1. There are no nitrates in the types of Michigan peat soil examined.
2. The amount of ammonia is small, ranging from a few thousandths to a few hundredths of one per cent., this representing the nitrogen available immediately as plant food. In the case of the brown peat, the amount of ammonia is sufficient to meet the needs of one or two crops, as is evident from the following: There are in an acre-foot in round numbers 170 tons of oven-dried peat, with 0.041 per cent. ammoniacal nitrogen, making 0.0697 ton or 139.4 pounds nitrogen as ammonia.
3. Practically all the nitrogen in the peat is of organic nature.
4. The bulk of the organic nitrogen, namely from two-thirds to three-quarters calculated upon the nitrogen in solution, by boiling with acids, is present in the form of monamino acids, about one-quarter in the form of amides and the rest of the nitrogen represents diamino acids.
5. Through weathering, the organic nitrogenous bodies present in the brown peat change quite slowly.

REVIEW.

SOME RECENT ADVANCES IN ORGANIC CHEMISTRY.

Jan. 1, 1908–July 1, 1909.

By L. H. Cone.

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Among the advances in organic chemistry during the last few years which have been remarkable for the difficulty of the experimental work involved are those which have been made at the border line between pure organic and physiological or biochemistry. These have deservedly attracted very wide attention.

Proteins.—Naturally one thinks first of Fischer's already classic work on the proteins when biochemistry is brought under discussion. This work has been steadily continued and polypeptides have been prepared of every naturally occurring amino acid, with the exception of five, which are very difficult to obtain or for which special methods will have to be worked out. The number of polypeptides isolated from the partial hydrolysis of proteins has constantly increased and five of these so isolated have been found to be entirely identical with those previously prepared synthetically in the laboratory.[1] Thus Fischer's theory of the protein constitution has been steadily strengthened. A discussion of the impetus which this theory has given to the more scientific study of problems of digestion, of assimilation, and of ferment action, lies without the province of this review, but a casual glance at the physiological literature will show the valuable service which the theory is rendering.

Early in the study of the polypeptides it became apparent that in order to obtain any large number of derivatives of the hydroxyamino acids some method would have to be devised for the temporary protection of the hydroxyl group so that hydroxyamino acid chlorides could be pre-

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[1] "Abderhalden-Physiologische Chemie," 2nd Edition, p. 258 (1908).

pared. Fischer[1] has solved the problem by shaking the hydroxy acid to be protected, in alkaline solution with chlorocarbonic methyl ester, when the carbomethoxy group is introduced.

$$HOC_6H_4CH_2.CH.NHR.COOH + CH_3OCOCl = CH_3OCO.OC_6H_4CH_2.CH.NHRCOOH + HCl.$$

The derivative thus obtained can be readily changed into the acid chloride by the action of phosphorus pentachloride and the acid chloride can be used for condensations. In the condensed product the hydroxyl group can easily be regenerated by hydrolysis with alkali. By means of this reaction a tetrapeptide, hitherto unattainable, containing tyrosine, has been prepared. The method has, however, a wider application in the synthesis of aromatic hydroxyketones, of which Fischer has prepared a number hitherto obtainable only with difficulty. He has carried the reaction still further and has prepared a number of gallic acid derivatives, among them a crystalline compound which was probably digallic acid.[2] This has not as yet been obtained entirely pure, so its relation to tannic acid is still uncertain.

Fischer's studies of the optical properties of the amino acids have also led to valuable results. Together with Raske[3] he treated the ethyl ester of *l*-serine with phosphorus pentachloride and obtained α-amino-β-chloropropionic ethyl ester. On reduction this yielded *d*-alanine. By treating the same chlorine derivative with barium hydrosulphide they obtained *l*-cysteine, which on oxidation gave *l*-cystine. This series of reactions proves that *l*-serine, *d*-alanine and *l*-cystine, the naturally occurring forms of these acids, all have the same configuration. Previously Fischer and Jacobs[4] had shown that *l*-serine gives *l*-glyceric acid with nitrous acid, Neuberg and Silberman[5] had shown that *l*-glyceric acid and *l*-tartaric acid have the same configuration, and Fischer had connected the configuration of *d*-tartaric acid with rhamnose, so that if all steps in the work were correct we have the beginning of a rational classification of the optically active mono-amino acids. Some doubts have been thrown on the correctness of the results of Neuberg and Silbermann however, so that the relationship between the amino acids and glucose is not yet entirely certain.

The results obtained by Fischer and Scheibler[6] in their study of "Walden's reversal" are interesting but too complex to be given here.

Nucleic Acids.—The problem of the constitution of the nucleic acids has been a difficult but attractive field. It has been known for some time that the nucleic acids have three constituents, carbohydrate, phosphoric acid, and purine or pyrimidine bases. The manner and order of linking of these constituents have not been known nor has the carbohydrate constituent been identified beyond question. That the carbohydrate in most nucleic acids is a pentose is now generally agreed, and Levene and Jacobs[7] have very recently shown that in four nucleic acids examined by them

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[1] *Ber.*, 41, 2860 (1908).

[2] *Ibid.*, 41, 2875 (1908).

[3] *Ibid.*, 40, 3717 (1907); 41, 893 (1908).

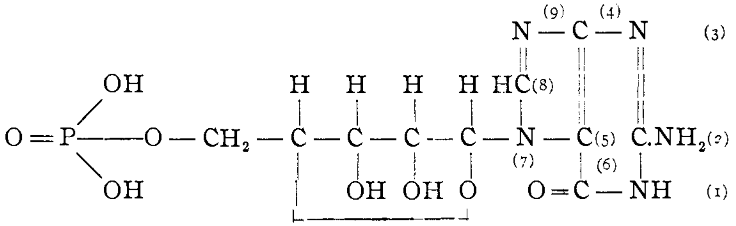
[4] *Ibid.*, 40, 1057 (1907).

[5] *Z. physiol Chem.*, 44, 134 (1905).

[6] *Ber.*, 41, 889, 2891 (1908).

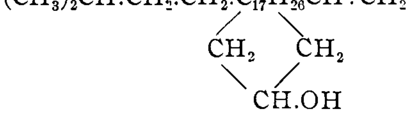
[7] *Ibid.*, 41, 2703 (1908); 42, 335, 1198, 2102, 2469 and 2474 (1909).

the same pentose is present and this pentose is very probably *l*-ribose. Burian, through his studies upon the diazonium compounds of the purine bases, has rendered it very probable that the purine group is bound in the nucleic acid molecule through its imide hydrogen in the position seven.[1] No sharp experimental evidence has, however, been brought to show the order of coupling of the constituents in the molecule till recent papers by Levene and Jacobs.[2] By acid hydrolysis they obtained a phosphoric acid-pentose complex which had strong reducing power and in which therefore the aldehyde group of the pentose was free. By neutral hydrolysis of the barium salts of several nucleic acids they then obtained a purine base-pentose complex which had no reducing power. From these facts they conclude that the pentose must be coupled ester-like through one of its hydroxyls to the phosphoric acid and glucoside-like through the aldehyde group to the purine base. Guanylic acid would be then as follows:



Such a complex they call a "mono-nucleotide" and suggest that the nucleic acids are made up of several of these complexes all alike or different as the case may be, linked together through the phosphoric acid, just as the proteins are composed of polypeptides bound together and the polysaccharides of mono-saccharides coupled in chains of varying length.

Cholesterol.—Through the painstaking work of Windaus[3] a great deal has been added to our knowledge of the constitution of cholesterol. By the judicious application of different oxidizing agents in rotation he has been able to break off various side chains till finally an acid, very resistant to oxidation, has been obtained with the compact formula $C_{17}H_{26}(COOH)_4$. The various steps in the oxidation process are too numerous to be given here, but from the results Windaus concludes that he is justified in writing cholesterol, which has the empirical formula $C_{27}H_{46}O$, as



$$\begin{array}{c}(CH_3)_2CH.CH_2.CH_2.C_{17}H_{26}CH:CH_2\\ CH_2\quad CH_2\\ CH.OH\end{array}$$

From the structure given it is apparent that of the twenty-seven atoms of carbon in the molecule the functions of ten have been determined.

Chlorophyll.—Although the work of Willstätter[4] and his co-laborers

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[1] Cf. "Abderhalden-Physiologische Chemie," 2nd Edition, p. 385. *Ber.*, **37**, 696, 708 (1904).

[2] *Loc. cit.*

[3] *Ber.*, 40, 2637 (1907); 41, 611, 2558 (1908); 42, 3770 (1909).

[4] *Ann.*, **350**, 1, 48 (1906); **354**, 205; **358**, 205, 267 (1908).

on chlorophyll began to appear several years ago, it has continued into the time supposed to be covered by this review. The conclusions which they have reached may be summarized very briefly. Chlorophyll occurs in at least two different forms, amorphous and crystalline. The amorphous chlorophylls, which apparently predominate in most plants, are all esters of the same high molecular weight unsaturated alcohol, phytol, $C_{20}H_{40}O$, with different complex acids. The crystalline varieties, if they are esters at all, contain only low molecular weight alcohols so soluble in water that they have escaped detection. Both varieties of chlorophyll contain magnesium in the acid part of their molecules, so combined as to be very resistant to alkalies. This magnesium is readily split off by dilute acids and the organic residues remaining may be broken up by severe treatment with strong acids and alkalies into less complex products, a number of which have been isolated and analyzed. Willstätter's results have generally been accepted. Stoklasa[1] has, however, recently published a series of analyses of samples of chlorophyll prepared by himself, in all of which he found very appreciable quantities of phosphorus. The phosphorus is bound in such a labile manner, according to him, that Willstätter removed it by his process of purification. The majority of chemists will probably accept Willstätter's conclusions, however, that the phosphorus is an adhering impurity properly removed during purification.

Carbohydrates.—A number of articles of interest have appeared dealing with the carbohydrates and their derivatives. Fischer and Raske[2] have applied the methods of König and Knorr[3] for the preparation of glucosides from acetobromoglucose and alcohols. The essential point of this method is that the alcohol and the acetobromoglucose are shaken together in a neutral organic solvent in the presence of silver carbonate. The silver binds the hydrobromic acid so that the reaction goes to end in neutral solution. The tetraacetylglucosides were obtained in crystalline form and the acetyl groups removed by hydrolysis with barium hydroxide. By this method glucosides of aliphatic, aromatic, and hydroaromatic alcohols were prepared. The glucosides of menthol and borneol thus obtained are the first terpene glucosides to be described. All of the glucosides prepared were hydrolyzed by emulsin and are therefore probably β-glucosides.

Hudson[4] has pointed out certain relations between the molecular rotations of the various sugars. Evidence indicates that α- and β-glucose are both lactones and differ from each other only sterically. This steric difference must be entirely in the fifth, new asymmetric carbon atom which is produced when the aldehyde group of glucose is hydrated and then dehydrated to form a lactone. If the theory of optical superposition holds[5] the optical effect of the four asymmetric carbon atoms common to both forms must be the same. Let this effect be B. The rotation produced by the fifth asymmetric carbon atom will be the same numerically in both forms but will be different in sign, and can therefore

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[1] *Ber. deutschen bot. Ges.*, 26a, 69 (1908).

[2] *Ber.*, 42, 1465, 1476 (1909).

[3] *Ibid.*, 34, 957 (1901).

[4] THIS JOURNAL, 31, 66 (1909).

[5] Cf. Rosanoff, *Ibid.*, 25, 525 (1906).

be represented by ±A. One form will thus have a rotation of A + B and the other of —A + B, the sum of which will be 2B and the difference 2A. Other aldoses differ from glucose in the configuration of the four originally asymmetric carbon atoms. In their α- and β- forms the fifth or end asymmetric carbon atoms are identical with those in the two forms of glucose, respectively, *i. e.*, ±A. Their rotations may then be represented by A + B′ and —A + B′, the sum of which is 2B′ and the difference 2A. This means that the α- and β-forms of all aldohexoses should have a common difference 2A. The same reasoning may be applied to other sugars. The theory was tested on a number of sugars whose α- and β-forms are known and found to agree fairly well with the facts. If the principle proves to have general application it will be of value in predicting the rotatory power of forms which have not as yet been isolated and will aid in the rational classification of forms as α- or β-derivatives.

Two years ago Slator[1] showed that lactic acid which is added to a sugar solution undergoing alcoholic fermentation is not affected and can be recovered at the end of the fermentation unchanged. He concluded therefore that lactic acid cannot be an intermediate product in the alcoholic fermentation of sugar. Buchner and Meisenheimer[2] did not accept his conclusions at the time but recently they have repeated his experiments, found them correct, and are inclined to accept his conclusions.[3]

Alkaloids and Terpenes.—The constantly growing volume and complexity of the work on alkaloids and terpenes makes it exceedingly difficult for one not specializing in these fields to choose from among the mass of material those results which stand for real advances.

Leuchs[4] has obtained crystalline acids as the result of the oxidation of strychnine and brucine in acetone solution with potassium permanganate. The acids from the two alkaloids are very similar and each contains four atoms of oxygen more and two atoms of hydrogen less than the alkaloid from which it was produced. From this the conclusion seems justified that a group $\underset{|}{\mathrm{HC}} = \underset{|}{\mathrm{CH}}$ was changed into two carboxyl groups and that a secondary alcohol group was oxidized to a ketone carbonyl. In a later paper Leuchs and Schneider[5] describe crystalline sulphonic acids of both alkaloids which they prepared by treating their solutions in sulphurous acid with manganese dioxide. The reaction apparently proceeds according to the following general equation:

$$O + HO_3SH + H.R = RSO_3H + H_2O,$$

and should therefore yield sulphonic acids of any substance RH, in which H is fairly easily oxidized away. The study of these new derivatives of strychnine and brucine bids fair to aid very materially in throwing light upon their constitutions.[6]

Wollfenstein[7] has described and patented a new method for the preparation of atropine and similar alkaloids from tropine and tropic acid or

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[1] *Ber.*, 40, 123 (1907).

[2] *Ibid.*, 41, 1414 (1908).

[3] *Chem. Zentr.* 1909, II, 730.

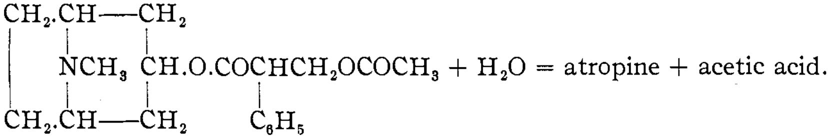
[4] *Ber.*, 41, 1711 (1908).

[5] *Ibid.*, 41, 4393 (1908).

[6] Leuchs und Weber, *Ber.*, 42, 770 (1909).

[7] *Ber.*, 41, 723, 733 (1908).

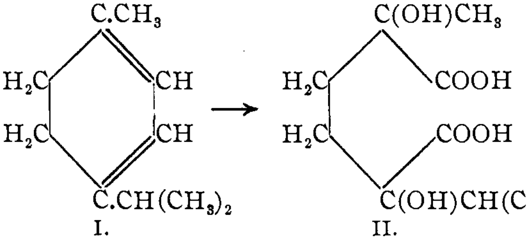
from tropine and other hydroxy acids as the case may be. Atropine is an ester of tropine and tropic acid, and therefore if tropic acid chloride could be prepared and would react normally with tropine the preparation of atropine would probably be very much more quantitative than by the methods at present in vogue.[1] Tropic acid is α-phenyl-β-hydroxypropionic acid and here, as in the case of Fischer's work with tyrosine, the hydroxyl group led to complications. Wollfenstein therefore prepared acetyl tropic acid, from this the acid chloride, and then condensed the acid chloride with tropine. The acetyl atropine thus obtained hydrolyzes into acetic acid and atropine merely by dissolving in water.



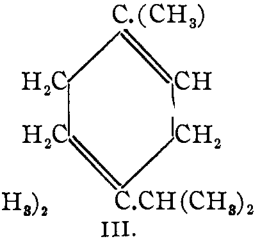
$$\begin{array}{l} CH_2.CH\text{—}CH_2 \\ \quad\; NCH_3\;\; CH.O.COCHCH_2OCOCH_3 + H_2O = \text{atropine} + \text{acetic acid.} \\ CH_2.CH\text{—}CH_2 \qquad\quad C_6H_5 \end{array}$$

Acetyl atropine.

Wallach[2] has shown that ordinary terpinene is not a homogeneous substance but that it is a mixture of which the main constituent is certainly α-terpinene or $\Delta^{1,3}$-dihydrocymol (I). Samples of terpinene prepared by four different methods, on oxidation all gave an erythrol, $C_{10}H_{16}(OH)_4$, which, on further oxidation yielded α,α'-dihydroxy-α-methyl-α'-isopropyladipic acid (II),



I. II.



III.

This acid could come only from α-terpinene (I). Besides the above oxidation products another erythrol was obtained which could not be further oxidized to a substituted adipic acid. This proves that another hydrocarbon is present with α-terpinene in ordinary terpinene, and Wallach concludes that this other hydrocarbon must be γ-terpinene (III). The reasons for this conclusion are too complex to be given here.

A long paper in Liebig's *Annalen* by Merling and Welde[3] on the synthesis of violet perfumes is a valuable contribution to that complex field. Their object was to determine as far as possible the constitutional conditions essential for this especial odor. They first proved that only those aldehydes of cyclo-citral which contain methyl groups in the positions adjacent to the aldehyde group give a compound with the odor of violets on condensation with acetone. This configuration is present in β-irone, the natural oil of violets, which is the condensation product of Δ_4-cyclocitral aldehyde (I) with acetone:

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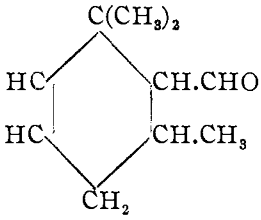
[1] *Arch. Pharm.*, **240,** 498 (1902).

[2] *Ann.*, **362,** 285 (1908).

[3] *Ibid.*, **366,** 119 (1909).



I.

They then tested non-cyclic derivatives with the aldehyde group between methyl groups as *e. g.*, isopropyl ethyl acetaldehyde,

$$C_2H_5.CH(CHO).CH(CH_3)_2,$$

and found that the acetone condensation product of this, while it had a pleasant odor, had no suggestion of violets. The presence of the aldehyde group in a hydroaromatic ring, between methyl groups, seems then to be essential for the production of a violet perfume. The remainder of their paper is taken up with a description of the methods of preparation of the materials for the synthesis of α- and β-irone which are Δ_3- and Δ_4-cyclocitral aldehyde condensation products with acetone, respectively. They conclude that α-irone has no perfume value above that of the natural oil of violets, which is β-irone, and neither have any advantage over the ordinary commercial product which is a mixture of α- and β-ionone, the Δ_2- and Δ_1 derivatives of the same cyclocitral aldehyde condensation product with acetone as the two irones. In passing, it may be worth mentioning that the German patents on ionone expired in April of 1908.

Chemistry of Dyestuffs.—Important advances have been made in the field of the natural dyestuffs so that the constitution of brazilin, haematoxylin, and their derivatives, may be considered as in the main established. Credit is chiefly due to W. H. Perkin, Jr.,[1] and his co-workers for these results, but the work is too complex to permit its being given even in outline in this paper.

Aniline black in its extreme insolubility and great stability has long defied attempts to gain an insight into its constitution. Willstätter,[2] in his characteristically concise manner, has attacked this problem with co-workers and has apparently been able to solve it. He has shown that the oxidation of aniline to quinone does not take place by way of phenylhydroxylamine as an intermediate product, but that aniline black is certainly produced as one of the steps. The amount of oxygen necessary to form aniline black was found to be 1.25 atoms for every molecule of aniline and the black thus produced had the composition $C_6H_{4.5}N$. The questions remaining to be settled were, how many of these units, $C_6H_{4.5}N$, are there in the molecule of aniline black, and how are they combined with each other? The first question was answered by hydrolyzing samples of the black with sulphuric acid when exactly one-eighth of the total nitrogen was split off as ammonia. Quantitative measurements of the amount of quinone obtained by the oxidation of the aniline black answered the second question. A yield of 93–95 per cent. of quinone was obtained. The only compound which seems to satisfy these facts is that one whose leuco base is the following:

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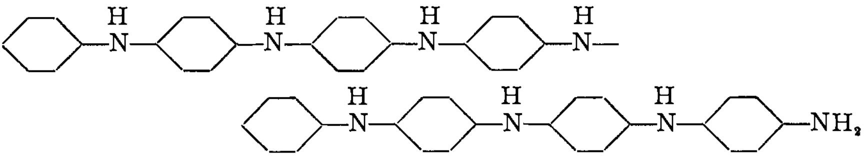
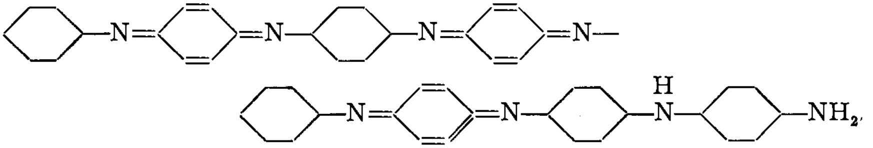
[1] *J. Chem. Soc.*, 93, 489, 1115 (1908).

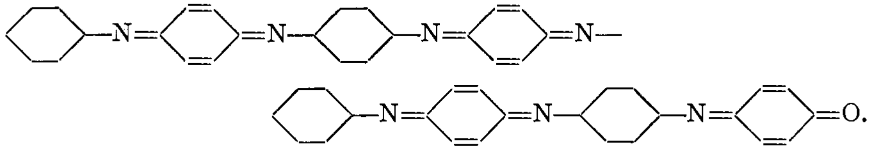
[2] Willstätter und Dorogi, *Ber.*, 42, 2147, 4118 (1909).



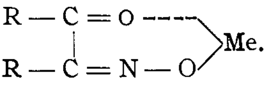
A chain of this type, with continuous para linkings, is the only one which could give a quantitative yield of quinone. The terminal amino group in such a chain is the only one which would be affected by hydrolysis, and therefore if the compound gives up one-eighth of its nitrogen on hydrolysis the molecule must contain eight amino groups, and therefore eight aniline residues in all. The black under discussion would then be $(C_6H_{4\cdot5}N)_8$ or $({}_{48}H_{36}N_8)$, which demands that six hydrogens be oxidized away from the above leuco base to form the dye.



This aniline black is in color blue-black and forms green salts, so it is not the valuable aniline black of commerce. To distinguish it from other blacks Willstätter calls it a triquinoid black. By further regulated oxidation a tetraquinoid black is produced in which the terminal benzene ring substituted with the amino group has become quinoid. This black, whose salts are also green, gives quinone quantitatively on oxidation and also yields one-eighth of its nitrogen on hydrolysis. By this hydrolysis a pure black is produced which does not change color with acids and which seems to be identical with the commercial black. This product must be represented by the following formula:



Werner[1] has made use of his theory of inner complex salts in an attempt to explain the nature of the metallic compounds (lakes) formed by mordanting dyes. He assumes the metal in these compounds to be a member of a heterocyclic ring, held there by one principal and by one secondary valence. The differences in color between the true salts of the metals and their lakes are ascribed to the peculiar influence of the secondary valence. The great stability of the lakes and the failure of the metals in them to respond to the ordinary ionic tests are explained on the same basis. The metallic compounds of many simple substances were discussed as illustrations of the theory, as *e. g.*, those of mono-oximes of diketones which he supposes to have the constitution



$$\begin{array}{l} R-C=O\text{----}\searrow \\ \quad\;\;| \qquad\qquad\qquad \rangle Me. \\ R-C=N-O\nearrow \end{array}$$

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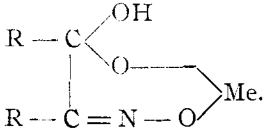
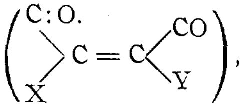
[1] *Ber.*, **41**, 1062 (1908).

Liebermann[1] replies to Werner by claiming that the peculiarities of the lakes may all be explained by his old theory of the formation of a heterocyclic ring in which the metal is held by two full valences. Compounds of the type of the above mono-oximes may be explained by assuming that they react in their hydrated form and produce a metallic compound with the structure

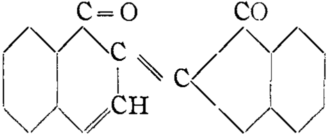


Liebermann's view-point has the advantage of employing only the accepted theory of valence.

Great interest has centered in the last few years in the preparation of dyes suitable for use in the hydrosulphite vat. The majority of these dyes are either of the indigo type or derivatives of anthraquinone. The valuable properties of thioindigo have greatly stimulated the preparation of new dyes of the indigo type. Friedlander[2] has coined the word "indigoid" as a class name for all compounds containing the chromophoric complex



in which the ring systems may be either aromatic or aliphatic and in which X and Y may be C, N, S or O. A great variety of compounds of this type can be prepared, of which the compound obtained by the action of isatine chloride on α-naphthol may be cited as an example:



Naphthalin-indole-indigo.

The technically important dyes of this class have been mostly derivatives of thioindigo because the introduction of substituents in the indigo molecule does not very materially alter the color.[3] Some halogenated indigos have been put successfully on the market and Friedländer[4] has shown that the "antique purple" of the classic period was a dibromo indigo obtained from a variety of snail *Murex brandaris* still common in the Mediterranean. Of thioindigo and its halogenated derivatives there are some fifteen different commercial marks for sale, which yield shades from red over orange to the blue and bright blue-violet. A number of these are unsymmetrical derivatives from hydroxythionaphthene and isatin or their derivatives as *e. g.*, thioindigo-scarlet R, which has the following structure:

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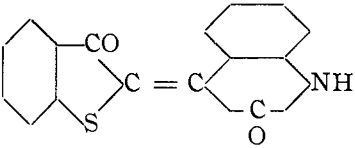
[1] *Ber.*, 41, 1436 (1908).

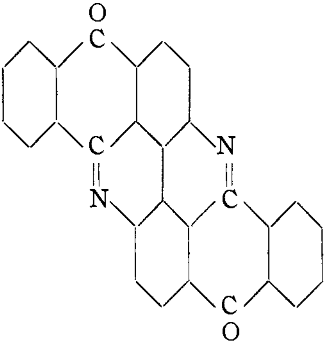
[2] *Ibid.*, 41, 772. *Monatsh.*, 30, 271 (1908).

[3] Cf. J. Rosenberg, *Z. angew. Chemie*, 22, 2129 (1909).

[4] *Ber.*, 42, 765 (1909).



The commercial success of indanthrene and flavanthrene has served to stimulate the production of anthraquinone dyes till at present a very wide range of colors can be obtained with these products. The chemistry of flavanthrene has been studied by Roland Scholl[1] who, in 1907, prepared the compound synthetically, showing it to have the following constitution:



In continuing his work Scholl has obtained seven reduction products of flavanthrene, finally preparing the oxygen-free base flavanthrine.[2]

Constitution and Color.—The vibratory nature of light makes it seem reasonable to conclude that colored substances, which are so by virtue of their power to absorb certain frequencies of vibrations, must have some sort of vibratory motions within themselves which give to them their selective absorptive power. In its ultimate analysis then the cause of color is vibration within the molecule. Whether or not we know enough of molecular physics to attempt at the present time the statement of theories as to the nature of these vibrations is an open question. A number of English investigators[3] have stated such theories, basing them on the results of their spectroscopic studies. Whether or not these theories will be of value to the science, time only will tell.[4] Their experimental work has, however, been of inestimable value in drawing attention to the necessity of applying spectroscopic methods to the study of the problem of color. Many of their observations have shown interesting analogies or have contributed to the settling of structural questions. Two examples from recent papers by Baly may be cited: 1,4,5,8-tetrahydronaphthalene has the same type of absorption spectrum as *p*-xylene, which serves to emphasize the similarity of their structures.[5]

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[1] *Ber.*, 40, 1691 (1907).

[2] *Ibid.*, 41, 2304, 2534 (1908).

[3] A review of these theories by W. J. Hale is to be found in *Pop. Science Monthly*, 72, 116 (1908).

[4] Cf. Michael, *Ann.*, 363, 45 (1908).

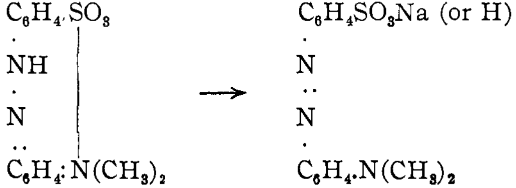
[5] *J. Chem. Soc.*, 93, 1902 (1908).

Cinnamylidenemalonic acid and its esters are yellow but its salts are colorless. The absorption spectra of all three, acid, ester, and salt are alike, thus showing that they are probably all similarly constituted.[1]

Hantzsch[2] has continued to bring forth much evidence in support of his theory that two substances differing in color, though they may be identical in all other properties, must be different in constitution. Hantzsch's theory is in fact a claim for the sufficiency of our present structural hypothesis in explaining color, as far as it can be explained in at all tangible terms. To him every change in color must be accompanied by a change in constitution, and such a change in constitution as can be expressed in terms of the generally accepted methods of structure writing.[3] The extensive debate between Hantzsch and Kaufmann during the past year or so has hinged upon this point. Kaufmann[4] claims that some substances with fixed constitutions will vary their real and their fluorescence color under the influence of mild external agents such as solvents, etc. There must be some variable in the molecule whose changes are casually connected with these variations in color. This variable, non-constitutional part he assumes to be "residual affinities" of the chromophore and the auxochrome groups. The state of these residual affinities, whether in combination with neighboring carbon atoms, with each other, or with molecules of the solvent determines the color of the substance. In terms of this theory all changes of color or of fluorescence can be readily explained, naturally enough, because residual affinities are of such elastic, undefined form that they can readily be molded to suit every demand made upon them. They and their near relatives, partial valences and secondary valences, are in fact the ghosts of modern chemistry. They walk among us constantly so that we all feel their presence, but no one has as yet been able to define their shapes or their sizes or to lay a hand upon them.

Hantzsch's theory, although it fails to explain much, certainly has the advantage of being tangible and of offering many opportunities for the application of experimental tests. A few examples from his work will suffice for illustration. Helianthin in its solid form is violet, in its solutions it is orange, and its sodium salt both in the solid form and solution is orange.[5] The absorption spectra of its orange solutions both as free acid and as salt are identical with similar derivatives whose azo character is not questioned. He concludes, therefore, that the orange forms are all azoid and that the violet form is quinoid as given in the following structures:

Violet. Orange.



$$\begin{array}{l} C_6H_4.SO_3 \\ \cdot \\ NH \\ \cdot \\ N \\ : \\ C_6H_4{:}N(CH_3)_2 \end{array} \longrightarrow \begin{array}{l} C_6H_4SO_3Na \text{ (or H)} \\ \cdot \\ N \\ : \\ N \\ \cdot \\ C_6H_4.N(CH_3)_2 \end{array}$$

Quinoid. Azoid.

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[1] *J. Chem. Soc.*, **93**, 1808 (1908).

[2] *Ber.*, **41**, 1171, 1189, 1204, 1216, (1908); **42**, 889, 966, 986, 1000, 1007 (1909).

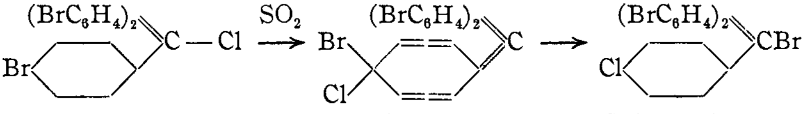
[3] In his last papers Hantzsch describes certain color changes which he claims are not accompanied by actual structural variations. Attempting to explain these facts he also falls back on secondary valences, whose variations he supposes to cause these more subtle color changes. *Ber.* **42**, 985 (1909).

[4] *Ibid.*, **41**, 4396, 4413 (1908).

[5] *Ibid.*, **41**, 1187 (1908).

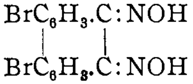
In another paper he describes a large number of salts of oximino ketones, R—CO—CNOH—R, with colorless cations.[1] These salts exist in the greatest variety of colors and mixed shades and he concludes that every salt with a distinctive color must be constitutionally different from salts of other colors and from the colorless form. In the work there is, however, a notable lack of distinctive proof, by reaction or by synthesis, which would positively connect a constitution with a color. The above assumption, for example, that the violet form of helianthin is a quinoid derivative is at best only very probable and it is devoid of actual experimental proof, other than the optical examination of similar derivatives with similar colors.

Gomberg[2] has been able to furnish definite experimental evidence that certain changes from colorless to colored forms in the triphenylmethane series are accompanied by a simultaneous transformation from benzoid to quinoid configurations. *p*-Tribromotriphenylcarbinol chloride, a colorless solid, dissolves in the ordinary organic solvents to a colorless solution but its solution in liquid sulphur dioxide is orange-red. When any of its colorless solutions in organic solvents are evaporated to dryness the original colorless carbinol chloride is recovered unchanged. If, however, the colored solution in liquid sulphur dioxide is evaporated to dryness the result is entirely different. A colorless solid is obtained which is mostly *p*-*p*′-dibromo-*p*″-chlorotriphenylcarbinol bromide. This means that the carbinol chlorine has exchanged places with one of the nucleus bromine atoms. The mechanism of the transformation will be clear if the following equation is examined:



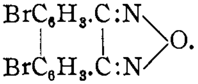
Solid-colorless. In solution orange-red. Solid colorless.

As this exchange of nucleus and carbinol halogen only takes place in colored solutions of the carbinol chlorides, and the exchange can be explained only by assuming the formation of a quinoid derivative, the latter state seems certainly to be connected with color as cause and effect. To conclude that because the quinone structure and color are related in the triphenylmethane series every quinone derivative must always be colored would, however, be stretching the theory further than the facts at present known warrant. A case recently observed by Schmidt and Mezger[3] illustrates this point. 2,7-dibromophenanthraquinone and its dioxime are both colored, but the oxime anhydride which still has the quinone configuration unchanged is colorless:



$$\begin{array}{l}BrC_6H_3.C:NOH\\ \quad |\qquad\ \ |\\ BrC_6H_3.C:NOH\end{array}$$

Ocher-yellow.



$$\begin{array}{l}BrC_6H_3.C:N\diagdown\\ \quad |\qquad\ \ |\qquad\ \ >O.\\ BrC_6H_3.C:N\diagup\end{array}$$

Colorless.

Tautomerism.—Michael[4] has discussed the phenomena of tautomerism and has concluded that two distinct types of reactions are ordinarily

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[1] *Ber.*, 42, 966 (1909).

[2] *Ibid.*, 42, 406 (1909).

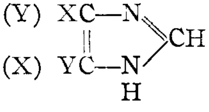
[3] *Ibid.*, 40, 4560 (1907).

[4] *Ann.*, 363, 20 (1908).

classed under this one head. These two classes he distinguishes as (1) desmotropism which is the reversible change of one form into another by the shifting of a hydrogen atom within the molecule and (2) merotropism, which is the irreversible change of one substance into the derivative of another under the influence of an active chemical agent. Both reactions are resultants of two factors, the free energy in the molecule, which naturally tends toward a minimum, and the chemical affinities of the specific groups undergoing change. These ideas Michael has illustrated on numerous examples. With various co-laborers[1] he then investigated several reagents to determine their value as diagnostic agents for stable keto or enol forms. Acetic anhydride, acetyl chloride and phenylisocyanate he found to give unreliable results, but tertiary amines, especially triethyl- and tripropylamine he found gave very consistent results. Tertiary amines unite with enols to form ammonium salts but do not form additive compounds with keto derivatives. The tertiary amines have little power to change keto derivatives over into enols so that only with desmotropes are the results of such a character that they require care in interpretation. A stable keto merotrope will not react with tertiary amines, but a stable enol merotrope will form ammonium salts with considerable evolution of heat, which ammonium salts will yield the free enol again on treatment with acid. A keto desmotrope may be changed over into the enol form, or *vice versa*, under the influence of tertiary amines, according to the stability relations of the two forms. From results with this tertiary amine reaction Michael and Smith classify a number of compounds as stable keto derivatives which have ordinarily been considered to be mixtures of the two forms in equilibrium with each other, *e. g.*, diacetylmethane and acetoacetic ester. This conclusion is not in harmony with the results of numerous physico-chemical investigations, but Michael and Smith point out that these physico-chemical results do not harmonize among themselves and are therefore never to be accepted when they contradict chemical evidence. It is interesting to note in this connection that Auwers[2] has called attention to the fact that physico-chemical methods have been of much less value in clearing up the constitution of the hydroxyazo compounds than have the purely chemical methods.

Mannich and Hancu[3] have shown that cyclic ketones, and Hancu[4] has shown that symmetrical aliphatic ketones are tautomeric substances (merotropes according to Michael), in that they yield more or less of the acetyl derivatives of their enol forms on long heating to high temperatures with acetic anhydride. On saponification the acetyl derivatives yield only the original ketones.

Gabriel[5] has shown that where two substituted imidazoles of the form



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[1] Michael and Smith, *Ann.*, **363**, 36, Michael and Cobb, p. 64, Michael and Murphy, p. 94 (1908).

[2] *Ann.*, **360**, 11 (1907).

[3] *Ber.*, **41**, 564 (1908).

[4] *Ibid.*, **42**, 1052 (1909).

[5] *Ibid.*, **41**, 1926 (1908).

would be expected only one can be obtained by synthesis. He therefore concludes that this is a case of "virtual tautomerism," where the imide hydrogen atom is in equilibrium between the two nitrogens.

Catalysis.—The mechanism of the catalysis of various organic reactions by acids and bases has been the subject of a number of investigations. Stieglitz[1] and Acree[2] have both obtained experimental evidence in favor of the theory that the catalyzer forms salts with some substance in the reaction undergoing catalysis. Stieglitz investigated the hydrolysis of imino esters and concluded that the rate of hydrolysis of the esters in acid solution is proportional to the concentration of the cation formed by the ester with the acid, and in alkaline solution is proportional to the concentration of the anion formed by the ester with the base. Acree studied the formation of acetooxime from acetone and hydroxylamine and concluded that the catalysis of this reaction by acids and bases depends in both cases upon salt formation with the hydroxylamine. Both investigators agree that the definition of catalysis, as accepted a few years ago, covers only certain ideal cases. Further study is needed before a satisfactory new definition can be formulated. The majority of chemists will probably agree with Stieglitz, Acree and others, that catalyzers exert their influence through the formation of intermediate unstable compounds which probably are salts. Since the work of Collie, Werner, Baeyer, and a host of others on the oxonium theory, the idea that these intermediate compounds are in most cases oxonium salts has steadily gained ground. That they may be carbonium salts has been suggested by Stieglitz,[3] but he concludes that at present the preference must be given to the oxonium form. The author of this review believes, however, that in the end evidence will be found to indicate that these compounds, if salts at all, are really carbonium salts. He bases this view on two things: first, the position of carbon in the periodic system, which would indicate a base-forming power greater than that of either nitrogen or oxygen, and second, on the generally unsatisfactory nature of the evidence in favor of the oxonium theory.

Rosanoff and Prager,[4] and Michael,[5] have simultaneously called attention to the fact that hydrochloric acid, which has always been assumed to be, with a few exceptions, a favorable catalyzer for esterifications, is in a good many cases a negative catalyzer. Michael uses this fact as an argument in support of the theory discussed above, that the catalytic influence of hydrochloric acid upon esterification is due to an intermediate salt formed with the alcohol. Hydrochloric acid will then increase or diminish the rate of esterification according as the acid being esterified reacts more readily with this hydrochloric acid-alcohol complex or with the free alcohol. The chemical nature[6] of the acid undergoing esterification will thus determine whether hydrochloric acid will

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[1] *Am. Chem. J.*, **39**, 29, 166 (1908).

[2] *Ibid.*, **39**, 300 (1908).

[3] *Ibid.*, **39**, 48 (1908).

[4] THIS JOURNAL, **30**, 1895 (1909).

[5] *Ber.*, **42**, 310, 317 (1909).

[6] Cf. Stewart, "Stereochemistry," p. 321.

act as a positive or a negative catalyzer. To determine the real rates of esterification of acids the reaction must be studied in the absence of all catalyzers. V. Meyer based his rule in regard to the esterification of di-*o*-substituted aromatic acids upon results obtained in the presence of hydrochloric acid. Hydrochloric acid acts toward the esterification of these acids as a negative catalyzer, but by heating them with alcohols alone they can be readily esterified. V. Meyer[1] was always very careful to state that his law held only for esterification in the presence of hydrochloric acid, therefore these new facts serve more to broaden his law than to contradict it. Rosanoff and Prager suggest the following wording so as to make the law general: "Aromatic acids, in which one or both of the positions ortho to the carboxyl group are occupied by substituents, unite with alcohols slower but not less completely than acids otherwise constituted."

Willstätter and Mayer[2] have revived a method, already patented and known in the chemical literature, for the reduction of unsaturated compounds with hydrogen at ordinary temperature in the presence of finely divided platinum. From phytol they thus prepared dihydrophytol, oleic acid ester gave stearic acid ester and benzoic acid gave some hexahydrobenzoic acid. Paal[3] has obtained the same results by the use of colloidal palladium.

The use of finely divided nickel oxide for the catalytic reduction of volatile organic substances at high temperatures has become general. Ipat'ev[4] has made several interesting observations on the finer details of this process. Nickel oxide, in an atmosphere of hydrogen, is reduced to metallic nickel at 200°, but when benzene is being reduced to hexahydrobenzene the nickel oxide is heated considerably higher without appreciable production of metallic nickel. If the nickel oxide is heated over the blast before using, its efficiency as a catalyzer is very considerably impaired. By analysis Ipat'ev showed that the unignited nickel oxide held a few per cent. of water and he attributes its better catalytic effect to this moisture. Senderens[5] has shown that silica and aluminium oxide have very peculiar effects upon the decomposition of alcohol and various organic acids at high temperatures. According to the previous history of the silica or the aluminium oxide employed as catalyzer, and the temperature at which the reaction is carried out, alcohol will produce a gas which is pure ethylene, or a mixture of ethylene and hydrogen, or practically all hydrogen. Acetic acid decomposes at 350° in the presence of aluminium oxide into acetone and carbon dioxide.[6] Ethyl ether breaks up at 300° into ethylene and water. If alcohol is passed over aluminium oxide below 300° at, *e. g.*, 240–260°, a good yield of ether is obtained with only slight quantities of ethylene.[7] Sabatier and Mailhe[8] have shown that a mixture of alcohol and ammonia passed over thorium

[1] Cf. *Ber.*, **41**, 4695 (1908).

[2] *Ibid.*, **41**, 1475 (1908).

[3] Paal und Jerum, *Ibid.*, **41**, 2273 (1908).

[4] *Russ. Phys. Chem. Soc.*, **40**, 1 (1908).

[5] *Compt. rend.*, **146**, 125 (1908).

[6] *Ibid.*, **146**, 1211 (1908).

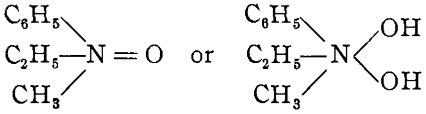
[7] *Ibid.*, **148**, 227 (1909).

[1] *Ibid.*, **148**, 898 (1909).

oxide at 360° will form primary ethylamine with some secondary amine and traces of the tertiary amine.

Stereochemistry.—The theory of Guye, that optical activity is a function of the differences between the weights of the groups about the asymmetric carbon atom, has been again brought into discussion. Recent writers[1] on stereochemistry agree that the theory is entirely insufficient, but because it is the only general theory of the relation between constitution and optical activity it still continues to suggest experimental work. Fischer and Flautau,[2] on the suggestion of van't Hoff, prepared propyl isopropyl cyanacetic acid and resolved it into its constituents. The theory of Guy requires that these constituents should be optically non-active, as the propyl and isopropyl group are identical in weight, but they were found to have an activity of ±11.4. Everat and Jones,[3] and Jones and Hill,[4] have examined a number of optically active ammonium derivatives and concluded that the constitutions of the groups about the asymmetric nitrogen have more influence than their weights. Bose and Willers[5] examined 42 optically active substances with seventeen different groups and conclude from their results that the theory of Guye is entirely at variance with the facts. Bose[6] suggests a modified form of Guye's equation for the asymmetry product in which no assumption is made as to the nature of the constants which represent the activity produced by each group about the asymmetric carbon atom. He then shows how such a modified expression suggests experimental tests which will either disprove or will furnish strong evidence in favor of the correctness of Guye's fundamental idea in regard to the asymmetry product. For the mathematical details of Bose's reasoning the original articles must be consulted.

Meisenheimer[7] has been able to prepare an optically active ammonium derivative where two of the five valences of the nitrogen are attached either to oxygen or to two hydroxyl groups:



Ethyl-methyl aniline oxide is optically active in aqueous solution as the free base, or in the form of its salts. As an explanation of this activity he assumes that four valences of the nitrogen atom are directed to the four corners of a tetrahedron and the fifth remains without fixed direction. The space arrangement then becomes similar to that about the asymmetric carbon atom. The two hydroxyls are not alike if the molecule is thus constructed, as one is fixed in position and the other is free to wander, so that the case under consideration would then really belong to the class of optically active ammonium derivatives having five unlike radicles. That the two hydroxyls of the hydrate form in its

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[1] Stewart, "Stereochemistry", p. 101; Werner, "Stereochemie", p. 133.

[2] *Ber.*, 42, 2981 (1909).

[3] *J. Chem. Soc.*, 93, 1789 (1908).

[4] *Ibid.*, 93, 295 (1908).

[5] *Z. physik. Chem.*, 65, 702 (1909).

[6] *Physik. Z.*, 9, 860 (1908); *Z. physik. Chem.*, 65, 695 (1909).

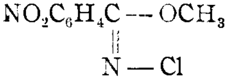
[6] *Ber.*, 41, 3966 (1908).

unionized state are really unlike seems very improbable to the writer of this review.

The phenomenon of auto-racemization so characteristic of the optically active ammonium salts has been investigated by E. Wedekind and his co-workers.[1] They have shown that when the active halogen salts are dissolved in chloroform the iodides racemize the most rapidly, the bromides next, and the chlorides are the most stable. This auto-racemization they proved to be due to the splitting of the ammonium salt into an alkyl halide and a tertiary amine, both of which are non-active.

Stieglitz and Hilpert[2] have isolated two forms of the chloroimido esters of several nitrobenzoic acids. These forms differ distinctly in physical properties, yet all of their reactions indicate that they are structurally identical. They must, therefore, be stereoisomers, probably geometrical isomers, of which one is the syn- and the other the anti-form:

$$\begin{array}{l} NO_2C_6H_4C-OCH_3 \\ \quad\ \ \| \\ Cl-N \end{array}$$



$$\begin{array}{l} NO_2C_6H_4C-OCH_3 \\ \quad\ \ \| \\ \quad\ \ N-Cl \end{array}$$

This is the first example of geometrical isomerism among derivatives where the nitrogen is attached on one side to a single element.

The limited space allotted for this review makes it impossible to even mention a great many of the valuable results obtained in organic chemistry during the past eighteen months. In view of the recent paper in THIS JOURNAL by W. A. Noyes[3] on "Molecular Rearrangements" that subject, which is at present receiving as much attention as any one field of organic chemistry, has not been discussed. Discussions of the special applications of general reactions, as Grignard's, and Friedel and Crafts' reactions, have been omitted, as well as descriptions of the synthesis of a vast number of new compounds belonging to already well-established classes.

UNIVERSITY OF MICHIGAN, ANN ARBOR.

NEW BOOKS.

Einführung in die allgemeine und anorganische Chemie auf elementare Grundläge. von DR. ALEXANDER SMITH, unter Mitwirkung des Verfassers übersetzt und bearbeitet von DR. ERNST STERN, Assistent am Königl. Material-prüfungsamt zu Gross-Lichterfelde-West. Mit einem Vorwort von Dr. FRITZ HABER, ord. Professor an der Technischen Hochschule zu Karlsruhe. G. Braun, Karlsruhe, i. B., 1909, pp. 677. Price, M. 9.

American chemists who owe so much of their advanced training to the German universities cannot fail to note with satisfaction that in reforming their methods of elementary chemical instruction the Germans are taking the American curriculum as a model. The German translation of Alexander Smith's laboratory manual which appeared some years ago has been widely adopted, and this excellent translation of the author's

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[1] E. and O. Wedekind, *Ber.*, 41, 1029 (1908); E. Wedekind and Paschke, *Ibid.*, 41, 2659 (1908).

[2] *Am. Chem. J.*, 40, 36, 150 (1908).

[3] THIS JOURNAL, 31, 1368 (1909).