THE AMERICAN CHEMICAL SOCIETY[1]

DIVISION OF ORGANIC CHEMISTRY

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The relative reactivities of the hydroxydehydrogen atoms of certain alcohols: JAMES F. NORRIS and A. A. ASHDOWN. The rates at which several alcohols react with p-nitrobenzoyl chloride in ether solution were determined. The second order velocity constant of methyl alcohol at 25° C. was 0.184. Taking this value as 100 the other alcohols give the following numbers: Ethyl 45.0, n-butyl 40.2, n-propyl 35.9, beta-phenyl-ethyl 21.6, isobutyl 16.7, alpha-phenyl-prophyl 10.7, benzyl 9.3, isopropyl 5.4, secondary butyl 4.0, tertiary butyl 1.46. The significance of these numbers will be discussed.

The dissociation into free radicals of derivatives of dixanthyl: J. B. CONANT and A. W. SLOAN. The salts of 9-benzylxanthenol on reduction with vanadous chloride yield dibenzylxanthyl, which, like diphenyldixanthyl, dissociates with the formation of a free radical. The molecular weight determinations in benzene indicate about 10 per cent. dissociation; the substance rapidly absorbs oxygen, forming a peroxide. Dibutyldixanthyl prepared in a similar manner shows none of the characteristic reactions of a free radical, and like the parent substance dixanthyl appears to be undissociated, although it absorbs oxygen very slowly. The influence of the benzyl group in causing dissociation is of interest in connection with the problem of the stability of trivalent carbon compounds.

A comparative study of the Kjeldahl-Gunning-Arnold and boric acid method for the determination of nitrogen: KLARE S. MARKLEY and RAYMOND M. HANN. The paper summarizes a series of experiments designed to show that the boric acid method, which utilizes a 4 per cent. solution of boric acid as an absorption medium for the liberated ammonia following its conversion to $(NH_4)_2SO_4$ by digestion with sulfuric acid containing 10 per cent. P_2O_5 and subsequent release with an excess of alkali, is equally as accurate as the official Kjeldahl-Gunning-Arnold method of the A. O. A. C. Tables will be shown giving comparative results on soils, solutions, alkaloids and organic compounds; a discussion of the indicators used and the advantages of the boric acid method in regard to economy of time, materials and standard solutions will also be given.

The ketenic decomposition of the ketones: CHARLES D. HURD and WILLIAM H. TALLYN. The optimum conditions for the preparation of ketene from acetone have been ascertained. Consistent yields of 35 per cent. are obtainable, and yields considerably higher than this have been obtained. Acetyl acetone, pinacoline and diacetyl have all been subjected to pyrogenic decomposition. Theoretically these represent three very interesting types, when the possibilities of ketene fission are considered.

The beta-chlorovinyl arsine reaction and further derivatives: W. LEE LEWIS and H. W. STIEGLER. As previously published (*Jour. Ind. and Eng. Chem.*, March, 1923) it is believed that the catalyst complex in this reaction is $Al(CHCl = CHCl)_3As$, formed first by the addition of three moles of acetylene to one of aluminum chloride with subsequent addition of dissociated arsenic chloride to this. If this is correct then the halogen on the arsenic will determine the halogen in the final arsine after the intermediate compounds are hydrolyzed. Experimentally it was found that arsenic bromide gave bromo arsines, and arsenic chloride gave chloro-arsines, regardless of whether aluminum bromide or chloride was used. The study is being extended to the action of mercury halides in catalyzing unsaturated reactions. Among the derivatives of the chloro-vinyl arsines prepared were: Beta-chloro-vinyl-arsenious sulfide; 7-beta-chloro-vinyl-7, 12-dihydro-gamma-benzo-phenarsazine; bis-beta-chloro-xinyl cyanide (and sulfide); bis-beta-chlorovinyl-methyl (and ethyl) arsine; tris-beta-chlorovinyl-methyl-arsonium iodide.

The preparation of alpha oxy-indole propionic acid and its halogen derivatives: E. C. KENDALL and A. E. OSTERBERG. Alpha oxy-indole propionic acid is prepared from its hydro derivatives by oxidation in glacial acetic acid followed by reduction of the resulting bromo derivatives with sodium amalgam in alkaline solution. It is precipitated from the alkaline solution by acids. It can not be reduced with sodium amalgam to the di and tetra hydro derivatives. In water it adds on bromine to the N, which then migrates to No. 6 carbon. More bromine will give the 4, 6, dibromo. With excess bromine it will take up seven bromine atoms. The relation of these compounds to thyroxin will be discussed.

Some condensation products of furfural: S. A. MAHOOD and S. B. JORDAN. Heating furfural with benzene in the presence of zinc chloride causes polymerization of the furfural into a solid. Unlike the condensation of benzaldehyde with benzene which forms triphenyl-methane, no evidence of the analogous compound, diphenyl-furylmethane, was found. From the data obtained the product is a polymer of furfural. Phosphorous halides give a similar product rather than fural halides. Furfural with phenyl-magnesium-bromide yields an addition product which with water gives an unstable oil which is apparently phenyl-furyl-carbinol. All attempts to esterify it, however, were unsuccessful and led to polymerization products.

The relation between the structure of organic halides and the reactivity of the halogen atom: J. B. CONANT, W. R. KIRNER and R. E. HUSSEY. The velocity constant of the reaction $RCl + KI \rightarrow RI + KCl$ in absolute acetone has been measured. The temperature coefficient of the reaction seems to be nearly the same for all substances studied. Ethyl chloride is about 2.5 times as reactive as n-propyl chloride, normal chlorides of higher molecular weight have about the same reactivity as propyl and butyl chlorides; secondary and tertiary halides are less reactive. The influence of so-called negative

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groups such as C_6H_5, C_6H_5CO, CN, etc., can be expressed by the equation:

$$2 \log R = \log K_A - \log K_{H_2O} = \log K_{NH_3} - \log K_B,$$

where R is the relative reactivity of RCH_2Cl referred to butyl chloride, K_A the dissociation constant of AOH as an acid, and K_B the dissociation constant of ANH_2 as a base.

Positive halogen in organic compounds. II—The propinyl halides: Lloyd B. Howell and Gaylord Johnson. Satisfactory methods have been found for preparing $CH_3 - C \equiv C - Br$ and $CH_3 - C \equiv O - Cl$. Failure of previous workers using methods successful for $CH_3 - C \equiv C - I$ (halogenating silver allylide suspended in water) was probably due to interfering oxidation and halogenation of the triple bond. Preliminary study of these propinyl halides and also review of Nef's work with $CH_3 - C \equiv C - I$ indicates his conclusion that compounds of type $R - C \equiv C - X$ are non-toxic, unexplosive and generally unreactive (in contrast to type $X - C \equiv C - X$) is not justified. Chloro-allylene and bromo-allylene are as pronouncedly nauseating, toxic, spontaneously inflammable and chemo-luminescent as are the halogen substituted acetylenes. Reactions of the propinyl halides indicate distinct positive polarity of the halogen atom present.

A modification of organic combustion analysis adapted to volatile liquids (Lantern): L. M. Dennis and F. E. Hance. In the analysis for carbon and hydrogen the usual train of reagents and combustion tube containing copper oxide are used. Suction is applied at the exit of the train, the copper oxide is heated, the sample in a small, sealed tube, having a constricted neck, is dropped in a U tube placed in the chain at the entrance of the combustion chamber. The neck of the sample tube is broken by a glass rod, the stopper being quickly replaced. An electrically heated oil bath is used to maintain the sample at about 20° below its boiling point, the vapor picked up by air, passing by a long thin tube, through the combustion tube, directly to the heated copper oxide. Condensation of the sample in the cooler portions of the combustion tube is prevented by a secondary stream of air which is drawn into the tube at the forward end.

Some interesting facts concerning the ultra-violet absorption spectra of certain organic compounds (Lantern): Helen L. Wickoff, C. E. Boord and A. W. Smith. The ultra-violet absorption of benzene, monobromobenzene, paradibrombenzene, monochlorobenzene, paradichlorobenzene, cyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, diethylether, dinormalpropylether, dinormalbutylether, methylnormalamylether and other related derivatives have been studied in a comparative way. The complexity of the ultra-violet absorption pattern of these derivatives seems to be a function of the molecular symmetry. The absorption patterns of all these substances are very similar and certainly can not, in some cases, be attributed to the oscillation of double bonds.

Thymolsulfonephthalein, the intermediate acid (p-hydroxy-m-isopropyl-o-methyl-benzoyl benzene-o-sulfonic acid) and some of their derivatives: W. R. Orndorff and R. T. K. Cornwell. Preparation of thymolsulfonephthalein and dithymyl-o-sulfobenzoate from the chlorides of o-sulfobenzoic acid and thymol. Preparation of thymolsulfonephthalein and the intermediate acid (p-hydroxy-m-isopropyl-o methyl-benzoyl benzene-o-sulfonic acid) from the anhydride of o-sulfobenzoic acid and thymol. Action of ammonia on the intermediate acid, its barium salt and the dibenzoate. Conversion of the intermediate acid by heat alone and by heating with thymol into thymolsulfonephthalein. Action of ammonia on thymolsulfonephthalein. The monosodium and disodium salts of thymolsulfonephthalein, the diacetate, the dibenzoate, the dimethyl ether, the aniline derivative. Dibromothymolsulfonephthalein and its diacetate.

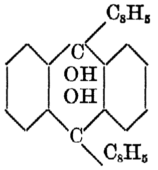
The chemistry of Jaffe's reaction for creatinine. II—The effect of substitution in the creatinine molecule: Isidor Greenwald. In a previous publication, it has been shown that Jaffe's reaction for creatinine is due to the formation of red tautomer of creatinine picrate. The following derivatives of creatinine do not give the reaction: dimethylolcreatinine, benzylidine acetylcreatinine, *benzylidine creatinine and tribenzoylcreatinine.* Reduction of benzylidenecreatinine with zinc and acetic acid gives a solution which gives Jaffe's reaction and from which *benzyl creatinine picrate* was isolated. Jaffe's reaction is given by methylcreatinine, benzoylcreatinine and methylglycocyamidine (isocreatinine). There appear to be two forms of benzoylcreatinine. (Substances italicized are new.)

Ketene in the Friedel and Craft's reaction: Charles D. Hurd. Ketene, in the presence of aluminum chloride, will convert several types of aromatic compounds, such as benzene, anisole, naphthalene, etc., to ketones. A mixture of ketones nearly always results, and it seems that in many cases more than one "$-COCH_3$" group is introduced. Ketene forms a white addition compound with aluminum chloride, suspended in CS_2. When aromatic compounds are added to it, HCl is evolved and ketones are formed as before.

The preparation of di and tetra-hydro oxy-indol propionic acid: E. C. Kendall and A. E. Osterberg. 1-alpha-glutaric acid 2-keto-cyclohexane reacts with ammonia in absolute alcohol to form tetra-hydro alpha oxy-indol propionic acid. In glacial acetic acid bromine oxidizes this to 3, monobromo-5, 6, di-hydro alpha oxy-indol propionic acid. The properties of these two derivatives of alpha oxy-indol and their relation to thyroxin will be discussed.

Derivatives of 3, 4-diamino-phenyl-arsonic acid: W. Lee Lewis and H. S. Bent. The study had for its main objective, which was achieved, the preparation of the arseno compound of sulfoxilated tryparsamide $(As\,C_6H_3\,(NH\,CH_2\,CONH_2)NH\,CH_2 - OSONa)_2$. A preliminary study of the stability of the arsonic radicle to heat was necessary, as well as the reactivity of the diamino-phenyl-arsonic acid to various aliphatic and aromatic acid chlorides, chloro-carbonates, alcohols, etc. Of interest are: N-(Phenyl-1-amino-4-arsonic acid) glycineamid; 1, 2-dihydro-3-amino-6-arsono quinoxaline; 1, 2-dihydro-3-hydroxyethylamino-6-arsonoquinoxaline; N-(phenyl-4-arsonic acid) amino malonamide; 1, 2-dihydro-2-formamide-3-amino-6-arsono quinoxaline.

9, 10-diphenyl anthracene: LLOYD B. HOWELL and E. E. DUNLAY. Attempted inner dehydration of:



resulted in reduction to 9, 10-diphenyl anthracene, a bright yellow solid. When, however, this hydrocarbon is made by method in literature (reduction of above diol by KI) a white solid results. Both forms melt alone or mixed at 261°, oxidize directly to original diol, upon chlorination give the same 9, 10-dichloro compound, but by no physical process could either modification be changed to the other. No adequate explanation of such two forms of 9, 10-diphenyl-anthracene is evident. The original diol made from anthraquinone and phenyl magnesium bromide (yield 10 per cent. in older literature m. p. 240–1° and 247°) was produced in yields of 80 to 90 per cent. of high purity (m. p. 263°) by merely adding a solid solvent for anthraquinone.

A new technique for preparing and handling zinc diethyl: L. M. DENNIS and F. E. HANCE. This article deals with a new method of preparing, purifying and handling zinc diethyl. Due to its spontaneously inflammable character, this reagent is handled in a closed chain of apparatus in a stream of carbon dioxide. Reaction is brought about between a zinc-copper couple and ethyl iodide. During this reaction ethyl iodide is refluxed against a slight pressure of carbon dioxide, this portion of the apparatus being vented to the room through a mercury trap. The product, zinc ethyl iodide, is converted to zinc diethyl and is passed along the apparatus by distillation from the zinc-copper reaction mixture. By fractional distillation the product is purified and the constant boiling alkyl is delivered to receptacles for further treatment, while the lower and higher boiling portions are diverted to another container in the chain. These operations are conducted in their proper sequence without exposing the alkyl to room air. The variations of gas pressure during the refluxing operation, in subsequent distillations and in the movement of the alkyl through the train, were all controlled by a series of simple mercury traps, by-pass connections and a vacuum oil pump. The entire apparatus may be readily constructed from ordinary laboratory material.

Some derivatives of p-hydroxy-methyl benzoic acid: F. H. CASE. In the esters of p-hydroxy-methyl benzoic acid, the local anesthetic effect of benzyl alcohol should be combined with that of aromatic esters in general. The object of this work has been the synthesis of such esters and some of their derivatives. p-hydroxy-methyl benzoic acid has been synthesized by a new and convenient method. Its ethyl, propyl, butyl, isobutyl and benzyl esters have been prepared, as well as the urethane, phenyl urethane, benzoyl and amino benzoyl derivatives of the ethyl ester. The benzyl and diethyl amino ethyl esters of p-ethoxy-methyl benzoic acid are described.

The two crystalline forms of glycine: C. A. BRAUTLECHT and W. W. PURDY. The results of a large number of experiments are given to determine whether any difference exists between the needle and plate forms of glycine when treated with sulfur dioxide alone, and in the presence of water-free liquids, carbon disulfide alone and in the presence of water-free liquids and acetyl chloride. As in the experiments with hydrogen chloride and bromine (C. A. Brautlecht and N. F. Eberman, *J. A. C. S.*, 45, 1924), using all means possible, no chemical difference between the two forms can be detected. Water brings about an equilibrium between the two forms and sulfur dioxide, carbon disulfide and acetyl chloride react with glycine only in the presence of water or atmospheric moisture.

The addition compounds of di-bromo-o-toluidine with metallic salts: RAYMOND M. HANN and G. C. SPENCER. A series of addition compounds prepared to study the effect of certain metals in organic combination upon the determination of nitrogen by the boric acid method. Dibromo-o-toluidine combines with $HgCl_2$, $ZnCl_2$, $CdCl_2$, $CdBr_2$ and certain other metallic compounds to give derivatives of the type $2\,C_6H_2(CH_3)(Br_2)NH_2 - MX_2$. Antimony trichloride combines in the ratio 1: 1. Comparison of results for nitrogen determination shows the boric acid method applicable to this class of compounds.

Nitration from a physical-chemical viewpoint: P. M. GIESY. Since the addition of sulfuric acid to a mixture of water and nitric acid raises the vapor pressure of the nitric acid, it must also raise the concentration of nitric acid dissolved in any immiscible liquid in equilibrium with the mixture and should therefore aid in the nitration of such a liquid. The suggestion is made that all mixed acids having equal vapor pressures of nitric acid should behave the same in nitrating, unless sulfuric acid dissolves sufficiently in the organic liquid to lower the vapor pressure of nitric acid from it.

The crystallography and optical properties of substituted 3-methoxy-4-hydroxy-benzaldehydes: RAYMOND M. HANN and EDGAR T. WHERRY. The crystallography of a series of substituted 3-methoxy-4-hydroxy-benzaldehydes is discussed from the chemical side. The effect of atomic volume upon crystal structure is pointed out. Topic axes are calculated and the resultant data included. Finally the optical properties of the derivatives are tabulated and a scheme for their separation and identification by optical means appended.

Reactions of divinylacetylene: J. A. NIEUWLAND. Reactions of divinylacetylene that gives additional proof of the formula ($CH_2 \equiv CH - C \equiv C - CH = CH_2$) of this acetylene polymer have been worked out. A tetrabromide has been prepared and purified (M. P. 87°). A hexabromide, the highest halogen containing derivative was obtained (M. P. 118°). Its formula is $CH_2Br - CHBr - CBr = CBr - CHBr - CH_2Br$. No octabromide could be obtained. The most interesting reaction of divinylacetylene is that by which formaldehyde is obtained by passing air into the warm hydrocarbon in the presence of $CaCl_2$ as a catalyst. Action of other reagents such as NOCl, N_2O_3, NO_2, Cl_2, I_2, H_2SO_4, HBr, CuCl (neutral in NH_4Cl or alkali chloride solutions). Polymerization products. In general it is even more reactive than C_2H_2. (Note on the preparation of pure dichlor ethylene ($CHCl = CHCl$).)

Preparation of several phenyl-alkyl hydantoins: T. J. THOMPSON. Several patents have been issued pertaining to the preparation of phenylethyl hydantoin, Nirvanol, a soporific introduced in 1917. These patents indicate three general lines of procedure, which may be used to synthesize 4, 4-aryl-alkyl hydantoin: (1) The reaction of carbonyl chloride with disubstituted amino-acetamid; (2) the reaction of alkali cyanate with disubstituted amino-aceto-nitril; (3) the reaction of alkaline hypohalites with disubstituted cyano-acetamides and malonamides. In this investigation phenylethyl hydantoin and four other substituted hydantoins, phenylpropyl, phenylisopropyl, phenylbutyl and phenylisobutyl hydantoin have been prepared by each of the last two methods. Phenylpropyl and phenylethyl hydantoin are mentioned in the patent literature. Preliminary tests indicate that the general physiological reaction of phenylpropyl and phenylisobutyl hydantoin is about the same as phenylethyl hydantoin Nirvanol, whereas phenylisopropyl and phenylbutyl have no action physiologically.

Aryl-arseno-acetic acids: C. SHATTUCK PALMER. Attempts to produce compounds of the type $RAs = AsCH_2COOH$ by simultaneous low-temperature reduction of an aryl arsonic acid and arsono-acetic acid gave mainly symmetrical aromatic arseno-compounds and arseno-acetic acid. This result suggested certain experiments now in progress to confirm the writer's view that the action of a primary arsine on a primary arsine oxide produces not by direct elimination of water to give the unsymmetrical arseno-compound but by formation of two symmetrical arseno-compounds which on further heating rearrange. An aryl-arseno-acetic acid is formed when molecular equivalents of an aryl water-soluble arseno-compound and sodium arseno-acetate are heated in slightly alkaline solution. (By title.)

Polyhydroxy methyl anthraquinones. IV—Condensation of opianic acid with substituted phenols and orientation in the preparation of anthraquinone: R. A. JACOBSON and ROGER ADAMS. Aromatic aldehyde acids condense with various p-bromo phenols by means of sulfuric acid to give substituted phthalides where condensation has taken place ortho to the hydroxyl group. The phthalides thus produced are readily reduced with zinc and sodium hydroxide to benzyl benzoic acid which can be converted to anthraquinones.

Molecular rearrangement in the acetylation of peri-aminonaphthol: L. CHAS. RAIFORD and E. P. CLARK. The study of mixed o-acyl-N-acyl derivatives of aminophenols has shown (*J. Am. Chem. Soc., 45,* 1738 (1923) and *46,* 430 (1924)) that when acyl radicals differ very much in weight and the reacting groups (amino and hydroxyl) are attached to adjacent carbon atoms (ortho), migration of acyl may occur under certain conditions. When these groups are on para carbon atoms this migration has not been observed. It has now been shown that when these groups are in the pori position, rearrangement may occur. Thus, benzoylation of 8-acetylamino-1-hydroxynaphthalene gives 8-benzoylamino-1-acetyl-oxynaphthalene. This supports the theory of Kaufler (Ber., *40,* 3250 (1907)) used to explain the observations of Kaufler and Karrer (*ibid.,* 3262) on 2, 7-naphthalenediamine.

Isophenolphthalein and some of its derivatives. A new class of phthaleins: W. R. ORNDORFF and W. R. BARRET. Ortho-para-phenolphthalein has been prepared by condensing phenol with o-hydroxybenzoyl-o-benzoic acid. It yields triclinic crystals which melt at 200° C. Its solution changes with alkalis from colorless to yellow at pH 8.4. The useful range is between pH 8.4 and pH 12.0 with a color change from yellow to purple. It has no laxative effect. Its solubilities and absorption spectra have been compared with those of phenolphthalein. Its reactions with bromine, iodine, ammonia, hydrazine, acetic anhydride, hydrohylamine, etc., are similar to those of phenolphthalein. When fused with caustic potash, the isophthalein yields o-p-dihydroxybenzophenone and benzoic acid. On reduction it yields isophenolphthalein and p-hydroxy-triphenylmethane carboxylic acid. This is the beginning of a series of new phthaleins which are under investigation in this laboratory.

Platinum oxide as a catalyst in the reduction of organic compounds. VII—A study of the effects of numerous substances on the platinum catalysis of the reduction of benzaldehyde: WALLACE H. CAROTHERS and ROGER ADAMS. (1) When ferrous chloride is added to pure catalyst which has been completely deprived of its activity by shaking with aldehyde, none of the activity is restored to the platinum, but if the mixture which contains the exhausted platinum is shaken with air, either before or after the addition of the ferric salt, the activity of the catalyst is partially restored and the restoration is permanent. (2) The power to accelerate the platinum catalysis of the reduction of benzaldehyde was found to be common to all the compounds of iron examined, namely, metallic iron, ferrous hydroxide, ferric hydroxide, ferric oxide, ferric chloride, ferrous chloride, ferrous sulphate, ferric acetate and ferric nitrate. (3) A variety of salts of other metals have also been tested in their effect upon platinum catalysts of the reduction of benzaldehyde. Manganese chloride and acetate, cobalt chloride and acetate, nickel chloride and acetate and chromic chloride are powerful accelerators. A variety of other salts had either no effect or only a slight effect. (4) Hypotheses which might account for the mechanism for the promoter effects have been suggested.

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