

back and right edge of the slide. These are then cut down to a height slightly exceeding the thickness of a slide. The edge at the point α should not be turned up but permitted to project very slightly beyond the back line, thus furnishing a secure contact with the back of the stage. This holder is more rigid than the first but requires more time and equipment to make it.

The left front end of the holders is formed to give space to the slide clamp.

The use of the holders alters the relation of the slide to the condenser by somewhat less than a millimeter, but this has not been found objectionable for ordinary work.

H. W. GRAYBILL

THE AMERICAN CHEMICAL SOCIETY

(Continued)

DIVISION OF ORGANIC CHEMISTRY. II.

The action of ultra violet light upon di-ketones: C. W. PORTER. Diacetyl, $\text{CH}_3\text{CO.CO.CH}_3$, when exposed to the radiation of a mercury arc lamp, decomposes with the production of ethane and carbon monoxide. Acetone may be an intermediate product; but acetone, under similar treatment, yields the same decomposition products. Benzil, $\text{C}_6\text{H}_5\text{CO.Co.C}_6\text{H}_5$, in the solid or in the molten state is not decomposed by u. v. l. When vaporized and exposed to u. v. l. it slowly decomposes, forming benzophenone, carbon monoxide and a charred residue. In dry benzene solution benzil is not affected by light. An aqueous solution of benzil, in absence of air, yields benzoic acid, benzaldehyde and benzoin. Benzilic acid is not produced. Solutions of benzil in mixtures of alcohol and water yield the same products. In the presence of oxygen a water-alcohol solution of benzil (2 g. per liter) yields benzoic and salicylic acids. The reaction is completed within twelve hours.

Motion picture demonstrations of laboratory apparatus: H. T. CLARKE.

The determination of mucic acid: E. O. WHITTIER. Mucic acid, tartaric acid or racemic acid may be determined in acid solution by oxidation with excess of standard potassium permanganate solution at boiling temperature, followed by a back titration with standard oxalic acid and standard permanganate. The relationships between these acids and permanganate are not stoichiometric, due to formation of some formic

acid. Oxalic acid and mucic acid may be precipitated together quantitatively as calcium salts, dissolved and determined in the presence of each other, the oxalic acid being titrated at 50°C ., the mucic acid at 100°C .

Dipropargyl methylene ether: HERBERT H. GUEST. This communication is a preliminary description of the preparation and properties of the methal of propargyl alcohol, and the attempt, so far unsuccessful, to utilize this acetal in the synthesis of the higher acetylenic alcohols of the type $\text{RC} = \text{C}-\text{CH}_2\text{OH}$. Bis (2.3 dibromopropyl) methylene ether (A) $(\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2\text{O})_2-\text{CH}_2$ viscous oil $b_{10\text{mm}}$ 220° was prepared by the action of a 2 per cent. HCl solution of 2.3 dibromohydrin on paraformaldehyde, and also by the use of anhydrous FeCl_3 and CaCl_2 , respectively, as catalysts. Bis (2 bromoallyl) methylene ether (B) $(\text{CH}_2 = \text{CBrCH}_2\text{O})_2\text{CH}_2$, oil $b_{10\text{mm}}$ $135-40^\circ\text{C}$, from A by the action of finely powdered KOH in Et_2O solution. Di propargyl methylene ether (C), $(\text{CH} = \text{C}-\text{CH}_2\text{O})_2-\text{CH}_2$, oil $b_{10\text{mm}}$ $75-80^\circ\text{C}$. was obtained in 50 per cent. yield from either A or B by heating with 4 mols. KOH dissolved in 4 vols. EtOH at 100°C . C reacts with Et Mg Br with evolution of C_2H_6 and formation of an oil insoluble in Et_2O . It gives an insoluble Ag salt $(\text{AgC} = \text{C}-\text{CH}_2\text{O})_2\text{CH}_2$ which explodes on heating and reacts very slowly with Na. These metallic derivatives of C were treated under varying conditions with alkyl halide, e.g., $\text{C}_4\text{H}_9\text{Br}$ in the attempt to form $(\text{C}_4\text{H}_9\text{C} = \text{C}-\text{CH}_2\text{O})_2\text{CH}_2$, but without any evidence of this reaction taking place.

The reaction between aryl esters of sulfonic acids and organomagnesium halides: CHARLES H. MEYERS and HENRY GILMAN. In connection with a study of methods for the introduction of aryl groups, an investigation is being made of the reaction between aryl esters of various acids, organic and inorganic, and organomagnesium halides. It has been found that when aryl esters of aromatic sulfonic acids are used the chief products are sulfones.

Secondary aliphatic-aromatic arsines, $\text{C}_6\text{H}_5\text{AsRH}$: C. SHATTUCK PALMER. This new series of arsines has been prepared by the action of alkyl halides on an alcoholic solution of the sodium derivative of phenylarsine, $\text{C}_6\text{H}_5\text{AsNH}_2$. The products are colorless oils, which fume strongly in the air, but are not spontaneously inflammable. They are oxidized by air to a mixture of arsine oxide, $\text{C}_6\text{H}_5\text{R As}-\text{O}-\text{AsRC}_6\text{H}_5$, and arsinic acid, $\text{C}_6\text{H}_5\text{RAsO}_2\text{H}$, in which the latter constituent is present in much the larger pro-

portion. With halogens arsine halides, C_6H_5RAsX are formed, and with alkyl halides, quaternary arsonium halides, $C_6H_5R_3AsX$. The reaction with secondary arsine halides, R_2AsCl and $RR'AsCl$, has made possible the preparation of several previously unknown types of cacodyls.

Arsenated N-arylamino alcohols (By title): CLIFF S. HAMILTON. Ethylene chlorohydrin reacts with sodium arsanilate to give p-arsono-2 anilino-ethanol. Its sodium salt separates from alcohol in colorless crystals. By treating the arsonic acid with sodium hydrosulfite the corresponding arseno-compound is prepared. In a similar manner, trimethylene chlorohydrin reacts with sodium arsanilate to give p-arsono-3 anilino-propanol. Its sodium salt and the corresponding arseno derivative have been prepared. Other compounds are in the course of preparation.

A new photochemical color reaction (with demonstrations): LAWRENCE W. BASS AND OSKAR BAUDISCH. It has been found that a mixture of bromoform, iodoform and indol, which is stable in the dark, is very sensitive to diffused daylight or electric light, giving a deep red color in a few seconds. Because of the rapid color change in daylight the reaction is particularly valuable for various photochemical lecture experiments. At the same time the reaction may be used as a sensitive test for indol.

The syntheses of some derivatives of the tetrahydro benzo-furane ring: A. E. OSTERBERG AND E. C. KENDALL. Thyroxin is a tetrahydro derivative of indol. Compounds which are tetrahydro derivatives of benzo-furane with the double bonds in the molecule bearing the same relationship as in thyroxin have been prepared. The chemical and physical properties of these compounds are described. Their reaction toward halogens, the ease with which the lactone and ester groups saponify and their stability toward oxidation and alkalis are discussed.

Acetyl-benzoyl derivatives of o-hydroxybenzylamine and o-aminobenzyl alcohol: L. CHAS. RAIFORD AND E. P. CLARK. In work previously reported from this laboratory (*J. Am. Chem. Soc.*, 41,2068 (1919); 44,1739 (1922) and 45,469 (1923)) it has been shown that when 2-acetylaminophenol is benzoylated in accordance with the Schotten-Baumann method, the benzoyl radical attaches itself to nitrogen, while acetyl migrates to oxygen, but that this rearrangement does not take place when para derivatives are involved. In continuation of this work and particularly on account of the results obtained by McConnan and Titherly and Auwers and collaborators, in which it was found that acetyl wandered from oxygen (bound to the nucleus) to nitrogen (situated on

a side chain), the behavior of the derivatives of o-hydroxybenzylacetamide and its isomer o-acetylaminobenzyl alcohol have been examined. No migration of acetyl was observed but, instead, two isomeric acetyl-benzoyl derivatives were isolated in each case.

The reduction of benzalpinacoline: G. A. HILL AND C. S. SPEAR. Benzalpinacoline was treated with a variety of reducing agents and yielded three compounds, a high boiling point liquid, a monomolecular reduction product melting at 142 degrees and a dimolecular reduction product melting at 208.5 degrees. The liquid, a ketone, the only substance formed in catalytic reduction, was synthesized and is omega-benzylpinacoline. The solid melting at 142 degrees is presumably the corresponding secondary alcohol, but attempts to establish its structure were unsuccessful. The other compound is 2, 2, 9, 9, tetramethyl, 5, 6, diphenyl decandione, 3, 8. It was synthesized from the hydrochloric acid addition product of benzalpinacoline.

The mercurization of methylene blue: LYMAN CHALKLEY, JR. Attempts to mercurize methylene blue in the ordinary way have been failures. The proposed explanation has been that methylene blue probably forms such a stable complex with mercuric acetate that the concentration of mercuric ion is reduced below the value necessary for mercurization to proceed readily. Therefore, mercurization with a large excess of mercuric acetate was tried. It was found that benzoyl-leuco-methylene blue could be mercurized if about three molecules of mercuric acetate were used. The work upon methylene blue itself is not complete, but small yields of two organic mercury derivatives have been obtained.

Structure of isocampholactone: P. K. PORTER WITH W. A. NOYES. When isocampholactone is heated for some days with moderately strong nitric acid, the two principal products formed are nitroisocampholactone and a lactone acid: $O_2N-C_8H_{13}-CO$ and $HOOC-C_7H_{11}CO$.

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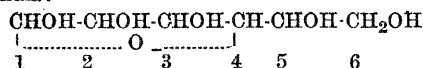
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This lactone acid gives an amide which on treatment with sodium hypobromite is converted to a ketone acid $HOOC-C_7H_{11}=O$. This ketone on treatment with methyl magnesium iodide regenerates isocampholactone and also forms another acid which is probably the trans hydroxy acid which might be expected. This series of reactions demonstrates that isocampholactone contains methyl groups in the 1, 2, 3 positions instead of the 1, 2, 2 positions of camphoric acid. Nitroisocampholactone on treatment with an alkali gives, almost quantitatively, acetone and a nitro acid which probably has the structure,

$\text{CH}_2\text{-C}(\text{CH}_3)\text{-COOH}$. The work on the acid is
 $\begin{array}{c} \text{CH}_2\text{-C}(\text{CH}_3)\text{-COOH} \\ | \\ \text{CH}_2\text{-CH-NO}_2 \end{array}$
 not, however, completed.

The biological and chemical significance of gamma sugars: J. C. IRVINE. The paper deals historically with the accumulation of evidence showing that reducing sugars can react in isomeric forms which differ in the position occupied by the internal oxygen ring. The general expression "gamma sugars" has been applied to the varieties in which the ring is displaced from normal stable position and the reactions of these sugars proceed with a facility which distinguishes them sharply from ordinary forms. No gamma sugar has been isolated in the free state, but their properties are indicated by the reactions of their methylated derivatives, several examples of which will be described. The suggestion is put forward that the elaboration of sugars in plants and their subsequent utilization by animals depend primarily on the transient formation of gamma sugars and not on the stable isomerides which constitute our standard examples of aldoses and ketoses.

A survey of the glucose molecule with reference to the formation of disaccharides and polysaccharides: J. C. IRVINE. If the molecule of glucose is considered in the light of its capacity to form derivatives such as disaccharides and polysaccharides, it is clear from the results of recent research that attention must be focussed on two positions, indexed as 1 and 5 in the following formula:

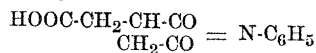


The No. 1 position, which constitutes the reducing group, takes part in the formation of glucosides and of non-reducing disaccharides such as sucrose. On the other hand, position 5 is involved in the formation of certain reducing disaccharides as, for example, lactose and cellobiose. In the case of the polysaccharides which are based on glucose, both of the hydroxyl groups (1 and 5) take part in the coupling, the best example being provided by cellulose in which no other linkage is present. Precisely the same structural feature is present in starch and in glycogen, where at least one maltose residue is attached to glucose through positions 1 and 5. This dissection of the function of each hydroxyl group in glucose serves to illustrate the simplicity and uniformity of the linkages involved in complex natural carbohydrates.

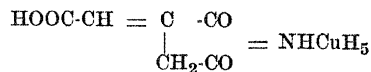
The oxidation of mannitol, sorbitol and dulcitol: CARL W. HOLL AND W. L. EVANS. These hexitols were oxidized with alkaline and neutral potassium permanganate at 25, 50 and 75 degrees.

The final reaction products were carbon dioxide, oxalic and acetic acids. Oxalic acid reaches a maximum value and the carbon dioxide a minimum value at about 0.1 N alkali. In studying the mechanism of these reactions, l-arabitol, d- and l-arabinose were also oxidized under the same conditions as the hexitols. No difference was detected in the amounts of the reaction products obtained in the arabonic series at a given alkalinity, the final products being the same as those obtained in the hexitols. The following compounds and mixtures were also oxidized: Glycerol, glyceric aldehyde (solid), erythritol and glycollic acid, l-arabinose and formaldehyde.

The aniline derivatives of citric and aconitic acids: E. B. BROWN AND J. R. BAILEY. Pebal prepared the so-called citranilic acid, to which has been assigned the structure



In a previous paper before the organic section of the society we reported experiments aimed at the preparation of the isomeric citranilic acid by the action of aniline on methylene citric anhydride, with subsequent hydrolysis of the methylene anhydride. This method of preparation gives a substance different from the Pebal compound, but under certain conditions the two products yield identical reaction products. We find that the two compounds with PCl_5 give the same aconityl anil and with $\text{C}_2\text{H}_5\text{OH-HCl}$ the same ethyl citranilate. This ester with alcoholic ammonia yields first an amide anilide ester of citric acid, which on further reaction with ammonia gives a diamide anilide of citric acid. With alcoholic KOH the ester gives a potassium salt of an anilide ester of citric acid and with PCl_5 there is produced an anil ethyl ester of aconitic acid. Skinner and Ruhemann prepared an aconityl anil to which is assigned the formula



while W. Bertram made the corresponding methyl and ethyl esters. Our aconityl anil, its methyl ester made from this by $\text{CH}_3\text{OH-HCl}$ and the ethyl ester prepared as described above, all differ from the corresponding derivatives to which reference has been made. We do not wish to advance structural formulas for the different substances involved in our work until further investigation has cleared up certain doubtful points.

Dimethylcyclopentenealdehyde: R. R. READ AND HAROLD HIBBERT. The structure of the aldehyde produced by the electrolytic reduction of crotonaldehyde has been established by its synthesis from the latter through the intermediate products

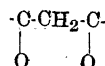
b-brombutyraldehyde diethyl acetal and the tetra ethyl acetal of 3.4 dimethyl hexanedial.

The preparation of the benzilmonoximes and a monotropic modification of gamma benzilmonoxime: FREDERICK WILLIAM ATTACK AND ALICE HARRINGTON ATTACK. In the course of an attempt to prepare the third isomeride of benzilmonoxime, which should exist in accordance with Attack's theory of the structural isomerism of oximes (J. C. S., 1921, 119, 1175), the existence of a monotropic modification of gamma benzilmonoxime has been noted. Alpha benzilmonoxime has been prepared by Forster and Dunn (J. C. S. Trans., 1909, 95, 431) by the interaction in pyridine solution of benzil and hydroxylamine, prepared by the action of powdered sodium hydroxide on powdered hydroxylamine hydrochloride in pyridine suspension. It has now been found that if the hydroxylamine is prepared by the action of sodium bicarbonate on hydroxylamine hydrochloride in presence of a limited amount of water, continuing the preparation in pyridine solution by the method of Forster and Dunn, almost pure gamma benzilmonoxime is obtained, the crude material being identical with that obtained by Auwer's method (action of hydroxylamine hydrochloride on benzil dissolved in hot sixty per cent. ethyl alcohol). The crude material melts in each case at 102-104 degrees C. and mainly consists of an apparently monotropic modification of the gamma benzil monoxime, which can be isolated in a pure form from alcohol solution (m. pt. 106 degrees); on recrystallizing from benzene and heating to remove benzene present in the addition compound, the known gamma benzilmonoxime of m. pt. 113 degrees is obtained. This can be reconverted into the modification of lower melting-point by solution in alcohol.

Ethers of diethyl malonate and barbituric acid: A. J. HILL AND DEWITT T. KEACH. As an extension of previous work, the writers have shown that chloroethers of the general formula, $R-O-CH_2Cl$ ($R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5CH_2$, etc.) may be utilized for the alkylation of diethylmalonate and its mono-alkylated derivatives, in particular, diethyl ethyl malonate. These new malonic esters combine smoothly with urea, in the presence of alcoholic sodium ethylate, giving ethers of barbituric acid. The investigations are primarily designed to establish new facts bearing on the relation between the chemical constitution of barbituric acid ethers and their physiological properties.

Condensation reactions of acetylene: HARRY HOFFMAN AND J. A. NIEULAND. Formation of cyclic ethylidene ethers results when glycols are

treated with varying parts of strong sulfuric acid not over twenty per cent., usually less than ten per cent., to which less than .01 per cent. of mercury sulfate is added as catalyst and dry pure acetylene gas is passed into the mixture. In this way a new compound, tetraethylethylidene ether (B.P. 95 degrees C.) is obtained, also trimethylene ethylidene ether, etc. The labile hydrogen in groups



is also thus replaceable forming, *e.g.*, in case of malonic ester and acetylene, ethyldenemalonic ester, etc. Benzaldehyde and its homologues introduce acetylene with the formation of cinnamic aldehyde according to the reaction $C_6H_5CHO + CH \equiv CH + (cat.) = C_6H_5CH = CH-CHO$. The best synthetic yields hitherto obtained result from the process.

The constitution of coal tar: JOHN MORRIS WEISS AND CHARLES RAYMOND DOWNS. A description is given of an exhaustive analysis of coal tar based on the distillation in the plant of about 20,000 gallons of coal tar oil and its separation into very close fractions which we later examined in the laboratory. By this means analytical methods for the principal compounds in coal tar were developed. The paper does not give these analytical methods in detail but does give the results of the composition of an average sample of American coke oven tar, showing the proportions of the constitutions in the tar which exist in appreciable amounts.

On derivatives of the sulfur analog of choline: R. R. RENSHAW AND N. BEKUNOWITZ. Several sulfonium compounds have been prepared including the acetyl formocholine analog. Their physical and chemical properties are being compared with corresponding derivatives of nitrogen and phosphorus, and attempts will be made to correlate these properties of the different compounds with their curare, nicotine and muscarine effects. Reid Hunt is making the pharmacological investigation of these substances. This work is being carried on with funds donated from the Bache Fund.

The constitution of N, N, 2, 2, dichloro-hydroxyethylidene-bis-nitroanilines: A. S. WHEELER AND S. C. SMITH. In a paper published by Wheeler in 1903 the constitution of these compounds was given as $(NO_2C_6H_4NH)_2CHCCl_2OH$. Since other compounds containing the grouping $-CCl_2OH$ are not known, these products were re-examined and constitutional studies now show that in the preparation of these compounds from the trichloro derivative by the action of alco-

holic potash the OH group has wandered to the alpha carbon, the true arrangement therefore being $(\text{NO}_2\text{C}_6\text{H}_4\text{NH})_2\text{COHCCl}_2\text{H}$. The proof is given in the reaction of the product with hot 30 per cent. sulfuric acid which splits the para compound into p-nitroaniline and p-nitrodichloroacetanilide, $\text{NO}_2\text{C}_6\text{H}_4\text{NHCOCCL}_2\text{H}$, which melts at 127 degrees and is identical with the product of the action of dichloroacetic acid upon p-nitroaniline in the presence of P_2O_5 . The corresponding ortho compounds possess the same melting point, 70-72 degrees.

The problem of alternating polarity in chain compounds: J. B. CONANT and W. R. KIRNER. The relative reactivity of the chlorine atoms in two series of organic halides of the type ACH_2Cl , $\text{ACH}_2\text{CH}_2\text{Cl}$, $\text{ACH}_2\text{CH}_2\text{CH}_2\text{Cl}$, etc., has been studied by measuring the rate of the methesis with KI in absolute acetone. The values obtained show that the position of the activating group ($\text{C}_6\text{H}_5\text{CO}$ or C_6H_5) influence the reactivity of the halide in the following diminishing order: $\alpha > \gamma > \delta > \beta$. The gamma and delta positions were nearly equivalent in the one case studied (the C_6H_5 compound). These facts seem to indicate that there is no simple alteration in reactivity in chain compounds but that spatial effects are of primary importance.

The influence of certain gases on ferrous bicarbonate: LAWRENCE W. BASS and OSKAR BAUDISCH. Our researches on the reduction of nitrates with ferrous hydroxide, on the splitting of pyrimidines with ferrous bicarbonate and on the aging of ferrous bicarbonate have not solved the question as to whether or not the action of these substances is due only to the nature of the surface of the freshly precipitated compound (absorption power). It is probable that another vital factor is the chemical nature of the various hydrates of the iron complex. To study the question further, an investigation was made of the activity of the ferrous bicarbonate when precipitated in the presence of various gases such as air, nitrogen, oxygen, nitrous oxide, acetylene and carbon monoxide. It has been proved that the activity of the compound is different, as shown by the quantity of thymine split, a fact which indicates that the second factor must be taken into consideration.

A new catalyst for use in catalytic oxidations in the vapor phase: FREDERICK WILLIAM ATTACK. In the course of an investigation of the catalytic effect of certain porous materials, the activity was traced to the presence of titanite oxide. It is a matter of doubt whether this substance is as effective as the vanadic acid or molybdic acid

catalyst, but it was found possible to oxidize naphthalene to phthalic acid and, more readily, anthracene to anthraquinone by passing the vapor mixed with air over the heated catalyst.

Fluoro and iodo-benzoyl-benzoic acids and their condensation to anthraquinone derivatives: F. C. HAHN and E. EMMET REID. Fluorobenzene and o- and p-fluorotoluenes have been condensed with phthalic anhydride in presence of aluminum chloride, the resulting benzoyl-benzoic acids and their condensation to fluoro and methyl-fluoroanthraquinones studied. The fluorine derivatives correspond in constitution to the chloro compounds analogously obtained and resemble them in properties. The fluorine in p-fluoro-benzoyl-benzoic acid is replaced by hydroxyl on boiling with strong alkali. When iodobenzene is condensed with phthalic anhydride in the same way, most of the iodine is set free and the product is a mixture of benzoyl benzoic acid with about 12 per cent. of the p-iodo-benzoyl-benzoic acid which can be isolated by conversion to the iodoso chloride from which it is regenerated by reduction.

The reaction between benzyl bromide and alkyl magnesium bromides: H. T. CLARKE, W. W. HARTMAN and M. R. BRETHEN. On adding benzyl bromide to an ethereal solution of butyl magnesium bromide, a vigorous reaction takes place, the main products being dibenzyl, alpha-butylene and butane. n-Amyl benzene is formed in only very small amount.

The preparation of acetylenes from dihalides: A. J. HILL and F. T. TYSON. It is well known that acetylenes of the normal type $\text{R}-\text{C}\equiv\text{CH}$, rearrange into more symmetrical configurations by the action of alcoholic potash, yet there appears to be a lack of information, from a quantitative standpoint, on the extent of molecular rearrangement when hydrogen halide is removed from symmetrical (1) and unsymmetrical (2) dihalides, either by solution methods, or in the gaseous phase with soda lime. (1) $\text{R}-\text{CHX}-\text{CH}_2\text{X}$. (2) RCHX_2 . 1, 1 dichloroheptane, a representative of type 2, has been investigated with respect to the products resulting from gaseous phase dehalogenation with soda-lime in an electrically-heated tube. The results have thus far indicated that the tendency for molecular rearrangement is very pronounced, and even under the most favorable conditions the yield of the normal acetylene, $\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{CH}$, is not above 30 per cent. calculated on the basis of the unsaturated compounds formed in the reaction, or 10 per cent., referred to the dichloroheptane.

CHARLES L. PARSONS,
Secretary.