	Part of the organism used	Number of individuals tested ♀	♂
Mice	blood	12	9
Sheep	blood	2	2
Pigeon	blood serum	3	3
Fruit flies (Drosophila virilis)	.5–1.5 g. of flies	2	2
Cladocera sp.	.2 g. of animals	3	2
Salix sp.	catkins	5	7
Populus sp.	catkins	2	6

It may be noted that the reaction is very sensitive. A slight mistake in the method or fault in the material may give inconclusive results. It should be mentioned that nine more male mice than these previously listed were used in investigations. Six of them gave inconclusive results and with the other three a reaction was obtained which was classified as female. It is very likely that in those cases, due to our unfamiliarity with technic, reacting enzymes were destroyed and the expected reaction failed to occur.

As pointed out by Manoilov in making the chlorophyll extract, it is essential not to have alcohol stronger than 60 per cent. and not to leave the material in alcohol over 24 hours. Otherwise the enzymes which produce the reaction are likely to be destroyed.

The authors are indebted to Dr. C. B. Davenport for mice and sheep material, to Dr. A. M. Banta for Cladoceras and to Dr. O. Riddle for pigeon material.

Sophia Satina
M. Demerec

Department of Genetics
Carnegie Institution of Washington
Cold Spring Harbor, N. Y.

HYDROGEN-MAGNESIUM HALIDES[1]

The intermediate formation of hydrogen-magnesium halides is postulated in current theories to account for the reducing action of the Grignard reagent on the carbonyl linkage. Several attempts have been made to prepare such compounds: first, the action of hydrogen halides on magnesium at low temperatures; second, the heating of sec-butylmagnesium bromide at 150° in a high vacuum, and, third, the catalytic reduction of RMgX compounds. Catalytic reduction of triphenylmethyl-magnesium chloride gave results which are indicative of the formation of hydrogen-magnesium chloride.

The reaction of RMgX compounds with azo compounds and the formation of colored intermediate compounds when the Grignard reagent reacts with carbonyl compounds suggests the intermediate formation of magnesium halides analogous to the metal ketyls. The free radical (R) so formed then dissociates to give hydrogen and the corresponding unsaturated compound. This hydrogen then combines with the trivalent carbon.

Russell M. Pickens

THE AMERICAN CHEMICAL SOCIETY[1]

The use of the sodium salt of dimethylglyoxime for the qualitative and quantitative determination of nickel: Waldo L. Semon and Gilbert Swart. Dimethylglyoxime forms a crystalline hydrated sodium salt. It is extremely soluble in water and insoluble in alcohol. A 3 per cent. (0.1M) *aqueous* solution is recommended for use in qualitative and quantitative analysis to replace the 1 per cent. alcoholic solution of dimethylglyoxime. Analyses for Ni are given in the presence of Co, Cr, Mn, Zn and Fe and in various alloy steels.

Esters of 3-amino-4-hydroxymethyl-benzoic acid: Francis H. Case. Ethyl 3-amino-4-hydroxymethyl-benzoate is prepared as follows: p-cyanobenzyl chloride is nitrated, and the 3-nitro-4-chloromethyl-benzonitrile converted to the acetate. This compound on hydrolysis with alcoholic hydrogen chloride yields ethyl 3-nitro-4-hydroxymethyl-benzoate. The latter is reduced to the amino ester by tin and alcoholic hydrogen chloride. Better yields were obtained with colloidal platinum in acetic acid solution. The butyl amino ester is similarly prepared from the butyl nitro ester. The hydrochlorides are soluble in water. The local anesthetic action of these esters will be investigated. A simple method of preparing p-chloromethyl benzoic acid has been found, in which the corresponding nitrile is hydrolyzed with conc. HCl, and the acid recrystallized from alcohol; yield, 80 per cent. On attempted recrystallization from water, p-hydroxymethyl benzoic acid results. Under the same hydrolytic conditions p-cyanobenzyl bromide is also converted into p-chloromethyl benzoic acid.

The reactivity of the hydroxyl group in certain alcohols: James F. Norris and Henry D. Hirsch. The reactivity of the hydroxyl group in nine straight chain aliphatic alcohols was measured by determinations of their rates of reaction with aqueous hydrobromic acid at 100°. The rates were found to be related in a quantitative manner to the structure of the alcohols. If a

---

[1] Abstract of a paper presented before the meeting of the American Chemical Society at Baltimore.

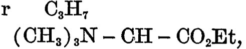
[1] The Los Angeles Meeting, August, 1925, of the Divisions of Organic Chemistry and of Medicinal Products.

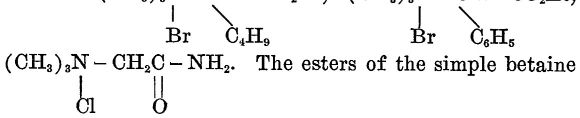
hydrogen in each position relative to the hydroxyl group be assigned a certain number, called the reaction number, then the reaction constant for any of the nine alcohols can be found simply by finding the total of the reaction numbers of all the hydrogen atoms in the molecule. Designating the H on the carbonol carbon as "a," the next as "b," etc., we find that the reaction numbers of the hydrogen atoms are as follows: position a, .000109; b, .000015; c, .000066; d, .000010; e, .000045. Thus the reaction constant of n-propyl alcohol is $2 \times .000109 + 2 \times .000015 + 3 \times .000066 = .000446$. The experimental values were found to check the calculated values within a few per cent.

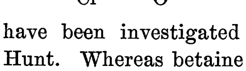
The behavior of acetylene and cuprous chloride catalysts in an ammonia system. II: EUGENE WILLIHNGANZ and J. A. NIEUWLAND. Acetylene condenses with aniline in the presence of the chlorides of copper or mercury to form a substance thought to be a polymer of ethylidine aniline. When this is heated in the presence of a small amount of acid, rearrangement takes place with the formation of products similar to those obtained by the action of aldehyde on aniline. Quinaldine and hydroquinaldine are present. N-ethyl aniline has been isolated, as also o- and p-ethyl anilines. Lepidine and gamma-methyl quinaldine are probably present as evidenced by reaction products. A new explanation of the mechanism of the Skraup synthesis of quinoline is offered.

The preparation of dihydroxymethylxanthene: EUGENE WILLIHNGANZ and J. A. NIEUWLAND. Acetylene reacts with resorcinol in a cold 10 per cent. sulfuric acid solution in alcohol, in the presence of mercuric sulfate, to give ethylidene diresorcinol. This compound readily loses water with the formation of dihydroxymethylxanthene. Paraldehyde may be substituted for the acetylene without decreasing the yield. When paraldehyde is used, the yield in all cases is about 50 per cent., based upon resorcinol used.

On the basis for the physiological activity of certain onium compounds. Derivatives of the betaines: R. R. RENSHAW and H. T. HOTCHKISS. The following derivatives of the betaines have been prepared by condensing the alpha halogen substituted acid derivatives with trimethyl amine. The methyl, ethyl, butyl and benzyl esters of the simple betaine,


$(CH_3)_3\underset{Br}{N} - CH_2 - CO_2R$,


$(CH_3)_3\underset{Br}{N} - \underset{CH_3}{CH} - CO_2Et$, $(CH_3)_3\underset{Br}{N} - \underset{C_3H_7}{CH} - CO_2Et$, $(CH_3)_3\underset{Br}{N} - \underset{C_4H_9}{CH} - CO_2Et$, $(CH_3)_3\underset{Br}{N} - \underset{C_6H_5}{CH} - CO_2Et$,


$(CH_3)_3\underset{Cl}{N} - CH_2\underset{\overset{\|}{O}}{C} - NH_2$.

The esters of the simple betaine have been investigated pharmacologically by Dr. Reid Hunt. Whereas betaine seems to be devoid of muscarine, nicotine and curare actions, these esters give distinct actions. The methyl and ethyl esters are the most active and give the muscarine effect greater than does either choline or murine. This change of activity brought about by muzzling the hydrogen atom of the carboxyl group through esterification is believed by the authors to give further evidence for the idea that to show these activities the substances must have (1) a definite spacial configuration and (2) they must exist in the blood stream as cations. On this theory the inactivity of betaine is explained by its existence in the blood as the electrically inert inner salt [bipolar ion, $^{+}(CH_3)_3N - CH_2COO^{-}$].

Studies on the formation of condensation products of furfural: S. A. MAHOOD. Condensation products of furfural are more difficult to obtain than those of benzaldehyde, due to the greater tendency of the former to polymerize. Benzene and furfural in the presence of zinc chloride give an insoluble solid polymer of the aldehyde but no diphenyl-furyl-methane. Attempts to make the latter through the fural halides led to similar polymerization products. With aryl amines, however, furfural condenses under the influence of inorganic acids or zinc derivatives, depending upon the conditions under which the condensation is brought about and the type of the amine used.

The preparation of l-arabinose from mesquite gum: ERNEST ANDERSON and LILA SANDS. Arabinose is readily prepared by the hydrolysis of mesquite gum for three hours at 80° in six times its weight of 4 per cent. sulfuric acid. After removal of the acid as barium sulfate the neutral solution is concentrated, the salts precipitated by alcohol, the alcohol solution of the sugars concentrated and allowed to crystallize. The yield of crystalline sugar varies from 27 to 36 per cent. of the gum used. The sugar can be recrystallized from water, mixtures of water and alcohol or from glacial acetic acid. Mesquite gum can be purchased in large amounts in the southwest.

The ultra-violet absorption spectra of N-methyl-gamma-pyridone, gamma-pyridone, pyrone and related compounds: E. RAYMOND RIEGEL and MELVIN C. REINHARD. The absorption spectra of nine bodies, which fall in three groups, have been studied: Group A: N-methyl-gamma-pyridone, gamma-pyridone, pyrone. Group B: N-methyl chelidamic acid, chelidamic acid, chelidonic acid. Group C: N-methyl-gamma-oxy-piperidine, gamma-oxy-piperidine, tetrahydro-pyrone. A quartz Hilger sector spectrophotometer was used, with a spark under water giving a continuous source of light; the solvent was water in each case. The molecular extinction coefficient was plotted against wave lengths. All the members of group A and group B give selective absorption; those of group C are almost transparent. The persistence of the band for the members of group A is of the same order of magnitude; this is true also for group B; the average persistence for group A is three times the average for group B. Various observations of the effect of substitution of N – H for N – CH$_3$ and for O and of the introduction of the two carboxyl groups are made; previous investigations are reviewed, and the bearing of the results on the present theories of light absorption is discussed.

Studies in vapor pressures. II. The mono-nitro toluenes: J. F. T. BERLINER and O. E. MAY. The vapor pressures of the ortho and meta nitro toluenes have been measured from 50° C. to temperatures slightly above their boiling points at atmospheric pressure, using the method devised by Smith and Menzies. Their latent heats of vaporization were determined by utilizing the Clausius-Clapeyron equation of state. The vapor pressures were also calculated and were in close agreement with the observed values. The entropies of vaporization have been derived.

Pyrogallolsulfonephthalein, 2, 3, 4-trihydroxybenzoylbenzene-o-sulfonic acid (the intermediate acid) and some of their derivatives: W. R. ORNDORFF and N. FUCHS. Pyrogallolsulfonephthalein was made by heating 2, 3, 4-trihydroxybenzoylbenzene-o-sulfonic acid either alone or with pyrogallol. It was also made by heating (1) saccharin, (2) the chlorides of o-sulfobenzoic acid and (3) the anhydride of o-sulfobenzoic acid with pyrogallol. When heated to 200° the derivatives of pyrogallolsulfonephthalein are converted into the corresponding derivatives of sulfonegallein by the loss of a molecule of water of constitution. Pyrogallolsulfonephthalein, its dibromo derivatives and sulfonegallein react as tautomeric substances forming *colored* derivatives of the *quinoid* form and *colorless* derivatives of the *lactoid* form. Pyrogallolsulfonephthal*in* and its zinc salt were made.

The mechanism of addition of halogens to double bonds: A. W. FRANCIS. In neutral aqueous solution, bromine and unsaturated compounds produce chiefly bromohydrin compounds, but this is not due to hypobromous acid. It can be prevented by a high concentration of neutral bromide or chloride, giving respectively the dibromo- and the chlorobromo-compounds. With sodium nitrate and bromine, ethylene gives some bromoethyl nitrate. Iodine gives similar mixed derivatives using sodium chloride or bromide. It is suggested that the halogens dissociate to some extent in aqueous solution, *e.g.*, to Br^+ and Br^-. The former is "nascent bromine," and reacts with the unsaturated compound forming a positive radical $(RCHBrCHR'—)^+$, which then may combine with any negative ion such as OH^-, Br^-, Cl^-, NO_3^-.

The chlorination of vanillin and derivatives of chlorovanillin: RAYMOND M. HANN and G. C. SPENCER. Vanillin is readily chlorinate in glacial acetic solution, the chloro-vanillin separating out in part in brilliant colorless tetragonal crystals. The analysis of the compound indicates it is a monochloro substitution product, chlorine entering the 5 position, adjacent to the hydroxyl group. Derivatives were prepared—the oxime, hydrazide, phenyl hydrazide, semicarbazide; the semicarbazide and diphenyl hydrazide are all beautifully crystalline solids. Condensation with ethyl cyano-acetate yields ethyl alpha-cyano-3-methoxy-4-hydroxy-5-chloro-cinnamate. Upon hydrolysis with concentrated HCl this yields 3-methoxy-4-hydroxy-5-chloro-cinnamic acid.

The optical identification of the naphthalene sulphonic acids by means of their benzyl-ψ-thiourea salts: RAYMOND M. HANN and GEORGE L. KEENAN. The optical properties and indices of refraction of analyzed benzyl-ψ-thiourea salts of alpha and beta mono-naphthalene sulphonates and 1, 5: 1, 6: 2, 6: and 2, 7 di-naphthalene sulphonates were determined. These constants give a means of identifying the various acids, not only when isolated, but also in mixtures. A diagnostic table was prepared showing a ready means of determining which acid of the series is present by successive immersion in two refraction liquids. Photomicrographs showing the appearance of the various salts were also prepared.

The chlorination, iodination and nitration of dihydroxytriphenyl methane-o-carboxylic acid: RAYMOND M. HANN and S. F. ACREE. Dihydroxy-triphenyl methane-o-carboxylic acid was chlorinated to yield a tetrachloro acid by treatment with chlorine in cold glacial acetic acid. The compound yields a diacetate with acetic anhydride, a dibenzoyl derivative with benzoyl chloride and a hexachloro-triphenyl methane-o-carboxylic acid with phosphorous pentachloride. Dihydroxy-triphenyl methane-o-carboxylic acid gives a tetra-iodo derivative with iodine in the presence of strong reducing agents. Dihydroxy-triphenyl methane-o-carboxylic acid yields a di-nitro derivative upon treatment with HNO_3. Experiments upon the oxidation of these derivatives with dilute potassium ferricyanide are now in progress.

The condensation of aldehydes with diphenyl iso-thiohydantoin: RAYMOND M. HANN and KLARE S. MARKLEY. Diphenyl iso-thiohydantoin is condensed with various aldehydes—salicylic, chlorosalicylic, bromosalicylic, iodosalicylic, vanillin, iodo-vanillin, bromo-vanillin, chlorovanillin, nitro-vanillin, iso-butyric and other aldehydes—and the products purified and analyzed. These derivatives are to be used in studies of reduction products and in spectrophotometric studies.

The toxicity of local anesthetics (with special reference to apothesine): HERBERT C. HAMILTON. A substitute for cocaine should be not only effective and non-habit forming, but should be relatively much less toxic. Toxicity tests should be based on the ordinary use of the material in clinical practice, but in addition such tests should be made as will show the possible results from accidental or unusual forms of administration. Apothesine has been tested for toxicity in comparison with cocaine by subcutaneous, intravenous and intraperitoneal injections, and the effect of adrenalin is described, by which the latter acts as an antidote. Previous work is reviewed to demonstrate the comparative effectiveness of apothesine and cocaine.

FRANK C. WHITMORE,
Secretary

NORTHWESTERN UNIVERSITY,
EVANSTON, ILLINOIS