

and van Haagen's<sup>3</sup> recent determination of the atomic weight of boron, 10.900, indicates the proportions of these isotopes as nearly 1 to 9, the relative intensities of the positive-ray spectra<sup>4</sup> point to a considerably larger proportion of the lighter isotope. Since we have redetermined the atomic weight of boron by analysis of the chloride and bromide, and have obtained a result more nearly in accord with Aston's experiments than with those of Smith and van Haagen, it seems advisable to state the outcome of our preliminary experiments, without waiting for the completion of the investigation.

Boron was obtained by reduction of boric oxide with an excess of magnesium and extraction with either hydrochloric or hydrobromic acid. To prepare the chloride, dry chlorine was passed over the boron at about 700°. To prepare the bromide, helium saturated with bromine nearly at the boiling point of the latter substance was passed over boron at 700°. After removal of the excess of halogen with mercury both halides were repeatedly distilled with the use of Hempel fractionating columns in sealed all-glass vessels, with complete exclusion of air. Quantitative testing even before the completion of the fractionation showed the absence of silicon halides which constituted the worst impurity. Material was collected for analysis in sealed glass bulbs. Analysis was effected by comparison with silver in the usual way.

The results of the analysis of the chloride agree with those of the bromide in yielding the value  $10.83 \pm 0.01$  for the atomic weight of boron. On the assumption that constant boiling mixtures with the halogen acids were not formed and that no separation of the eight possible combinations of two isotopes of both boron and chlorine took place, this new value for the atomic weight of boron indicates the proportion of the heavier isotope to be about five times that of the lighter.

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<sup>3</sup> Car. Inst. Pub., No. 267 (1918).

<sup>4</sup> Aston, *loc. cit.*

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(Continued)

*Isomeric alkyl-pyrimidines and color phenomena:* ARTHUR W. DOX AND LESTER YODER. A series of alkyl-diketo-pyrimidines was prepared by condensing alkyl-malonic esters with amidines. In this series four types of isomerism occur, of which the following derivatives are examples: (a) 5-butyl and 5,5-diethyl; (b) 5-phenyl-2-methyl and 5-methyl-2-phenyl; (c) 5-isoamyl-2-phenyl and 5,5-diethyl-2-p-tolyl; (d) 5-allyl and cyclobutane-1,5-spiro. Some of these derivatives are white, others are bright yellow. Color is dependent upon the presence of an aromatic group on the 2-carbon and a labile hydrogen on the 5-carbon. The latter makes possible a rearrangement into a tautomeric enolic form with three double linkages in the ring. The only exception to the color rule is the spiro derivative, which is yellow. Spectroscopic examination of a typical yellow derivative showed an absorption band in the violet between 260 and 330  $\mu$ .

*An octet formula for benzene:* ERNEST C. CROCKER. Proposed formula is ring of six carbon atoms acting as single complex atom. Individual carbons bonded together by sharing single pairs of electrons (single bonds), with hydrogens associated with pairs of electrons, as usual. The six excess electrons of system are "aromatic" electrons, and vibrate between the carbons, in unison. "Aromatic" electrons cause two distinct patterns, o.p., and m., according to the influence of substituents in the ring. The theory accounts well for mono, di and tri substitution products of benzene. It accounts for aromatic structure in general; particularly thiophene, furane, pyrrol, naphthalene, and anthracene.

*Diisopropylhydrazine.* J. R. BAILEY, W. A. NOYES AND H. L. LOCHTE. Diisopropylhydrazine can be easily prepared by treating a solution containing acetone, hydrazine chloride, gum arabic and colloidal platinum with hydrogen under pressure. Dimethylketazine  $(CH_3)_2C:N=N:C(CH_3)_2$  is at first formed and this is reduced to diisopropylhydrazine,  $(CH_3)_2CHNHNHCH(CH_3)_2$ . The latter is a monacid base, which forms stable salts. The free base is very easily oxidized, even by exposure to the air, probably forming an azo compound. The investigation of this and other relations will be continued.

*The chlorination products of formanilide:* W. LEE LEWIS AND R. S. BLY. When formanilide is chlorinated in the presence of chlorides of sulfur

or phosphorus the principal product is 2,4-dichloroformanilide. With thionyl chloride, however, the following products were isolated: 2,4-dichloroformanilide, phenylimido phosgene, and mono- and di-chloro phenylimido phosgene. The last three compounds were identified by their conversion into the corresponding triphenyl guanidines, urethanes, and acetanilides.

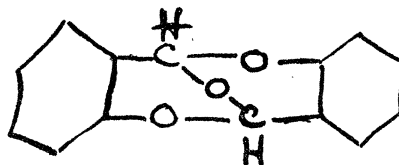
*The preparation of dialkyl mercury compounds from the Grignard reagent:* C. S. MARVEL AND V. L. GOULD. Diphenyl mercury, dibenzyl mercury and dicyclohexyl mercury have already been prepared from the Grignard reagent and mercuric chloride, but only in poor yields. This method may be applied to the preparation of various dialkyl mercury compounds in yields of 45-65 per cent., if the proper precautions are taken. In this reaction there is formed first, an alkyl mercury halide which is then converted into the dialkyl compound. The first step goes easily but a large excess of the Grignard reagent and long heating are necessary to bring about the second. The unreacted magnesium must be removed from the Grignard reagent solution in order to avoid reduction of the mercuric halide and consequent lowering of the yield.

*The chlorination of 5-hydroxy-1,4-naphthoquinone (juglone):* ALVIN S. WHEELER AND PAUL R. DAWSON. The chlorination of juglone in hot glacial acetic acid solution yields dichlorojuglone (A), probably the 2,8-isomer, orange red needles, m.151°. Benzoyl derivative, yellow needles, m.225°. Sodium salt, indigo blue, a direct dye for silk and wool. Alcoholic caustic soda gives a monochloro-hydroxy-juglone, yellowish brown needles, m.191°. Diacetyl derivative, yellow needles, m.147°. Monochloro-anilino-juglone, obtained by boiling A with aniline in alcohol, violet red needles, m.222°; o-toluidine derivative, dark red needles, m.151°; p-toluidine derivative, deep violet needles, m.235°. So far no oxidation products of A have been obtained which might locate the chlorine atoms.

*Kelp tar oils:* ALVIN S. WHEELER AND H. M. TAYLOR. The kelp tar oils came from the Summerland, California, kelp plant of the U. S. Department of Agriculture and were given to us for study by Mr. J. W. Turrentine, in charge. The oil is a mixture of compounds, for we found the boiling point to range from 200° to 300° at atmospheric pressure and from 50° to 170° at 12 mm. In the latter case two thirds of the distillate came over between 110° and 150° and 25 per cent. of the oil remained behind as pitch. The oils dis-

solve in all organic solvents and are unaffected by most reagents. The reaction with bromine is violent and hydrobromic acid is evolved. The redistilled product contains bromine. Molecular weight determinations of fractions from low to high boiling points gave values from 124 to 165. Specific gravity ranges around the point 0.94 and refractive index about 1.46. Hydrogenation and bromination studies are in progress.

*The structure of disalicylaldehyde:* ROGER ADAMS AND M. F. FOGLER. When salicylaldehyde is heated with acid chlorides, it is converted into disalicylaldehyde, a white solid, m.131°. This substance has been studied by previous investigators and shown to have the following properties: empirical formula  $C_{14}H_{10}O_6$ , stable to sodium hydroxide solution, unstable to concentrated sulphuric acid yielding two moles of salicylaldehyde; shows no reaction which would indicate a phenol or aldehyde group. No satisfactory formula has yet been suggested for this substance. The following one is proposed:



This structure is a double acetal and agrees with the properties above mentioned. The synthesis of analogous compounds which have the same chemical properties has been accomplished. New methods of preparation for disalicylaldehyde indicate that it has an acetal structure.

*Anthraquinone thioethers:* M. S. HOFFMAN AND E. E. REID. The study of the replacement of the sulphuric acid group in alpha anthraquinone sulphonic acid has been continued with the use of a variety of mercaptans, isopropyl, benzyl, nitrobenzyl, monothio-glycol, etc., and a great variety of anthraquinone thioethers thus prepared. Most of these have been oxidized to the sulphones.

*Some derivatives from p-nitrothiophenol:* W. R. WALDRON AND E. E. REID. A large number of bases of the benzidine type have been prepared, various groups  $-CH_2-$ ,  $-CH_2S-$ ,  $-CH_2SCH_2-$ , etc., being introduced between the two rings. In particular bases have been made from mustard gas which are readily converted into azo dyes. The whole work is a study of constitution and color.

*The reaction of propylene, butylene, and amy-*

*lene with selenium monochloride:* C. E. BOORD AND FRED F. COPE. *Bis* ( $\beta$  chloropropyl) selenide, bis ( $\beta$  chlorobutyl) selenide and bis ( $\beta$  chloroamyl) selenide and their respective dichlorides were described. The reaction between olefines and selenium monochloride both when the olefine is in excess and when the monochloride is in excess were discussed. Evidence was offered to show that selenium monochloride has the unsymmetrical structure.

*The use of olefines in the preparation of alkyl phenols (preliminary report):* C. E. BOORD, A. J. YANEY AND C. W. HOLL. A simple apparatus for the laboratory preparation of ethylene, propylene, butylene, and amylene is described. A description of the preparation of amylphenol and amyl catechol by the interaction of amylene and the phenol in the presence of anhydrous ferric chloride is given. An extension of the reaction between olefines and phenols in the presence of anhydrous chlorides for the preparation of alkyl phenols is proposed. It is also proposed to use this reaction in a study of the mechanism of the Friedel-Crafts reaction.

*The action of sulphuric acid on 1-phenylnaphthalene-2-3-dicarboxylic acid:* M. L. CROSSLEY. It has been shown by previous investigators that 1-phenylnaphthalene-2-3-dicarboxylic acid is converted by sulphuric acid into allochrysoketone-carboxylic acid. I have found that if the reaction is carried out at a higher temperature than that at which the ketone acid is formed, a product differing from the ketone acid and having the formula  $C_{22}H_{18}O_4$  is obtained. This forms an ethyl ester of the formula  $C_{24}H_{20}O_4$ . The acid crystallizes from pyridine in tufts of light yellow monoclinic needles and melts at about 375° C. without decomposition. It is insoluble in water and most organic solvents. The ester crystallizes from alcohol in long yellow needles, melting at 171° C. and is quite soluble in most organic solvents.

*Addition compounds of  $\gamma$ -pyrones and sulfur trioxide:* A. S. RICHARDSON.

*Compound formation in phenol-cresol mixtures:* JAMES KENDALL AND J. J. BEAVER. The isolation of stable compounds between phenol and the cresols has been cited by Dawson and Mountford as constituting an exception to the generalization that the stability of addition compounds decreases with increasing similarity in character of the components. The present authors have determined the specific conductivity, viscosity and

freezing-point depression curves in benzene for all six phenol-cresol systems. Without exception, the results indicate that no increase in molecular complexity occurs on admixture. The compounds obtained by Dawson and Mountford are therefore to be regarded as substitution rather than as addition compounds, being formed by the replacement of part of an associated molecule by a homologue.

*The oxidation of potassium acetate with potassium permanganate in the presence of potassium hydroxide:* W. L. EVANS AND PAUL S. HINES. The literature contains conflicting statements in reference to the stability of acetates towards alkaline potassium permanganate. The results of our experiments are as follows: (a) Potassium acetate is oxidized to potassium oxalate with potassium permanganate in the presence of potassium hydroxide. (b) The production of oxalic acid is proportional to the concentration of the alkali used. (c) An increase in the temperature is accompanied by an increase in the production of oxalic acid. (d) When the oxidation is carried on for several days it is found that potassium acetate is oxidized to potassium oxalate in neutral potassium permanganate solutions. (e) The yield of oxalic acid increases with the time of the oxidation. (f) The velocity of the oxidation is very small.

*The oxidation of acetol with potassium permanganate in the presence of potassium hydroxide:* W. L. EVANS AND ORA L. HOOVER. (a) Acetic, oxalic and carbonic acids are the final products of the oxidation of acetol with potassium permanganate in the presence of potassium hydroxide. (b) In the absence of potassium hydroxide, acetic and carbonic acids are the sole reaction products. (c) Acetic acid is formed in the largest amounts in neutral permanganate solutions, although the acetic acid present in these cases is less than the amount equivalent to two carbon atoms. These facts show that more than one oxidation reaction is taking place under these conditions. (d) The yield of acetic acid diminishes to a certain minimum with an increase in the initial concentration of the alkali, after which it increases to a certain constant yield with a continuing increase in the initial concentration of the alkali. (e) The production of carbon dioxide increases to a maximum point with an increase in the initial concentration of the alkali, after which it diminishes to a constant value. (f) The yield of oxalic acid is proportional to the

concentration of alkali used up to a certain constant value. (g) The general effect of an increase in temperature is that of an increase in the yield of oxalic acid and carbon dioxide and a decrease in the yield of acetic acid.

*The oxidation of propylene glycol with potassium permanganate in the presence of potassium hydroxide:* W. L. EVANS. (a) Acetic, oxalic and carbonic acids are the final oxidation products of propylene glycol with solutions of alkaline potassium permanganate. (b) Acetic and carbonic acids are the only products obtained in neutral solutions of potassium permanganate. (c) The oxalic acid production is proportional to the initial concentration of the alkali used. (d) The acetic acid production varies inversely with the initial concentration of the alkali. (e) At very low concentrations of alkali the production of carbonic acid is proportional to the initial concentration of the alkali. (f) The production of acetic acid diminishes with an increase in the temperature used. (g) The production of carbonic acid increases with an increase in the temperature used. (h) An increase in temperature has no marked effect on the production of oxalic acid.

*The condensation of citral, with certain ketones and the synthesis of some new ionones:* HAROLD HIBBERT AND LAURA G. CANNON. The best method for purifying citral is the one developed by Tiemann. Of the condensing agents hitherto employed, sodium ethylate is the most satisfactory, but metallic sodium is equally efficient. Better yields of a purer product have been obtained. The bisulfite method of purification is capable of general application in the purification of pseudo-ionones, giving yields of about 85 per cent. and chemically pure products. New ionones have been synthesized from methyl propyl ketone and acetophenone.

*The migration of acyl from nitrogen to oxygen:* L. CHARLES RAIFORD AND JOHN R. COUTURE. The present work is an extension and confirmation of that previously published from this laboratory (*J. Am. Chem. Soc.*, 41, 2068 (1919)) and was done to secure further evidence that the rearrangement involving migration of a lighter acyl from nitrogen to oxygen, when a heavier acyl is introduced into the molecule, is general for the specific case of acetyl and benzoyl, when the base employed is an orthoaminophenol. The rearrangement was found to occur with the derivatives of the base 2-amino-4-bromo-6-methylphenol.

When the radicals were propionyl and benzoyl, the rearrangement was not complete, which indicates that the weight of acyl is one of the important factors in this migration.

*Acylation with  $\alpha$ -naphthoyl chloride and the migration of acyl:* L. CHARLES RAIFORD AND CLARENCE E. GREIDER. (1) A further study of the general reaction indicated in the above report was carried out, using 2-aminophenol, 2-amino-4-methyl-6-bromophenol, and 2-amino-4, 6-dibromophenol as bases, and converting them into the  $\alpha$ -naphthoyl-acetyl and  $\alpha$ -naphthoyl-benzoyl derivatives, respectively. In each case the heavier acyl was found on nitrogen, regardless of the order in which they were introduced. (2) This study has also furnished evidence, so far as it has been carried, that  $\alpha$ -naphthoyl chloride does not undergo the Schotten-Baumann reaction.

*The migration of acyl: Effect of the relative positions of the amino and hydroxyl groups:* L. CHARLES RAIFORD AND H. A. IDDES. In a continuation of the studies mentioned above, the acetyl-benzoyl derivative of 2, 4-dibrom-3-methyl-6-aminophenol was found to undergo the rearrangement, and benzoyl was found on nitrogen; while the derivative of the isomeric base, 2, 6-dibromo-3-methyl-4-aminophenol did not suffer the migration. Here it was possible to isolate N-acetyl-O-benzoyl, and O-acetyl-N-benzoyl derivatives. The failure of this para compound to undergo this change was supported by the behavior of the derivatives of 4-aminophenol, 2, 6-dibrom-4-aminophenol, and 2-brom-4-amino-6-methylphenol.

*Stability of the C-Hg linkage in mercury derivative of maleric acid. Preliminary paper:* FRANK C. WHITMAN AND B. J. MARTIN. The sodium salt of hydroxymercuric maleric acid obtained from the action of sodium hydroxide on the reaction product of maleric acid with mercuric acetate contains an unstable C-Hg linkage. It reacts at once with sulfides. With sodium iodide it gives sodium maleate, sodium mercuric iodide and sodium hydroxide. The reaction is complete only on heating the mercury compound with a large excess of iodide. The calculated amount of iodide gives only one third of the calculated amount of base. If this base is neutralized and the mixture is boiled a little more base is formed. Many repetitions of this process give a total amount of base which gradually approaches the calculated volume.

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