(1)	(2)	(3)	(4)	(5)
Number of Brothers	Number of Sisters	Frequency	(1) × (3)	(2) × (3)
0	$n-1$	kn	0	$kn(n-1)$
1	$n-2$	$kn(n-1)$	$kn(n-1)$	$kn(n-1)(n-2)$
2	$n-3$	$\frac{kn(n-1)(n-2)}{2!}$	$kn(n-1)(n-2)$	$\frac{kn(n-1)(n-2)(n-3)}{2!}$
"	"	"	"	"
"	"	"	"	"
"	"	"	"	"
"	"	"	"	"
$n-3$	2	$\frac{kn(n-1)(n-2)}{2!}$	$\frac{kn(n-1)(n-2)(n-3)}{2!}$	$kn(n-1)(n-2)$
$n-2$	1	$kn(n-1)$	$kn(n-1)(n-2)$	$kn(n-1)$
$n-1$	0	kn	$kn(n-1)$	0
	Totals	$kn\ 2^{n-1}$	$kn(n-1)2^{n-2}$	$kn(n-1)2^{n-2}$

from the group is a boy, it will be proved that $(n-1)/2$ is the most probable value of the arithmetic mean of the number of a boy's brothers, and likewise of the number of his sisters. Consider a large number N of families and for convenience assume that N is a certain number of time 2^n, say $N = k2^n$. Then the *a priori* most probable numbers of families with 0, 1, 2, : : :, n boys is given, respectively, by the terms k, kn, $kn(n-1)/2!$, : : :, $kn(n-1)/2!$, kn, k in the binomial expansion of $k(1+1)^n$.

First note that k families out of $k2^n$ have no boy; second, that kn families have only one boy each and therefore they have kn cases of no brothers and $n-1$ sisters; third, that $kn(n-1)/2!$ families have two boys each, and hence they have $kn(n-1)$ cases of one brother and $n-2$ sisters; fourth, that $kn(n-1)(n-2)/3!$ families have three boys each, and hence they have $kn(n-1)(n-2)/2!$ cases of two brothers and $n-3$ sisters; and so on. The manner of the distribution seems sufficiently clear without further illustration.

Then we set up the ordinary form for finding the arithmetic means of the number of brothers and of the number of sisters in the accompanying table.

The totals of columns (4) and (5) are equal, and each divided by the total of column (3) gives $(n-1)/2$. Hence $(n-1)/2$ is the arithmetic mean of the number of brothers, and of the number of sisters.

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DIVISION OF ORGANIC CHEMISTRY

(Continued)

The electrochemistry of free radicals: J. B. CONANT, L. F. SMALL and A. W. SLOAN. The halochromic salts of triaryl and diaryl carbinols are rapidly reduced in acetic acid solution by vanadous salts to the corresponding ethanes which can be obtained in good yields. If these ethanes are dissociated with the formation of free radicals, a significant potential of the process can be measured by the titration method, or by mixing the free radical and the halochromic salt. Similar results can be obtained with certain more stable xanthylium salts even in an aqueous and alcoholic solution. These potentials are the equivalent of the single electrode potentials of the metals, and vary according to the nature of the free radical. The reduction of halochromic salts to free radicals is being used to prepare free radicals hitherto inaccessible; benzylxanthyl has been thus obtained.

Condensation of phthalic anhydride with aryl hydrocarbons: O. R. QUAYLE and E. E. REID. The condensation of phthalic anhydride with aromatic hydrocarbons containing fluorine has been studied, and a number of fluor-benzoyl-benzoic acids prepared. These have been condensed to form the corresponding substituted anthraquinones.

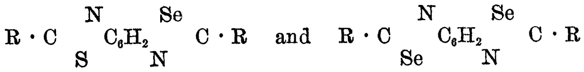
Condensation of cyclohexanone with aldehydes: C. E. GARLAND and E. E. REID. Cyclohexanone has been condensed with p-toluic aldehyde, p-brombenzaldehyde, furfural and anisic aldehyde. The complex ketones have been hydrogenated and also subjected to the Grignard reaction. The tertiary alcohols so formed have been dehydrated and the unsaturated hydrocarbons hydrogenated.

Reactions of unsaturated 1, 4 diketones: J. B. CONANT, R. E. LUTZ and L. F. LEA. Dibenzoyl ethylene and its derivatives combine with ammonia, aniline, malonic ester (in the presence of sodium alcoholate), hydrogen chloride, acetyl chloride and acetic anhydride yielding substituted 1, 4 diketones or, in certain cases, substituted furans; from the former, pyrrols can be prepared. Dibenzoyl ethylene dibromide easily loses two molecules of hydrogen bromide when treated with alkaline reagents; the resulting dibenzoyl acetylene combines at once with water, alcohol or phenol according to the nature of the reagent employed. The product in the first instance is a strongly enolic 1, 2, 4 triketone.

Benzylpseudothiourea salts of naphthalene sulfonic acids: R. F. Chambers and P. C. Scherer. The method of preparation of the benzylpseudothiourea salts of a series of the more common mono and disulfonic acids of naphthalene is given, and these salts have their properties described. The melting points, solubility curves in n/5 HCl, solubilities in organic solvents, crystal forms and water of crystallization have been determined and are described. On account of their extreme ease of preparation and definite melting points, these compounds are suggested as a means of identification of the naphthalene sulfonic acids.

Reduction potentials of polycyclic anthraquinones and the structure of anthracene: L. F. Fieser. The reduction potential of ang. benzanthraquinone ($\pi_0 = 0.226$) in alcoholic solution is considerably higher than that of anthraquinone ($\pi_0 = 0.155$) while lin. benzanthraquinone can not be reduced by zinc dust and boiling alkali, and attempted measurements indicate a reduction of potential of less than 0.100v. This difference in the effect of the phenylene group on the potential of anthraquinone, exhibited also in the dibenzanthraquinone series, is interpreted on the basis of the ortho-quinonoid structure of anthracene and the comparison of the properties of the quinonoid systems of the anthrahydroquinones in question with the properties of true quinones.

Researches on the selenium compounds—III. The synthesis of benzo-bis-selenazoles and thiazylbenzoselenazoles, new heterocyclic systems. The preparation of a selenium derivative of cinchophen type: M. T. Bogert and H. H. Hopkins. Benzalamino benzoselenazoles when fused with sulfur or selenium yield the following heterocycles:



$$R\cdot C\begin{matrix}N & & Se\\ & C_6H_2 & \\ S & & N\end{matrix}C\cdot R \quad \text{and} \quad R\cdot C\begin{matrix}N & & Se\\ & C_6H_2 & \\ Se & & N\end{matrix}C\cdot R$$

The thiazylselenazole adds bromine or acetyl chloride, and is easily nitrated. The bis-selenazole exhibits properties similar to those of the simple benzoselenazoles. Such bis-selenazoles also result from the fusion of the dibenzal derivatives of phenylene diamines with selenium. The 6-furalamino-2-phenyl-benzoselenazole is decomposed by fusion with either sulfur or selenium. From 6-amino-2-phenyl-benzoselenazole, the corresponding 6-cyano and 6-COOH derivatives were prepared, the latter being a selenazole analog of Cinchophen (Atophan), resembling the thiazole compound described by Bogert and Abrahamson (*J. A. C. S.*, 44, 826 (1922)).

Researches on quinazolines—XXXV. Stereoisomeric styryl derivatives of some 4-quinazolone alkyl iodides, and their bearing upon the problem of photosensitizing dyes: H. Clark and M. T. Bogert. (1) Great difficulty was experienced in the preparation of alkyl iodides of 2-methyl-quinazolines, although the corresponding derivatives of 2-methyl-4-quinazolones were obtained easily. (2) The non-reactivity of 2, 4-dimethyl-quinazoline with aromatic aldehydes is at variance with certain recent hypotheses concerning reactive methyl groups of nitrogen heterocycles. (3) Attempted "cyanine condensations" with 2-methyl-4-quinazolone alkyl iodides resulted negatively. (4) 2-Methyl-4-quinazolone alkyl iodides were condensed with p-dimethylamino benzaldehyde in the presence of acetic anhydride or piperidine, yielding the corresponding styryl derivatives. (5) Cis and trans forms of these styryl derivatives were separated by fractional crystallization from methyl alcohol. The two forms differed widely in appearance and in melting point. (6) The lower melting (labile) isomer was convertible into the higher melting (stable) one, but the reverse change could not be effected. (7) The products were devoid of photosensitizing properties and valueless as dyes. (8) The two stereoisomers gave identical mono-bromo dibromides when treated with bromine in chloroform solution. (9) In the course of the work, the following new compounds were prepared: cis and trans forms of the methyl iodides of 2-p-dimethylaminostyryl-4-quinazolone, of 3-methyl-4-quinazolone, of 3-ethyl-4-quinazolone, also of the ethyl iodides of 3-methyl-4-quinazolone, and their bromination products.

The preparation of oxindole derivatives from isatin: A. J. Hill and A. S. Schultz. Isatin, as well as its mono and dibrom derivatives, will condense with the activated methylene groups of diketopiperazine and hydantoin. The reduction and subsequent hydrolysis of these new condensation products should theoretically lead to the formation of oxindole amino-acetic acid (A), or oxindole acetic acid (B) and the corresponding halogen derivatives.

(A) $C_6H_4(NH\cdot CO : CH) - CH\cdot NH_2\cdot COOH$
(B) $C_6H_4(NH\cdot CO\cdot CH) - CH_2\cdot COOH$
(C) $C_6H_4(NH\cdot CO\cdot C) : CH\cdot COOH$

From the unsubstituted isatin condensation products, the writers have obtained (B) and its unsaturated homolog (C), depending upon the reagents employed. The amino acid has not been isolated, since deaminization occurs, even when mild hydrolytic agents are employed. Oxindole acetic acid may be obtained from (C) by reduction. The former is readily brominated in sulfuric acid solution. This method for the synthesis of oxindole derivatives is being extended to include not only the brominated, but also the iodated types which are somewhat related to thyroxin in their molecular configuration.

The substituted thioureas—V. The synthesis of thiazolidine derivatives: F. B. Dains, R. Q. Brewster, I. L. Malm and A. W. Miller. (a) The synthesis of alpha-aryl (or alkyl)-alpha-ethanol-beta-alkyl (or aryl) thioureas. $RN(CH_2CH_2OH)CSNHR'$ from the substituted aminoethanols and mustard oils. (b) The conversion of these thioureas into thiazols of known structure. (c) The formation of thiozolines from ethylene dibromide and thioureas of the type $RNHCSNHR'$, where R and R' are different groups. (d) Some di-thio-ethylene ethers from aryl-alkyl thioureas.

The oxidation of carbohydrates with air: H. A. Spoehr. Thus far it has been possible to oxidize the hexoses with air only in alkaline solution. While disodium phosphate catalyzes the oxidation of glucose with H_2O_2, it does not affect the oxidation with air. Glucose and other hexoses are oxidized with the formation of CO_2 by air in solutions containing Na_2HPO_4 and methylene blue. This reaction is greatly accelerated by small amounts of Fe salts. Sodium ferro pyrophosphate is a more active catalyst for the oxidation of carbohydrates than methylene blue. Not only are the hexose sugars thus oxidized, but sucrose, trehalose and other compounds which do not reduce Fehling's solution are easily oxidized. From a consideration of the rates of oxidation of different hexoses, it appears that glucose is first converted into levulose by the Na_2HPO_4.

The lactones of l-mannonic and d-mannonic acid: F. W. Upson and L. Sands. Nef and Hadenburg have shown that there are two d-mannonic acid lactones, one of specific rotation plus 112° and changing rapidly in solution to a rotation of about plus 28°. Nef called this provisionally the beta-lactone. The gamma-lactone, rotation plus 53°, changes very little in solution. We have the analogous lactones of l-mannonic acid. Further, we have shown that Nef's beta-lactone possesses in all probability a pentylene-oxide structure and that, further, the sugar, d-mannose, possesses also a pentylene oxide ring structure.

Separation of alpha and beta amylose. Properties of alpha and beta amylose: T. C. Taylor and H. A. Iddles. A study has been made of the possibilities of separating the alpha and beta components of corn starch through the agency of the electric current. Alpha amylose wanders to the positive electrode, while the beta amylose remains dispersed. The solution of the beta amylose can be decanted from residue of the alpha which collects in compact mass. Proper treatment of these two components gives the respective amyloses. The alpha contains 1.25 per cent. combined fatty acids, while the beta is apparently pure carbohydrate. The latter amylose goes into ''solution'' in water heating, to the extent of at least 6 per cent. It gives a pure blue color with iodine-iodide solutions and is very quickly hydrolyzed by malt diastase. Detailed investigation of the properties of these two components are under way.

Identification of fatty acids liberated by hydrolysis of corn starch: T. C. Taylor and L. Lehrman. Oleic acid and linoleic acid have been identified by their oxidation products and bromides as being the unsaturated fatty acids which together with palmitic acid are liberated by the acid hydrolysis of corn starch.

The catalyzed oxidation of galactose: E. C. Whittier. This oxidation by nitric acid is of interest in connection with the production of mucic acid from milk sugar or galactose. Vanadium pentoxide was the only substance tested that accelerated the oxidation of galactose by nitric acid. Thirty-five to forty per cent. is the optimum range of concentration of nitric acid for mucic acid production at 85°. Both higher concentration of oxidizing agent and addition of vanadium pentoxide increase the production of oxalic acid and carbonic acids at the expense of mucic acid.

The extraction of maltase from yeast: V. K. Krieble, E. L. Skau and E. W. Lovering. Previous investigations on maltose from yeast have shown that an acid is formed in the extraction, but have disagreed as to the best method of extraction, and the treatment of yeast previous to extraction. Our experiments have shown that maltase can be extracted either from fresh or dry yeast, a more active extract being obtained from dry yeast, and that the strength of the extract depends on the condition of the yeast, the length and temperature of extraction, and the P_h of the extractive medium. Maltase even at 15° is destroyed gradually in the extractive medium so that, as the extraction progresses, the activity of the extract rises to a minimum and then decreases—the rate of decrease being influenced by temperature and the medium of extraction.

Preparation of tartaric acid from maleic and fumaric acids (By title): N. Milas and E. M. Terry. The K. A. Hofmann method of oxidating maleic and fumaric acids to meso tartaric and racemic acids, respectively, has been materially improved by a study of the variation of yield at different hydrogen ion concentrations. The catalyst, osmium tetroxide, can be removed and reused. The mechanism of the reaction will be given in brief.

A study of directing influence of substituents in the benzene ring by means of rate of bromination: J. Johnson, A. J. Hill and A. W. Francis. Amino and phenolic compounds in aqueous solution are brominated rapidly in all available ortho and para positions. The rates are influenced greatly, however, by other substituents in the ring. The absolute velocities are far too great to be measured directly, but consistent relative rates have been estimated by means of a series of partition experiments, allowing insufficient bromine to react simultaneously with two compounds, and analyzing the products. In this way measures of the relative velocity of bromination in all positions of about 35 benzene derivatives have been ascertained. A comparison of the influence of the several groups under various conditions is thus possible.

A simple relation between composition and boiling point of organic liquids: E. Q. Adams. Longuinescu found an appropriate relation for normal organic liquids between the absolute boiling point, density of no. of atoms in the molecule: $T\sqrt{(D\,V\,n)}$ — 100 approx. An even more exact expression, not involving density, has been found. If the elements be weighed according to the row in the periodic table in which they occur (system of Rydberg), *i.e.*, H is disregarded; C, N, O, F count 1; Si, P, S, Cl, 2, etc., the relation T equals to the square root of 2000n holds within one unit of ''n'' for most organic liquids, and for many inorganic nonelectrolytes.

The chlorination of 2-amino-p-xylene: A. S. WHEELER and M. MORSE. 2-Amino-p-xylene was converted into its acetyl derivative and chlorinated at a low temperature. Chlorine was substituted in position 5. This was proven by converting it into 2, 5-dichloroxylene and oxidizing this to 2, 5-dichloroterephthalic acid. A new series of azo dyes was prepared by diazotizing 2-amino-5-chloro-p-xylene and coupling it with the following phenols: phenol, resorcinol, thymol, alpha-naphthol, beta-naphthol, Schaeffer's acid and Cleve's acid. Other dyes are in the course of preparation.

Borneol in spruce turpentine: A. S. WHEELER and C. R. HARRIS. The dark liquid residue left after removing most of the p-cymene from spruce turpentine by steam distillation was subjected to fractional distillation in vacuo. Direct heat was applied and a pressure of 3 mm. Using 900 cc of liquid, 400 cc proved to be p-cymene, b. p. 42°. The remainder was collected in 5 or 10 cc fractions, the last fraction collected boiling above 100° or above 300° at atmospheric pressure. All fractions were liquid except one boiling at 75–80° or 205–210° at atmospheric pressure. This was white crystalline compound of terpene-like odor (melting point 205° after recrystallizing). Analysis gave the formula $C_{10}H_{18}O$ corresponding to borneol. The melting point, crystalline form and solubilities also suggested borneol. Its phenylisocyanate gave the melting point of 141°, the same as that of borneol. The specific rotation, however, was — 12° 43′. This indicated l-borneol mixed with considerable of the dl-form.

Preparation of malic acid from maleic acid (By title): E. M. TERRY and L. EICHELBERGER. A method for the quantitative estimation of malic acid in the presence of maleic acid was first developed. Then a survey was made of the effect of different salts on the rate of addition of water to the double bond of maleic acid. Many salts were found helpful. The rate of the change when mercuric acetate was catalyst was studied in detail and an efficient method established for the preparation of malic acid from maleic acid. A theory of reaction will be given.

Study of nitration of benzoic acid (By title): H. M. SEVERANCE and E. M. TERRY. A study was made of the products of nitration of benzoic acid when the process was carried out first, with nitric acid with varying water content, and second, with pure nitric acid in acetic acid solution. For this purpose a new method was developed for analyzing mixtures of ortho and meta nitro benzoic acid in the presence of benzoic acid. This method is briefly outlined together with the results of the study.

Bromination of sodium benzoate (By title): E. M. TERRY and L. EICHELBERGER. Sodium benzoate was brominated by a new process. For the purpose of establishing the identity of the isomeric acids formed, a special method of analysis was developed. Finally good working conditions were found for the preparation of isomeric monobrombenzoic acids. It may be shown that the methods of analysis and preparation have a variety of possible applications. The mechanism of the reaction together with an outline of the above processes could be given.

Catalytic transmutation of maleic acid to fumaric acid (By title): L. EICHELBERGER and E. M. TERRY. A new theory of the mechanism of the catalytic transmutation of maleic to fumaric acids is given. It is shown to correlate the widely diversified conditions under which the process may be carried out. New experimental work is given in support of the theory.

Halogenation of maleic acid and of fumaric acid (Lantern): E. M. TERRY and L. EICHELBERGER. A new method of bromination and of chlorination of the neutral salts of mono-carboxylic acids will be presented. With the help of this method in large measure we may bring about either cis or trans addition of halogen at the double bond of the acid as we desire. A theory of the mechanism of the processes involved has been developed. This theory may be shown to apply to the Walden Inversion as well as the above-mentioned processes.

Condensation of carbon tetrachloride with phenol (By title): M. GOMBERG and H. R. SNOW. We find that, contrary to Heumann's claim (D. R. P. 68,976), the condensation of carbon tetrachloride and phenol takes place at ordinary pressures, and a good yield of aurin is obtained. In addition to aurin, several other products are produced. All these have been identified. Procedures have been worked out whereby either diphenyl carbonate or di-hydroxy-benzophenone or trihydroxy carbinols may be obtained to the almost complete exclusion of the others. A convenient method has been devised for the complete separation and purification of aurin. The properties of the latter were determined and many derivatives of it obtained. It has also been established that the technical product contains only about 50 per cent. of aurin, and the nature of impurities has been determined.

Unsymmetrical aliphatic arseno compounds: C. SHATTUCK PALMER. Several members of this previously unrecorded series have been prepared by simultaneous reduction of equimolecular proportions of two different aliphatic arsonic acids with 50 per cent. hypophosphorous acid in the cold. The products can be obtained as yellow needles but have a marked tendency to become gummy. They are practically insoluble in water and most organic solvents. Those in which one of the groups attached to arsenic is substituted by carboxyl form water-soluble sodium salts. If proper conditions of reduction are not observed, a mixture of two arseno compounds is obtained instead of the unsymmetrical derivative.

The effect of temperature on the equilibrium between benzaldehyde and benzoin: ERNEST ANDERSON and LEROY G. STORY. The value of the equilibrium constant between benzaldehyde and benzoin has been determined experimentally at six different temperatures and the results found to agree closely in each case with the value calculated by means of the Van 't Hoff equation.

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Secretary