - 2p_{1,2}$, $\lambda\lambda$ 10829.1, 30.3. Until we have a satisfactory theory of the helium arc spectrum speculation as to the new line will be useless.

An interesting feature of the spectrum of the thermionic discharge in lithium is the unusual development of the subordinate series. Eleven lines of the sharp series and 16 of the diffuse were plainly seen on one of the plates. Only six and seven, respectively, are listed in tables of series lines. The principal series was recorded to the tenth line.

F. L. MOHLER

BUREAU OF STANDARDS

ON THE DISPERSITY OF SILVER HALIDES IN RELATION TO THEIR PHOTOGRAPHIC BEHAVIOR

IN an article appearing in SCIENCE for October 26, 1923, under the above heading, Dr. Frank E. Germann and Mr. Malcolm Hylan query a conclusion reached by Wightman, Trivelli and Sheppard, on the relation of grain size and photographic sensitivity. Their first questioning of the conclusion that the sensitivity increases with the grain size is based on an example quoted in "Monographs on the theory of photography," No. 1, p. 104, where comparison of two emulsions showed that the one having grains one third the linear dimensions was more than 19 times as fast and that the same was true of individual grains in the same emulsion. The explanation of this discrepancy has been amply provided subsequently by discoveries concerning the function of sensitive specks in the silver halide grains.[1]

They quote further the conclusion of Koch and DuPrel that "it is not possible to formulate any definite relationship between the grain size and sensitivity with the information at present available," to which it may be replied that very much more data are now available than were at hand at the time that Koch and DuPrel made their statement.

With regard to the theoretical considerations they advance, we find ourselves in considerable disagreement with them. They conclude, on the nuclear theory (without specifying what they mean by the nuclear theory), that the speed depends on the *number of grains affected* without reference, therefore, to the size of the grains. It can be seen from the work of Svedberg and others that this argument is entirely in contradiction with the present nuclear theory, since the number of specks or nuclei increase with the size of grain and, therefore, the chance of a grain being made developable by light increases with its size. As we have pointed out in other papers,[2] this result is independent of whether the continuous wave theory or the quantum theory of the constitution of light be adopted. The decision between these two theories must be reached on other grounds. Consequently, we can not agree that "theoretically the smaller grained emulsion should be the more sensitive," but rather the reverse. We may point out in this connection that the writers have not defined exactly what they mean by "sensitivity." Speed, in the usual photographic significance of the term, depends on density measurements, that is, on the number and size of the developed grains conjointly. Sensitivity can be determined microscopically from counts of grains independently of density measurements and the sensitivity of grains of a given size can therefore be specified in a manner independent of such density measurements.

It does not appear necessary, therefore, to discuss their explanation of a discrepancy between experimental results and those theoretically expected, which discrepancy does not in our opinion exist.

We shall await publication of their experiments on removing adsorbed halide from silver bromide grains with interest, but prefer to postpone discussion of this until we have their fuller data.

E. P. WIGHTMAN
A. P. H. TRIVELLI
S. E. SHEPPARD

ROCHESTER, N. Y.

THE AMERICAN CHEMICAL SOCIETY

(*Continued*)

DIVISION OF ORGANIC CHEMISTRY

Frank C. Whitmore, *chairman*
R. R. Renshaw, *secretary*

The uses of acetylene in synthesis: J. A. NIEUWLAND. The evolution of acetylene in organic syntheses began with the introduction of catalytic agents to effect reactions. Some of the following important types of catalytic syntheses were discussed: A—The halogenation reactions, typified by (a) catalytic $AlCl_3$ reactions; (b) catalytic $SbCl_3$ reactions. B—Catalysis with mercury salts, as (a) acetaldehyde, glacial acetic acid and acetone; (b) paraldehyde synthesis; (c) synthesis of ethylidine diacetate, acetic anhydride, formaldehyde and methyl acetate; (d) synthesis of acetals and cyclic acetals; (e) synthesis of acetylene with aryl hydrocarbons; (f) synthesis of acetylene with phenols (bakelite), and the dinaphthylols; (g) synthesis with reacting substances in solution, aldehyde blue, and green, acridine and xanthene dyes. Quinaldine, indole, cinnamic aldehyde, nitro cinnamic aldehyde and indigo. C—Syntheses with Cu_2Cl_2, as (a) divinyl acetylene, and derivatives (HCHO); (b) quinaldine and quinoline de-

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[1] See papers of Svedberg, *Phot. Journ.*, 62, 186, 316 (1923); Toy, *Phil. Mag.*, 44, 352 (1923); *ibid.*, 45, 715 (1923); Silberstein, *Phil. Mag.*, 44, 252, 955 (1923); *ibid.*, 45, 1062 (1923); S. E. Sheppard and E. P. Wightman on "The theory of photographic sensitivity," SCIENCE, 1923, pp. 89–91.

[2] *J. Franklin Inst.*, 194, 485 (1922); *J. Phys. Chem.*, 27, 141 (1923).

rivatives. General remarks on the possibilities of future progress in synthesis with C_2H_2 were made.

Synthesis of a new bicyclic nitrogen ring. Isogranatanine derivatives. Preparation of an isomer of homococaine: S. M. McELVAIN and ROGER ADAMS. A method for the preparation of a derivative of a new bicyclic nucleus containing a nitrogen atom common to both rings has been developed. The new nucleus has been called isogranatanine because it is isomeric with granatanine. The particular derivative especially investigated was ethyl benzoyl isogranatoline carboxylate, prepared by reduction of the ethyl granatonine carboxylate and subsequent benzoylation. The ethyl benzoyl isogranatoline carboxylate hydrochloride is isomeric with homococaine hydrochloride, and is a powerful local anesthetic.

Recent developments in the chemistry of arsphenamine: WALTER G. CHRISTIANSEN. Arsphenamine, *i.e.*, salvarsan, as prepared by the customary process, *i.e.*, reduction of 3-nitro-4-hydroxyphenylarsonic acid with sodium hydrosulfite is not a pure substance, but contains at least three impurities—two sulfur compounds and one oxide. The amounts in which these impurities are present and the toxicity of the product are dependent upon the experimental conditions existing during the reduction. By the use of various modifications of these reactions, these impurities may be largely eliminated, but since a product which is satisfactory for clinical use can be secured by the above reaction, there is no necessity of abandoning this process. The colloidal properties of arsphenamine have an important bearing on the toxicity of this substance.

The electronic conception of valence and the heats of combustion of organic compounds: MORRIS S. KHARASCH. The paper concerns itself with the application of the notions developed in a previous paper to the explanation of a number of properties of organic compounds. Considered in this light the study of the heats of combustion furnishes us with a very powerful tool for the determination of the electronic structure of organic compounds. The heats of combustion of some 275 organic compounds calculated upon this basis agree very well with the values that have been determined experimentally.

Petroleum as a chemical raw material: B. T. BROOKS. Petroleum is sometimes referred to as a rich mixture of raw materials which should yield a wide variety of chemical derivatives comparable with the large number of substances which have been prepared or manufactured from coal tar. The problem of isolating pure substances from petroleum is, however, quite different and for the most part yet unsolved. Our present chemical knowledge of the hydrocarbons in petroleum enables us to make a certain limited survey of what might be expected in the way of a chemical development of this raw material. In this discussion the problem is considered more from the standpoint of research in organic chemistry than from the standpoint of the more or less well-known problems of the petroleum industry proper. The present discussion is limited more to an effort to indicate what organic chemists can reasonably expect to do with this raw material rather than to discuss any improvements or extensions in the application of petroleum products such as are now manufactured and utilized in the industries.

Wednesday—9.30 A. M.

SYMPOSIUM ON SYNTHETIC METHODS

The alkylation of primary amines with aluminum ethoxide to give pure secondary amines: W. A. LAZIER and HOMER ADKINS. Both aromatic and aliphatic amines (aniline, p-toluidine, n-pentyl amine, n-butyl amine) have been alkylated with aluminum ethoxide, isopropoxide, normal butoxide and isobutoxide at temperatures of from 275°–350° to give secondary amines entirely uncontaminated with tertiary amines. The reaction of aluminum ethoxide and aniline has been most thoroughly investigated. A 90 per cent. yield of mono ethyl aniline has been obtained at 350° in a sealed tube, 10 per cent. of the aniline remaining unchanged.

Methylation by means of dimethyl sulfate: H. F. LEWIS. Mass relationships have been studied in the methylations of the phenolic hydroxyl groups. Attempts have been made to develop a procedure for the utilization of the second methyl group in dimethyl sulfate. To a certain extent this has been accomplished.

Ethylation of aniline by means of diethyl sulfate: A. R. CADE. In the experimental work which forms the basis for this paper the reaction between diethyl sulfate and aniline has been studied. Varying mixtures of aniline, monoethylaniline and diethylaniline are prepared by varying the molecular ratio of the aniline and of the diethyl sulfate originally used in the reaction. The effect of the time and temperature of heating the reaction mixture has been studied. A method for preparing a high grade diethyl aniline, or a mixture of mono- and diethyl aniline free from unused aniline are recommended as a result of the data obtained.

The preparation of the simple olefine bromides: C. E. BOORD. The bromine addition products of ethylene, propylene, butylene and amylene are easily and rapidly prepared in quantity by generating the olefine by the contact process and passing the gas counter-current to bromine or a solution of bromine in carbon tetrachloride in a special absorbing device. The products are purified by fractional distillation or if necessary fractional distillation under diminished pressure. Since the product is in contact with bromine for only a short length of time substitution is reduced to a minimum.

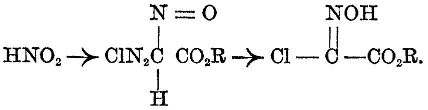
Modification of the Sandmyer synthesis of nitriles: H. T. CLARKE and R. R. READ. The standard method for the preparation of nitriles from aromatic amines suffers from the disadvantage that poisonous gases are evolved at two stages in the process, namely, cyanogen during the formation of the cuprous cyanide and hydrocyanic acid during the reaction of this with the acid diazonium solution. It has been found possible to avoid both of these difficulties; firstly, by preparing the cuprous cyanide solution by dissolving cuprous chloride in sodium cyanide and, secondly, by neutralizing the diazonium solution before adding it to the cyanide. The intermediate addition products formed under these conditions are extremely unstable, rapidly evolving nitrogen below 0°, and decomposing almost explosively unless the mixture is well agitated, preferably in presence of a diluent such as benzene. The yields fully equal those obtained by the standard procedure.

Methods of manipulating liquid ammonia solutions: E. C. FRANKLIN.

A new method of preparing alkyl halides: James F. Norris. Primary alcohols are readily converted into the corresponding halides by heating the alcohol with concentrated hydrochloric acid and anhydrous zinc chloride. Proportions found to give the best results were one mol. of alcohol, two of hydrogen chloride as concentrated hydrochloric acid and two of anhydrous zinc chloride. The yields varied from 60 to 80 per cent.

Simplification of the Gattermann synthesis of hydroxy aldehydes: Roger Adams and I. M. Levine. The Gattermann synthesis for the preparation of hydroxy aldehydes by the reaction of phenols, anhydrous hydrogen cyanide and dry hydrogen chloride in dry ether, sometimes with the addition of anhydrous zinc chloride, gives excellent yields of products. The method is not as frequently used as might be expected owing to the necessity of handling anhydrous hydrogen cyanide. The synthesis has been modified in such a way that this has been avoided. In place of the hydrogen cyanide, zinc cyanide is used, which is converted into anhydrous zinc chloride and anhydrous hydrogen cyanide in the reaction mixture. The zinc cyanide is readily prepared by treating an aqueous solution of sodium cyanide with magnesium chloride in order to precipitate the carbonate and hydroxide present, filtering and adding an alcoholic solution of zinc chloride. The precipitated zinc cyanide is filtered and dried. Experiments have shown that in several types of reactions anhydrous hydrogen cyanide has been previously employed, zinc cyanide may be substituted.

A new method for the synthesis of esters of chloroximino acids. Evidence of the existence of aliphatic diazonium salts: Glenn S. Skinner. In attempting to obtain evidence of the existence of aliphatic diazonium salts by working at low temperatures, using esters of glycocoll in the presence of a large excess of hydrochloric acid, the esters of chloroximino acetic acid were found to be the chief product. These compounds by treatment with sodium carbonate give good yields of the corresponding nitrile oxides or their polymers. A comparatively small amount of the esters of chloracetic acid is also formed. The possibility that the chloracetic ester is first formed and then oxidized to the chloroximino ester has been eliminated by the fact that it remains unchanged when subjected to similar conditions. A second explanation of the reaction is that the diazo ester is first formed and this then reacts with the elements of nitrosyl chloride from the excess hydrochloric and nitrous acids present. However, the diazo ester was shown to give none of the substance when treated with nitrosyl chloride. A study of the molecular weight of the nitrile oxide in four different solvents shows that it is an equilibrium mixture of the monomolecular form and the dimolecular form the so-called furoxandicarboxylic ester. The yield of the chloroximino compounds varied from 50 to 80 per cent. of the theoretical. The reaction should be formulated as follows: $ClN_2CH_2CO_2R +$



$$HNO_2 \rightarrow ClN_2\overset{\overset{\displaystyle N=O}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\;CO_2R \rightarrow Cl-\overset{\overset{\displaystyle NOH}{\|}}{C}-CO_2R.$$

Condensation reaction: Fred W. Upson. Certain points relative to carrying out the following reactions were discussed: (1) Reactions involving benzyl cyanide; (2) reactions between aniline and chlorohydrins; (3) addition of HCN to sugars.

Sodium amalgam as a reducing agent for oximes and aldehydes: L. Chas. Raiford and E. P. Clark. When sodium amalgam is prepared from pure mercury in accordance with the directions of the authors (J. Am. Chem. Soc., 45, 1740 [1923]) and used as specified, it is found to be a suitable agent for the reduction of certain oximes to the corresponding amines. Contrary to the results of Goldschmidt and Ernst (Ber., 23, 2740 [1890]), who found that only a poor yield of amine could be obtained by reduction of salicylaldoxime with sodium amalgam, although they tried several modifications of the method, we obtained a yield of 96 per cent. When salicyaldehyde was employed under similar conditions, with the exception that the liquid was kept faintly acid with acetic acid during the reaction, a yield of over 90 per cent. of the corresponding alcohol saligenin was obtained. The highest yield we have found reported in any other case is 63 per cent. Several other examples are being studied.

Tertiary butyl alcohol: Roland R. Read and F. A. Prisley. Isobutylene, prepared by the catalytic dehydration of the isobutyl alcohol, is passed into a light petroleum distillate kept at a temperature below — 10°. The saturated solution is agitated vigorously with 50 per cent. sulfuric acid, the temperature being allowed to rise slowly to that of the room. The aqueous layer is separated and neutralized. Tertiary butyl alcohol is then distilled out and dried.

The use of phenyl-hydrazine for the preparation of some derivatives of benzo-pyrrol: E. C. Kendall and A. E. Osterberg. The use of phenyl-hydrazine for the preparation of indol derivatives has long been known. Reduced benzo-pyrrol derivatives can be prepared by treating phenyl-hydrazones of cyclo-hexanone and its derivatives. To prepare members of the alpha-oxy-benzo-pyrrol series, the derivative of cyclo-hexanone must contain a side chain of two carbons terminating in a carboxyl adjacent to the ketone group, such as ortho-cyclo-hexanone acetic acid. If the hydrazone of ortho-cyclo-hexanone acetic acid is treated with acids, it will lose ammonia, producing a double bond within the ring, and will form the phenyl derivative of the open ring form of alpha-oxy-benzo-pyrrol. Derivatives in which a side chain is attached to the beta carbon of the benzo-pyrrol nucleus have also been prepared. The properties of these compounds depending upon the position occupied by the double bond will be discussed.

The oxidation of sucrose, glucose and fructose: C. D. Looker and W. L. Evans. Sucrose and an equivalent mixture of equal parts of glucose and fructose were oxidized by means of potassium permanganate at 50°, 75° and 100° C. In neutral solutions, carbon dioxide and acetic acid were obtained upon complete oxidation. In potassium hydroxide solutions of varying concentrations at 50° and 75°, oxalic acid was also obtained and increased in quantity up to about 0.1 N alkalinity and then decreased, but at 100° the amount of oxalic acid increased again beyond 1.0 N alkalinity. As oxalic acid increased, carbon dioxide always decreased proportionally. Acetic acid was nearly constant under all conditions.

Derivatives of the beta-chloro-vinyl arsines, II: W. Lee Lewis and H. W. Stiegler. In addition to previously reported derivatives, the following have been isolated in the pure state: beta-chloro-vinyl arsine sulphide; bis-beta-chloro-vinyl arsine sulphocyanate; tris-beta-chloro-vinyl methyl arsonium iodide; double salt of tris-beta-chloro-vinyl methyl arsonium iodide and mercuric iodide; double salts of tris-beta-chloro-vinyl arsine and silver nitrate with (a) 1 mole arsine and 1 mole $AgNO_3$ and (b) 2 moles arsine and 1 mole $AgNo_3$; double salt of tris-beta-chloro-vinyl methyl arsonium iodide and phenyl mercuric iodide.

Arsenoacetic acid and its polyarsenide: C. Shattuck Palmer. Hypophosphorous acid reduction of arsonoacetic acid, $H_2O_3As.CH_2.COOH$, leads to arsenoacetic acid, $HOOC.CH_2As = AsCH_2COOH$, yellow needles, which decompose above 200° but do not melt. The product is practically insoluble in water and common organic solvents, but readily soluble in pyridine and dilute aqueous alkali hydroxides and carbonates. Simultaneous reduction of one mol. As_2O_3 and two mols arsonoacetic acid gives the polyarsenide, $HOOC.CH_2.As = As - As = As.CH_2.COOH$, bright vermillion microcrystalline powder, resembling the simple arseno compound in solubilities and behavior on heating. The sodium salts of arsenoacetic acid and its polyarsenide are the first known water-soluble aliphatic derivatives of the arseno and polyarseno linkages.

The action of beta-chloro-ethyl chloroformate on amino-arylarsonic acids, and subsequent formation of arsonated N-arylamino alcohols. Preliminary Paper: Cliff S. Hamilton. The interaction of beta-chloro-ethyl chloroformate, prepared from ethylene chlorohydrin and phosgene, and amino-arylarsonic acids results in the formation of arsenated beta-chloro-ethyl carbanilates. These in turn give arsonated oxazolidones on treatment with alkali. The arsonated oxazolidones on further treatment with alkali yield, in some cases at least, arsonated N-arylamino alcohols.

The addition of mercuric salts to α, β-unsaturated ketones: Edmund B. Middleton. Unsaturated ketones reacted with alcoholic solutions of mercuric acetate. Ketones with one double bond like benzalacetophenone gave products whose composition is expressed by ketone plus $-HgOCOCH_3$ plus $-OR$, while dibenzalacetone gave products with two $-HgOCOCH_3$ and two $-OR$. They are α-acetoxymercuri-β-alkoxy ketones. If mercuric halides were used instead of mercuric acetate colored compounds consisting of one molecule each of ketone and mercuric halide resulted. The white products obtained with mercuric acetate gave reactions similar to those obtained from olefines: decomposition with acids, etc. With bromine, the mercury was replaced and α-bromo-β-alkoxy ketones resulted, for example, α-bromo-β-methoxy-β-phenyl propiophenone from benzalacetophenone. This lost HBr with alkali and the resulting unsaturated ketone reacted further with mercuric acetate to give diacetoxymercuri-dibenzoyl methane. On acidification, dibenzoyl methane was obtained.

The direct mercuration of benzine, and the preparation of mercury diphenyl: J. Lewis Maynard. Direct mercuration offers the simplest method of obtaining derivatives of the type C_6H_5HgX. However, the method has heretofore been impracticable because of the very low yield of desired product. Since acetic acid formed in the reaction $C_6H_5 + Hg(OAc)_2 = C_6H_5HgOAc + HOAc$ apparently prevents more complete forward reaction, HgO was added to neutralize the HOAc as rapidly as it formed. Based on the quantity of $Hg(OAc)_2$ used, the theoretical yield of C_6H_5HgOAc was obtained by refluxing the three reactants for 55 hours. $Hg(C_6H_5)_2$ may be obtained from C_6H_5HgOAc by heating it under pressure to 140° with alkaline sodium stannite solution.

Unsymmetrical mercuri-organic derivatives and the nature of valences of mercury: Morris S. Kharasch and Mildred W. Grafflin. The number of unsymmetrical mercuri-organic derivatives, of the type $RHgR_1$, recorded in the literature is limited to a few instances. The compounds are also claimed to be extraordinarily unstable and to decompose into two symmetrical molecules: $2\ R_1HgR \rightarrow R_1HgR_1 + RHgR$. The writers have evolved a method of preparing unsymmetrical mercury derivatives. Those prepared thus far are stable even at 200° and do not decompose into two symmetrical molecules. The decomposition of these molecules with acids should throw considerable light upon the nature of linkage of the mercury and the carbon atoms of the respective molecules.

The chemistry of furfural. The preparation of the furfural analog of benzoflavine or dimethyldiamino-furyl-acridine hydrochloride: S. A. Mahood and C. R. Harris. Furfural can be substituted for benzaldehyde to give condensation products with amines analogous to the derivatives of tri-phenyl-methane. When meta-phenylene-diamine is used tetraamino-ditolyl-furylmethane is obtained. This yields, with hydrochloric acid under pressure, dihydro-diamino-dimethyl-furyl-acridine hydrochloride which on oxidation gives a new dye, the furfural analog of benzoflavine. It is typical acridine dye; gives to silk, wool and unmordated cotton a rich brown color and in fastness and stability is indistinguishable from its analog. Contrary to the work of O. Fisher but in accordance with that of Renshaw and Naylor, the substitution of the furyl for the phenyl group in dyes does not appear to render them less stable.

The polymorphic forms and thermotropic properties of Schiff's bases derived from 3-methoxy 4-hydroxy-5 iodo benzaldehyde: Raymond M. Hann. A review of the previous work on the effects of actinic light, trituration and heat upon the color changes of the parahydroxy anils. Discussion of the theories for explaining these physical changes bringing in mention of the Hantzach Werner theory of molecular rearrangement, the molecular aggregation hypothesis and the possibility of stereoisomeric forms. Finally the effect of the introduction of a negative radical in the benzylidene group upon the polymorphic and thermotropic properties.

The ketenic decomposition of ketones: CHARLES D. HURD. Ketene was produced, not only from acetone, but also from methyl ethyl ketone and diethyl ketone when their vapors were passed through an electrically heated platinum coil in a partial vacuum. In addition, methyl ketene was obtained in small yields from methyl ethyl ketone and from diethyl ketone. High temperatures, apparently, decompose methyl ketene with the resultant production of ketene. Acetone and methyl ethyl ketone formed very small amounts of liquid condensation products. Much of the diethyl ketone, however, was changed to higher boiling material.

The addition of nitrogen trichloride to unsaturated hydrocarbons. II: G. H. COLEMAN and ELIZABETH PICKERING. Nitrogen trichloride adds to β-n-Amylene, α-n-amylene, and cyclohexene with the formation of C-chloro-N-dichloroamines. By the action of conc. HCl these amines are changed to C-mono-chloromines. The C-chloroamine obtained from β-N-amylene was reduced by sodium amalgam to the corresponding amyl amine.

Nitrophenols and nitrodiphenyl ethers: F. W. SULLIVAN, JR. 2, 4, 2′, 4′ tetranitrodiphenyl ether was obtained in 90 per cent. yield by the reaction between 2, 4 dinitrochlorbenzol and the potassium salt of 2, 4 dinitrophenol. On nitration with $NaNO_3$ in 50 per cent. fuming sulfuric acid, this yields 2, 4, 6, 2′, 4′ pentanitrodiphenyl ether, which melts at 205°. The constitution of this substance was proved because of its identity with the product obtained by the reaction between picryl chloride and the potassium salt of 2, 4 dinitrophenol. A small amount of a hexanitro compound melting at 258° is also obtained at the same time. This is believed to be the hitherto unknown anhydride of picric acid, but its constitution has not yet been proved. In connection with this work improved methods for the preparation of o-nitrophenol and 2, 6 dinitrophenol have been developed.

Derivatives of para-nitrobenzaldehyde: C. G. KING and ALEXANDER LOWY. p-Nitrobenzaldehyde was condensed with the following aromatic amines, forming "Schiff bases": o-nitroaniline, 2,6-dibromoaniline, 2,4,6-tribromoaniline, o-bromoaniline, m-bromoaniline, 3-bromo-4-toluidine, and p-xylidine. The first three would not condense satisfactorily in alcohol or glacial acetic acid, but did condense on direct fusion. Reduction of the nitro group on condensation products of the above type yielded unstable products. Dimolecular condensations were carried out with p-nitrobenzaldehyde and the following compounds: phenol (tetra-brominated and acetylated), resorcinol (dibrominated), thymol (dibrominated and benzoylated), o-nitrophenol and o-methyl anisol. In each case, bromination increased the depth of color. Oxidation of the phenolic products gave compounds analogous to the aurine dyes.

The electromotive force of organic compounds. II. The unsaturated hydrocarbon groups. S. B. ORENSON and D. J. BROWN. The observed potentials at 25°C. against the normal calomel electrode were $+ 0.09 - 0.03 \log (C_2H_4)(H+)$ for ethylene. Ethylene bromide and glycol seemed to have little or no effect on the observed potentials.

The composition of whale oil: C. H. MILLIGAN, C. A. KNUTH and A. S. RICHARDSON. The composition of whale oil has been studied by fractionally distilling the methyl esters of the solid, liquid and mixed fatty acids of the raw oil and also the methyl esters of the fatty acids of the hydrogenated oil. Whale oil, like other marine animal oils, contains a complicated mixture of fatty acids of carbon content varying from 14 to 22, probably with a small amount of C_{24} acids. The highly unsaturated acids are chiefly of 20 and 22 carbon content.

A contribution to our knowledge of orthoquinones: LEONARD T. CAPELL and C. E. BOORD. The substituted catechols were prepared by the action of potassium persulfate on para substituted phenols. The catechols were oxidized by the Willstatter method using dry silver oxide. The methyl, ethyl, terbutyl, teramyl and monochloro substituted derivative of o-benzoquinones were prepared. The absorption spectra of the green, red and yellow forms of these quinones were photographed and compared. All forms show the same absorption in dilute solution.

Basis for the physiological activity of certain onium compounds, III. Rates of Hydrolysis of esters and ethers of choline and of its analogs. Preliminary communication: R. R. RENSHAW and N. BACON. Dale has advanced the hypothesis that the extraordinary activity of acetyl choline and the evanescence of its action when compared with its ether and other esters may be due to the rapid hydrolysis of the former. The rates of hydrolysis of acetyl choline, the methyl ether of formocholine, acetyl formocholine and the acetyl derivative of the sulfur analog of formocholine have been studied at the temperature and hydrogen potential of blood. The preliminary experiment would seem to negative the suggestion of Dale.

The influence of high temperature on the decomposition of anthraquinone: H. F. LEWIS and SHERMAN SHAFFER. The action of dry heat and steam at atmospheric and elevated pressures has shown that there is a definite point beyond which anthraquinone begins to decompose rather rapidly. These upper temperature limits of stability approach 450 degrees with an air pressure of 35 pounds, 400 degrees with a steam pressure of 35 pounds, and 375 degrees with a pressure of 30 pounds of oxygen. A temperature of 500 degrees decomposes anthraquinone at such a rate that at the end of eight hours approximately 80 per cent. of the original anthraquinone has been decomposed. A study has been made of the decomposition products which shows that there are at least two new substances produced—one extremely stable and the other very unstable. The stable substance being of the nature of hydroxy-anthraquinone and the unstable substance indicating the condensation of two or more molecules of anthraquinone.

The action of acetylene on phenols: HERMAN WENZKE and J. A. NIEUWLAND. Acetylene in the presence of sulfuric acid and a mercury salt readily condenses with phenols to form ethylidene compounds. As in the case of ordinary phenol the position of linkage is usually para whenever that position is unoccupied. The tendency to form an aromatic acetal is slight, β-naphthol being the only compound tried that reacts in that way. The reaction with acetylene continues even after the theoretical quantity of 1 mol. of acetylene to 2 mols of phenol has been absorbed. A tarry, resinous body is formed when an excess of phenol is absorbed. The presence of negative groups in the benzene ring as NO_2, SO_2OH, COOH prevented the reaction with acetylene. The phenol ethers, anisol and phenetol do not react with acetylene. Most of the condensation products polymerized on heating or on long standing to form an insoluble body.

Synthesis of aspartic acid: Glenn S. Skinner and Harry E. Carswell. A study of the conditions affecting the yield of aspartic acid has been made in its production from maleic and fumaric acids by the action of ammonia. The reaction has been carried out at temperatures of 100°, 109°, 117°, 125° and 137° for periods of time ranging from five to more than a hundred hours. The temperature range 110°–125° is most satisfactory. The optimum pH value for the precipitation of the aspartic acid was found to be 4.5. The conditions employed by Emil Fischer and by Engel were found to be unsatisfactory and it has been found possible to increase the yield to 70 per cent. of the theoretical. The melting point of the pure acid is 215°–217° in a closed tube.

The oxidation of sugars: Fred W. Upson and M. H. Power. Glucose has been oxidized by air in the presence of saturated lime water. The oxidation is slower than in the presence of more concentrated alkali as used by Nef but the products are qualitatively the same. Formic, d-arabonic, d-erythonic, glycollic, oxalic and carbonic acids are among the oxidation products. Experiments on the speed of oxidation of glucose and fructose in the presence of six equivalents of NaOH have been carried out. Glucose and fructose oxidize at practically the same rate. The rate is no faster with oxygen under two atmospheres pressure than it is with air at atmospheric pressure.

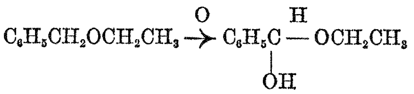
The oxidation of maltose in neutral and alkaline potassium permanganate solutions: W. L. Evans and M. L. Wolfrom. Maltose is oxidized by neutral permanganate solutions at 50° to acetic and carbonic acids. In alkaline solutions oxalic acid is also an oxidation product in addition to acetic and carbonic acids. The oxalic acid production reaches a maximum at about 0.1 N alkali, while the carbon dioxide reaches a minimum at about this point. At higher alkalinities the oxalic acid diminishes in amount to a small degree while the carbon dioxide increases.

The oxidation of propylene glycol in potassium permanganate solutions: E. C. Hytree and W. L. Evans. When propylene glycol is oxidized in potassium permanganate solution at 0°, lactic acid is obtained as one of the oxidation products in addition to acetic and carbonic acids. Evidence was also obtained for the presence of lactide in the reaction mixture. From a consideration of the possible oxidation mechanisms it is highly probable that lactic aldehyde is an intermediate compound in the formation of lactic acid under these experimental conditions.

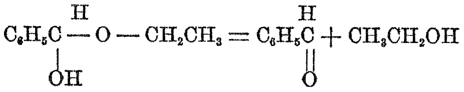
The relation between molecular structure and odor in tri-substituted benzenes. I. Derivatives of para-methoxy-acetophenone. M. T. Bogert and L. P. Curtin. Trisubstituted benzenes carrying three osmophores in 1:3:4 arrangement are not always odorous, even when sufficiently volatile. Although 4-methoxy-acetophenone itself is a perfume substance, the introduction of the osophores NO_2, NH_2, N_3 or CN, in position 3, results in odorless products. Certain new hypotheses are advanced concerning steric hindrance. The following new compounds are described:—the 3-sulfo, 3-amino, 3-acetamino, 3-p-nitrobenzal amino, 3-iodo, 3-iodochloride, 3-iodoso and 3-cyano derivatives of 4-methoxy-acetophenone; and from the 3-amino, the corresponding diazo perbromide, azido, diazoamino and aminoazo derivatives; also the 3-iodoso-4-hydroxy-acetophenone.

The synthesis of new rose alcohols of citronellol-rhodinol type: M. T. Bogert and E. M. Slocum. Iodohydrin acetates were condensed with sodio acetoacetic ester at 0°, the products hydrolyzed to the keto alcohols, and the latter subjected to Barbier-Grignard reactions, the primary-tertiary glycols first formed losing water with production of the desired olefin alcohols. Dimethyl-hexenols,—heptenols,—octenols, etc., were thus obtained from acetopropanol, acetobutanol, etc. Some of these products have fine rose-like odor. The odor of others is more of cedar oil type. Various new intermediates were synthesized in the course of the investigation, and some old methods of preparation were improved so as to give greatly increased yields.

The decomposition of benzyl ethyl ether in air: Ralph C. Huston. Benzyl ethyl ether appears to be less stable in air than the simple dialkyl ethers, the aryl alkyl ethers or the diaryl ethers. Its decomposition apparently takes place according to the following scheme:

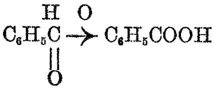


$$C_6H_5CH_2OCH_2CH_3 \xrightarrow{O} C_6H_5\overset{H}{\underset{\substack{| \\ OH}}{C}} - OCH_2CH_3$$



$$C_6H_5\overset{H}{\underset{\substack{| \\ OH}}{C}} - O - CH_2CH_3 = C_6H_5\overset{H}{\underset{\substack{\| \\ O}}{C}} + CH_3CH_2OH$$

The benzaldehyde formed is then further oxidized to benzoic acid:



$$C_6H_5\overset{H}{\underset{\substack{\| \\ O}}{C}} \xrightarrow{O} C_6H_5COOH$$

These changes take place when the pure ether (B. P. 185°) is allowed to stand for several weeks in an ordinary ground glass stoppered bottle. A small amount of the ether when placed on a watch glass and allowed to stand over night deposits crystals of benzoic acid. Benzyl alcohol is not oxidized under similar conditions. Since benzyl alcohol and acetaldehyde were not found in the decomposition products, it appears the CH_2 group between the oxygen and phenyl group is the main point of attack. The effect of other alkyl groups on the stability of the CH_2 between oxygen and phenyl group is being studied.

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Secretary