The next meeting will be held in Convocation Week, December, 1920, at Chicago.

CHARLES F. BROOKS, Secretary

WEATHER BUREAU, WASHINGTON, D. C.

THE AMERICAN CHEMICAL SOCIETY. III

The Kaufler-Cain formula for diphenyl derivatives: OLIVER KAMM and C. S. PALMER.

BB'-dichlorodiethyl ether: the oxygen analogue of mustard gas: OLIVER KAMM and J. H. WALDO.

The chlorination of acetone: A. W. Homberger and M. BORRIES. Technical acetone was purified and treated with dry chlorine in sunlight. During the chlorination three distinct steps were noted. The first step was completed at the close of the first half hour. No hydrochloric acid was liberated during this stage. The second step lasted two hours. The heat of reaction was much higher than in the preceding step and whenever the temperature rose over 80 degrees violent reaction, resulting in flames, took place. A third step took place after this second reaction with no violent action and a temperature maintained itself below 80 degrees, and no tendency to burst into flames. During the second and third step hydrochloric acid was liberated, much more during the second than the third step. The resulting liquid of chlorination was submitted to distillation under diminished pressure and three distinct fractions obtained. The three fractions, when redistilled, showed definite and well-defined boiling points and properties. Each of these products is being investigated at present.

The use of a chart in the study of organic chemistry: CHAS. W. CUNO. The studies are divided into three great divisions, the memory studies, the reasoning studies, and the constructive studies. The two great memory studies are history and the languages. History concerns itself with data and dates, or to put it abstractly, with sequence and facts. Language concerns itself with interpretation. If we examine the reasoning studies such as chemistry we find they have a language and sequence and data that need to be made a part of the memory before the student can very well reason intelligently. In organic chemistry the language is exceedingly difficult and the data and sequence very voluminous. The use of a chart such as the one published by the author has its use, therefore, to help the student in acquiring the data, sequence and language of organic chemistry.

The mechanism of some reactions involving the Grignard reagent: HENRY GILMAN. It has been conclusively proved that the reactions of ketenes are not restricted to primary addition to the ethylenic linkage. The benzoate of triphenylvinyl-alcohol was obtained when the addition compound of diphenyl ketene and phenyl magnesium bromide was treated with benzoyl chloride. The Grignard reagent, therefore, has added to the carbonyl group. Preliminary experiments on the mode of reaction of the Grignard reagent and phenyl isocyanate (and phenyl iso-thiocyanate), indicate the following: first, but one molecule of phenyl magnesium bromide adds; second, addition takes place on the carbonyl (and thio-carbonyl) linkage; and, third, addition is probably restricted to this linkage, as with the ketenes.

The nitration of certain halogenated phenols: L. CHAS. RAIFORD. In preparing halogenated o-aminophenols with which to test further the migration of acyl from nitrogen to oxygen (J. A. C. S., 41, 2068 (1919)), several of the brominated cresols were nitrated according to the method used by Zincke (J. pr. Chem. (2), 61, 561 (1900)), who found that in the meta series the halogen atom para to hydroxyl was replaced by the nitro group. while in the ortho and para series the atom ortho to hydroxyl was replaced. In none of these cases did he report the formation of isomeric nitro compounds in a single experiment. In the present work it has been found that the dibromo and tribromo-ortho cresols, to which Zincke has assigned the structures



both give isomers when they are nitrated as indicated above. The structures of the isomers, as well as the mother substances, are under consideration.

Action of aromatic alcohols on phenols in the presence of aluminum chloride: RALPH C. HUSTON. Earlier work has shown that aromatic alcohols (primary or secondary) are readily condensed with aromatic hydrocarbons such as benzene, toluene, etc., to form diphenyl methane or derivatives thereof. In the present work benzyl alcohol was allowed to react at relatively low temperatures with phenol in the presence of Al Cl₃. A good yield (40-50 per cent.) of p benzyl phenol was obtained, according to the equation

$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_8}C_6H_5CH_2C_6H_4OH + H_{20}.$

Slightly better yields of the ethers of this phenol were obtained by the condensation of benzyl alcohol with anisol or phenetol.

Derivatives of cyclohexane: ARNOLD E. OSTER-BERG and E. C. KENDALL.

The formation of organic reactions under the electron conception of valence, reaction of formaldehyde: H. C. P. WEBER.

A new color reaction for phenols based upon the use of selenious acid: VICTOR E. LEVINE. Phenols in contact with a solution of 0.5 per cent. selenium dioxide or 0.75 per cent. sodium selenite in concentrated sulphuric acid give rise to a pale green, olive green, emerald green, blue-green or purplish blue color. Often several colors are observed simultaneously. On standing, on heating or on the addition of water the characteristic color or play of colors disappears, giving way to a dark brown, reddish brown or brick red. The reactions is of great sensitivity and of wide applicability. The following types of phenols respond to the test: Mono-, di- and triphenols, phenolic ethers, aldehydes, alcohols and acids, glycosides yielding phenols on hydrolyses, dyes and alkaloids possessing phenolic groups. Nitrating the phenol abolishes the reaction, for o-nitrophenol, p-nitrophenol, diand trinitrophenol yield negative results. Phenolic aldehydes and acids give extremely faint reactions. The following compounds tested prove the general value of the reaction: phenol, amidol, anisole, phenetole, phenacetine, the cresols, salicylic aldehyde, salicylic acid, acetyl salicylic acid, methyl and phenyl salicylates; pyrocatechol, guaiacol, vanilin, vanillic acid, piperonal, resorcin, hydroquinone, pyrogallol, phloroglucine; eugenol, thymol, carvaerol, α - and β -naphthol, chrysarobin; the glucosides, arbutin, phloridzin; the opium alkaloids, morphin, heroin, dionin, narcotine, narceine, papaverin; the dyes, orcein, alizarin, purpurin. The reaction proves very useful in detecting phenols in solid or liquid state. Phenols dissolved in water or in an organic solvent should first be evaporated in a porcelain crucible and the test made on the dry residue. A beautiful ring test may be obtained by the addition of a chloroform or amyl alcohol solution of the phenol to the selenium reagent. A bright emerald green is observed at the point of junction of the two liquids. The green compound remains with the sulphuric acid and does not dissolve in the organic liquid. The course of the reaction may be explained on the ground that the phenol decomposes the selenous acid with the formation of free selenium. This dissolves with a green color in concentrated sulphuric acid to form selenosulphur trioxide.

A note on the differentiation of acetic anhydride from glacial acetic acid: VICTOR E. LEVINE. A. differentiation based upon chemical tests may be made as follows: (1) A few drops of 0.5 per cent. selenium dioxide in concentrated sulphuric acid added to acetic anhydride results in the formation of elemental selenium, which appears as brick-red colloidal solution or precipitate. Glacial acetic acid is not affected by the selenious acid reagent. (2) Ten drops of acetic anhydride are shaken with 2 c.c. chloroform in which a few crystals of cholesterol have been dissolved. On the addition of 20 drops of concentrated sulphuric acid a fleeting purple is developed changing to blue and finally to deep green. With or without glacial acetic acid a lemon yellow color forms, which quickly goes over to deep orange, cherry red or burgundy red.

The poly-phenyl ethers: HILTON IRA JONES.

The decomposition of amines at high temperatures: FRED W. UPSON.

Oxalyl chloride in the synthesis of the triphenylmethane dyes: HARPER F. ZOLLER. Oxalyl chloride may be used in the place of phosgene or Michle's ketone in the condensing of aniline and its derivatives for the production of dye stuffs of the magenta type. The use of fused zinc chloride increases the yield of the colored base just as was found true in the case of phosgene. The calculated molecular quantities of aniline or its derivatives are mixed with a corresponding amount of oxalyl chloride necessary to produce a given dye. This mixture is heated in a flask bearing a reflux condenser and suspended in a hot water bath. Crystal violet (hexa methyl tri amino triphenylmethane) para rosaniline (tri amino triphenylmethane) have been prepared using oxalyl chloride in their synthesis. No accurate study has been made of the yields of the dyes using these synthesis. The quantity obtained using the above method amounted to about 50 per cent. of the theoretical. The synthesis is described as a very convenient laboratory method of producing the dyes in small and very pure quantities.

The benzoic acid ester of trichlorotertiary butylalcohol or chloretone benzoic acid ester: T. B. ALDRICH. The benzoic acid ester of chloretone is prepared by heating molecular quantities of anhydrous chloretone and benzoyl chloride (slight excess) on the steam bath, until hydrochloric acid gas ceases to be given off. Any uncombined chloretone or benzoylchloride is eliminated and the resulting body recrystallized from alcohol. The ester is when pure a solid melting at $34^{\circ}-35^{\circ}$ and not a liquid as claimed by Willgerodt and Durr (J. f. praktische Chemie (Neue Folge), 39 and 40, p. 189). It may be distilled under reduced pressure without decomposition. Chlorine determinations (Carius) gave results which characterize the eompound as the benzoic ester:

$C_6H_5CO-OCC_3H_6Cl_3$.

The compound is readily soluble in the organic solvents, and practically insoluble in water. It is not readily saponified, being much more stable than the other esters studied. Boiling with con. nitric acid does not decompose it as is the case with the aliphate esters of both chloretone and brometone. It is not volatile in the air, but is slightly volatile with steam. Pharmacological tests would indicate that it possesses less hypnotic and anesthetic properties and is less toxic than the esters studied thus far. Its relative stability is greater than that of any of the esters studied previously.

The utilization of waste silk fibroin: TREAT B. JOHNSON and P. G. DASCHAVSKY. A statistical study of the development of the waste silk industry in the United States. The behavior of fibroin on distillation is described, and an improved method of obtaining tyrosine from fibroin has been developed. It is shown experimentally that fibroin is a valuable source of the drug "tyramine," $HO \cdot C_{e}H_{4} \cdot CH_{2}CH_{2}NH_{2}$.

The conversion of anilides of chloracetic acid into ketide-isothiocyanates: TREAT B. JOHNSON, ARTHUR J. HILL and ERWIN B. KELSEY. Isothiocyanates of the general formula

$SCN \cdot CH_2 \cdot CONHR$

have hitherto never been synthesized. A method of preparation has now been developed which eliminates any possibility of the formation of isomeric rhodanides NCS \cdot CH₂CONHR. The work is an extension of earlier researches on thiocyanates and isothiocyanates carried on in the Sheffield Chemical Laboratory, and has led to the development of a new method of entering the hydantoin series.

The condensation of formaldehyde with o-nitrophenol: TREAT B. JOHNSON and J. B. HISHMAN. A repetition of the work of several previous investigators has revealed the fact that o-nitrophenol condenses with formaldehyde to form two isomeric compounds, viz.: 3-nitro-4-hydroxy- and 3-nitro-2-hydroxybenzylalcohols. Several new derivatives of these compounds have been prepared.

The alkylation of aromatic amines by heating with alcohols: ARTHUR J. HILL and J. J. DON-LEAVY. A study of the influence of catalysts on the general reactions

 $\label{eq:rescaled} \begin{array}{l} R \cdot NH_2 + R' CH_2 OH \longrightarrow R \cdot NH \cdot R' + N_2 O \\ \text{and} \end{array}$

 $\text{RNH}_2 + 2\text{R'CH}_2\text{OH} \rightarrow \text{R} \cdot \text{N}(\text{R'})_2 \cdot + 2\text{H}_2\text{O}.$

The work so far has been confined to the study of aniline and the isomeric toluidines and the two alcohols ethyl and n-butyl. It has been found by experiment that these alkylation reactions are greatly stimulated by using certain inorganic salts as catalytic agents. The first contribution on this subject has already been accepted for publication in the Journal of Industrial and Engineering Chemistry.

The search for pressor substances in the pyrimidine series: TREAT B. JOHNSON and L. A. MIKESKA. A study of some new amidine condensations leading to the formation of new types of cyclic amine combinations in the pyrimidine series. The substances under examination will be submitted to a careful pharmacological investigation to determine their pressor or other specific action. The research will be extended to the hydantoin and purine series.

The oxidation of iso-propyl alcohol by means of alkaline potassium permanganate: WM. L. EVANS and LILY BELL SEFTON.

> CHARLES L. PARSONS, (To be continued) Secretary

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