classes of these nitrogen oxygen compounds behave altogether differently; and that only for the very limited group of nitroso compounds whose nitrogen atom is not directly linked to carbon is there anything like a clear comprehension of the details of the reaction.

EUGENE, OREGON,
August, 1901.

REVIEW.

A REVIEW OF SOME RECENT PROGRESS IN ORGANIC CHEMISTRY.[1]

It is with deep regret that I am obliged, at this first attempt of the Section, to bring a systematic review of recent progress in chemistry, to ask your kind indulgence for the many omissions and defects in this summary of the recent history of organic chemistry. The time at my disposal has been very short; the subject-matter, I need not say, is all too extensive. A painstaking German statistician has calculated that over 10,000 pages are needed to record the annual progress of organic chemistry. I have endeavored to report upon the work of some three years; the printed pages, if laid side by side, would make a solid field of type covering some 6,000 square feet—a large area for a critic to weed over by lamplight. Under the circumstances, I have ventured to select a few of what have seemed to me the more important achievements, and have called this paper "A Review of *Some* Recent Progress."

NOMENCLATURE AND REGISTRATION.

The important problem of naming organic compounds has not advanced much beyond the work of the Geneva conference in 1893. It will be remembered that the Geneva rules are fairly satisfactory only for the simpler fatty compounds; they are too cumbersome for complex fatty derivatives, and fail almost completely with the vast majority of ring compounds. It is still possible for ten chemists to describe one and the same substance under ten different names, without recognizing the identity of their descriptions. An important discovery by M. M. Richter, however, promises to be of great assistance in simplifying this difficulty. Richter has pointed out that while the name of an organic compound may not be characteristic, *its empirical composition is absolutely definite*. He has, therefore, undertaken the truly Herculean task of gathering nearly 80,000 organic substances together into a dictionary, grouping these according to the increasing complexity of their atomic composition. The result is a

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[1] Read at the Denver meeting of the Society, August, 1901.

monumental work,[1] whose use enables the chemist to identify an unknown compound in the shortest possible time.

At first sight, it may appear that the Richter system has serious disadvantages. For instance, no less than 52 compounds of the formula $C_{12}H_{16}O_3$ are to be found in this dictionary. Even if we should ascertain this formula for a newly-found substance, a huge problem remains. On the other hand, it is to be observed first, that Richter is not responsible for the isomerism of these 52 compounds; and second, that by thus grouping them all together in one place, the comparison of data is greatly facilitated. As a matter of fact, the most superficial determination of properties, once the composition is known, is all that is needed to pick out the desired name from the list. The ability of the Richter system to stand the test of actual use is shown by its adoption for the index of several important journals; *e. g.*, the *Berichte*, the *Annalen*, and the *American Chemical Journal.*

This general use of Richter's system is interesting from two rather different points of view. For one, it will serve to increase the respect of the organic chemist for quantitative analytical work. He has been compelled to identify his substances largely by their general reactions and relationships. He has even been proud of his skill in dispensing with analysis. But the analytical route is now the shortest method of identifying substances, and the organic chemist must again be broiled over his combustion furnace as in Liebig's time. I venture to predict a speedy improvement of this venerable contrivance.

The second feature takes a speculative turn. The present development of organic chemistry is due to the discovery of isomerism; *i. e.*, of the fact that *empirical composition does not suffice* to characterize a substance. It is curious that the fruits of this discovery should bring us back to one of the earliest ideals of modern chemistry. How this would have pleased Berzelius!

In the way of special propositions in nomenclature, it is worth while to note the suggestions of Vorländer,[2] that *all* univalent hydrocarbon radicals, both fatty and aromatic, be designated by the old term *alkyl;* that fatty alkyls be called *alphyls*, and aromatic alkyls be named *aryls.* Mixed fatty and aromatic radicals, such as benzyl, are to be called *alpharyl.* Acid radicals are to have the class name *aryl*, from which are then derived *alphacyl* and *aracyl* for fatty and for aromatic acid radicals, respectively. These suggestions seem to have been widely adopted.

The need of some comprehensive method of naming and registering organic compounds has been shown by Rey and by Kaufman,[3] in rather alarming fashion. Assuming not more than nine different substituents, hydrogen included, in the naphthalene

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[1] "Lexikon der Kohlenstoffverbindungen."

[2] *J. prakt. Chem.*, **59**, 247 (1899).

[3] *Ber. d. chem. Ges.*, **33**, 1910, 2131 (1900).

nucleus, 10,766,601 derivatives are possible. Organic chemistry is not likely to perish for lack of material, it would appear.

We cannot do more than refer here to Baeyer's proposed nomenclature for the so-called condensed carbon rings.[1] As with all of Baeyer's proposals, this one is sure to be universally employed.

MISCELLANEOUS COMPOUNDS AND REACTIONS.

Under this heading will be given a number of interesting or important facts that cannot well be classified under other topics. The order of arrangement is merely one of convenience.

The *paraffin hydrocarbons* will soon no longer deserve their name. The difference between them and the aromatic hydrocarbons, once so marked, has been shown by Worstall to be only a matter of degree.[2] They are attacked both by concentrated nitric and sulphuric acids, yielding nitroparaffins and sulphonic acids, just as benzene does. The action is much slower than in the latter case, however, and seems to reach its equilibrium at a much lower percentage of transformation.

In the *sugar group*, Ruff[3] has discovered a new method of passing from one sugar to the next lower in the series. This method consists in the oxidation of the calcium salts of the corresponding acids with hydrogen peroxide. He was thus able to prepare *d*-erythrose from *d*-arabinose, and to establish the generic relationship of the former to the sugar series.

Graphitic acid, obtained by the oxidation of graphite, has long been regarded as one of the mysteries of chemistry. It has recently been investigated by Staudenmaier,[4] who concludes that it is likely to remain a mystery for some time to come. The formulas and properties that have been previously ascribed to its various derivatives are entirely unreliable. Staudenmaier has found a very easy method of preparing the acid, suitable for lecture demonstration.

It will be remembered that a few years ago Nef was able to bring to a conclusion a century's work on *fulminic acid*, by showing that this interesting acid is the oxime of carbon monoxide, $C{=}N{-}OH$. This has recently been substantiated in a curious manner by Scholl.[5] The Friedel-Crafts reaction of mercury fulminate, benzene and aluminum chloride leads to the synthesis of benzaldoxime:

$$C_6H_6 + C{=}N{-}OH = C_6H_5CH{=}N{-}OH.$$

The Friedel-Crafts reaction itself, which Baeyer has called the magic trunk of the wizard because of the wonderful things it

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[1] *Ber. d. chem. Ges.*, **33**, 3771 (1900).

[2] *Am. Chem. J.*, **21**, 210 (1899); **20**, 664 (1898).

[3] *Ber. d chem. Ges.*, **32**, 3672 (1899).

[4] *Ibid.*, **32**, 2824 (1899).

[5] *Ibid*, **32**, 3494 (1899).

furnishes in inexhaustible supply, has been the object of careful study by Perrier[1] and others; and before long we may hope to understand this important process to a degree befitting its importance.

The bitter struggle over the constitution of the *diazo compounds* is drawing to a close. It will be remembered that Hantzsch has contended for a stereochemical explanation of diazo isomerism, whereas Bamberger stood out for a structural explanation of these phenomena. It would take us too far afield to enter into the details of this controversy here, and a few observations must suffice. Bamberger for the last three years has been allowing his case to go by default, a sign that he has recognized his defeat. Quite recently he has made an important admission of error with reference to the metallic derivatives of the diazo compounds. Hantzsch, meanwhile, with the agility that has characterized the evolution of his views, has returned to the proposition he had so strenuously opposed at first, that the isodiazo compounds are true nitrosamines in the free state. In connection with the diazo compounds, Hantzsch has elaborated a new theory of chemical processes which will be considered below.

The *uric acid* group is witnessing a decided "boom" during the last few years. Fischer's syntheses in this group are too well known to refer to now. W. Traube has recently discovered an entirely new synthesis of uric acid and its numerous congeners.[2] The method is too complex for description here; suffice it to say that it starts with cyanacetic acid, a compound easy to obtain in large quantities, and that Traube has already succeeded in obtaining xanthine, guanine, uric acid, and numerous alkylated derivatives of these. The yields are said to be almost quantitative.

The remarkable activity of investigation and synthesis in the uric acid group undoubtedly owes its origin to the hope of commercial success. Fischer's work has shown a very close connection between caffeine and uric acid; and a moderate fortune awaits him who will be able to prepare caffeine cheaply by a synthetic process. Aside from this material interest, however, the uric acid group occupies an important position in the purely scientific aspects of chemistry. On the one hand, the function of uric acid and its derivatives within the animal organism is a topic of the profoundest importance to physiology and dietetics. Great progress is to be expected when the advertisements of the Michigan "health food" people will be published in befitting detail in the *Berichte*. And on the other hand, a very curious isomerism has been brought to light among the mono-methyl uric acids. Four of these are foreseen by structural theories, whereas Fischer and Ach[3] have already discovered six. No explanation is offered

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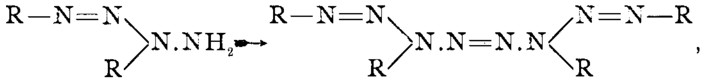
[1] *Ber. d. chem. Ges.*, **33**, 815 (1900).

[2] *Ibid.*, **33**, 3035 (1900).

[3] *Ibid.*, **32**, 2723 (1899).

so far, except that Fischer, than whom no man is a better judge, has expressed his conviction that stereochemistry and tautomerism have no application here.

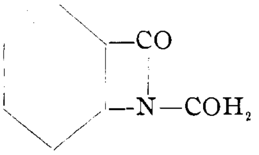
Among the large number of curious *nitrogen compounds and reactions* discovered during the past few years, a few must answer for the present. A long chain of nitrogen atoms has been prepared by Wohl and Schiff.[1] By oxidation of the so-called diazohydrazides,



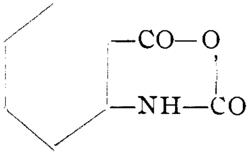
$$\genfrac{}{}{0pt}{}{R-N=N}{R}\!\!>\!N.NH_2 \longrightarrow \genfrac{}{}{0pt}{}{R-N=N}{R}\!\!>\!N.N=N.N\!<\!\genfrac{}{}{0pt}{}{N=N-R}{R},$$

which contain four nitrogens in a chain, octazons with eight atoms are produced. The mere existence of these chains is an important contribution to our knowledge of the combining power of nitrogen.

Another interesting datum with reference to this combining power is found in the structure of isatoic acid. Erdmann[2] has shown that this acid, which for a long time was supposed to have the formula I, really has the formula II:



I.



II.

The interesting feature of this discovery, which Erdmann seems to have missed, lies in the fact that until now isatoic acid was the only substance which had a free carboxyl group, —COOH, directly attached to nitrogen. Carbamic acid, $H_2N—COOH$, for example, is incapable of existing in the free state, and is known only in the shape of salts, esters, and other derivatives. It has now been shown that isatoic acid possesses a different structure than the one formerly assigned to it, so that we are forced to regard the combination of a carboxyl group with nitrogen as one of the incompatibilities of nature.

A third interesting discovery in the nitrogen territory was made independently by Wolffenstein, Bamberger, and Dunstan and Goulding. These investigators found that basic nitrogen atoms, as contained in the various amines, can be directly oxidized with hydrogen peroxide, yielding hydroxylamine derivatives. The most curious of these are the amine oxides, of the general formula

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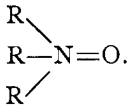
[1] *Ber. d. chem. Ges.*, **33**, 2741 (1900).

[2] *Ibid.*, **32**, 2159 (1899).



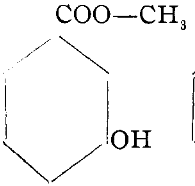
The amine oxides will play an important part in the future history of nitrogen.[1]

More or less connected with the chemistry of nitrogen, though in a manner by no means understood, are the *artificial medicaments*. It is a remarkable fact that very many of the most powerful drugs, including, of course, all the alkaloids, contain nitrogen. This is true of the artificial as well as of the natural members of the materia medica. I need only instance phenacetine and antipyrine. The study of the connection between chemical compositions and physiological action is steadily progressing, and the time seems not far distant when the scientific practitioner will invent new compounds off-hand at the bedside, instead of relying upon the pharmacopoeia. A long step in this direction has been taken by Einhorn,[2] who by systematic planning has obtained three new substitutes for cocaine :

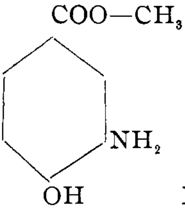
Orthoform, *p*-amido-*m*-oxybenzoic methyl ester (I).

Orthoform new, *m*-amido-*p*-oxybenzoic methyl ester (II).

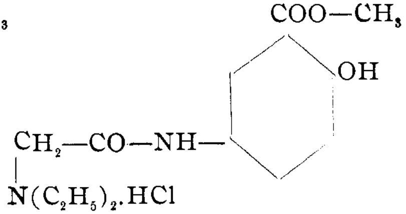
Nirvanin diethylglycocoll-5-amido-2-oxybenzoic methyl ester hydrochlorate (III).



I.



II.



III.

These anesthetics found immediate entrance into medical practice.

Attention should be called to a curious fact in all of the above formulae : *viz.*, that the *methyl* esters of the various substituted benzoic acids have been selected. The corresponding *ethyl* esters have no marked anesthetic properties. Here is a flagrant breach of the law of homology, which calls for protest from the systematists. It is a common statement in text-books of organic chemistry that all the members of a homologous series have identical chemical properties ; yet here we find the simple substitution of ethyl for methyl annihilating the most characteristic property of some rather complicated compounds. This remarkable influence

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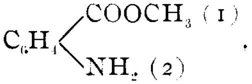
[1] *Cf.* Lachman : *Ber. d. chem. Ges.*, **33**, 1038 (1900).

[2] *Ann. Chem.* (Liebig), **311**, 33 ff (1900).

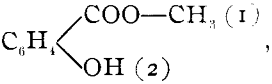
of the methyl group is not confined to drugs. It has recently been found that the *methyl ester of anthranilic acid*,



$$C_6H_4\begin{cases}COOCH_3\ (1)\\ NH_2\ (2)\end{cases}.$$

is one of the essential odorous principles of the orange blossom and the jasmine.[1] The corresponding *ethyl* anthranilate is almost odorless.

A similar instance is to be found in the esters of salicylic acid; methyl salicylate is the oil of wintergreen,



$$C_6H_4\begin{cases}COO{-}CH_3\ (1)\\ OH\ (2)\end{cases},$$

whereas ethyl salicylate has only a faint ethereal odor.

The above investigation of orange and jasmine oils furnished an additional surprise; for it transpired that the sweet, penetrating perfume of these flowers was due in no small part to *indol!!* Indol, a constant ingredient of feces, has long been noted for its penetrating qualities; its sweet perfume comes as a surprise to many a patient, long-suffering chemist. Yet there seems to be no doubt that pure indol has a decided perfume odor, and that the disagreeable smell of the substance as usually obtained is due to some impurities.

A friend of mine once advanced the theory that all pure substances were odorless, and that all odors were due to impurities. This theory was born of an article that harks back several years, but which is worth reviving here. It was found by Finckh[2] that the odor of the sulphides and mercaptans can be entirely removed by a simple process. Now the mercaptans have been known to cause public riots; and Emil Fischer once showed that 1/460,000,000 of one milligram of ethyl mercaptan can be detected by the average unaided human nose. Yet the pure mercaptan is odorless; so that this small amount of mercaptan that Fischer smelled owed its recognition to the much smaller amount of the impurity which it contained. An interesting corollary of my friend's theory is that even this impurity is odorless in the pure state, and owes its odor to the presence of some other impurity. The subject is a promising one for investigation.

The importance of *physical chemistry* for the development of organic chemistry is increasingly manifest, and grows day by day. I need not more than refer to the use of physical constants in the determination of molecular structure; the methods and results of "spectro-chemistry," molecular-volumetric studies, thermochemical investigations, etc., are sufficiently well known. It will be sufficient to emphasize the warning that all of these methods

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[1] Hesse: *Ber. d. chem. Ges.*, **32**, 2611 (1899); H. and E. Erdmann: *Ibid.*, p. 1213.

[2] *Ber. d. chem. Ges.*, **27**, 1239 (1894).

depend upon extrapolations the moment they are applied to new classes of compounds, and that they share with all other extrapolations the risk of running ahead of the facts. This seems notably true of the spectro-chemical studies of nitrogen compounds. Nor need I refer to the use of electrolytic conductivity for studying the dissociation of organic acids, bases and salts; these applications are sufficiently obvious.

It is in the use of the physico-chemical methods of thinking that organic chemistry will make the greatest progress. Thus, the study of reaction velocities, of the really active molecules when two or more substances are brought together, of the consequences rather than of the fact of ionization, have already made notable additions to our comprehension of organic reactions. A few examples will suffice.

Thus, Lewkowitsch was able to show by a study of reaction velocities that when fats are saponified the acid radicals attached to glycerine are separated one at a time, and not all three simultaneously.[1] Hantzsch has made continual use of electrolytic methods for tracing out the isomerization of diazo compounds (the references are too numerous to be cited). Walker has shown that the historical isomerization of ammonium cyanate to urea takes place between the ions of the salt, and is not a so-called "molecular rearrangement."[2] And numerous investigations of organic reactions have been carried out by H. Goldschmidt and his pupils upon a physico-chemical basis.[3]

The use of the electric current for oxidizing and reducing organic compounds affords another instance of the interrelation of physical and organic chemistry. The successful employment of the electric current calls for a very careful study of the electrical processes themselves, as may be seen from the recent work of Tafel.[4] Once the details are mastered, however, excellent results can be obtained.

It is to be hoped that the time is not far distant when the word "catalysis" will vanish from the chemist's daily vocabulary. At present, it is merely a mystifying cloak to conceal our ignorance. It will be shown below that in the case of auto-oxidation the function of the catalyzer is growing clearer. Meanwhile, the discovery of new catalyzers, that is to say, of deeper mysteries of reaction, proceeds with unabated vigor. Michael has recently made the remarkable observation that the presence of methyl cyanide greatly increases the reaction-velocity of metallic sodium on organic compounds.[5] Thus, methyl iodide reacts very slowly with sodium in the cold; a few drops of methyl cyanide cause the reaction to proceed almost with violence.

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[1] *Ber. d. chem. Ges.*, **33**, 89 (1900).

[2] *J. Chem. Soc.*, **71**, 489 (1897).

[3] *Cf. Ber. d. chem. Ges.*, **33**, 1140 (1900).

[4] *Ber. d. chem. Ges.*, **33**, 2209 (1900).

[5] *Am. Chem. J.*, **25**, 419 (1901).

The stereochemistry of carbon has made no notable progress during the last few years. A great deal of work has been done, but this has been devoted to extending our knowledge of the applications of stereochemistry rather than to enlarging our knowledge of the subject itself. In this connection, a recent utterance of Emil Fischer is of some significance.[1] He rebukes the general tendency to rush to stereochemistry as a final explanation of isomerism, and warns us to be ever mindful of its limitations and imperfections.

It is often the simplest cases of isomerism that are the hardest to explain. A simple case that *can* be explained therefore possesses a double interest. Keiser has obtained a second form of acetylene diiodide;[2] the best explanation is that of stereoisomerism :

$$\begin{array}{ccc} H-C-I & \qquad & H-C-I \\ \| & & \| \\ H-C-I & & I-C-H \end{array}$$

We are here crowding closely upon the final explanation of the isomerism of unsaturated compounds, for the geometrical interpretation does not please everybody.[3]

Another observation connected with stereochemistry deserves a moment's attention. W. A. Noyes has announced that optical activity may be present in substances that do *not* contain an asymmetric carbon atom.[4] Baeyer made a similar announcement a few years ago, and anent a very similar compound. Baeyer withdrew his announcement a few months later ; I fear the similarity will extend to the same point in the former instance. Noyes' observation is important—if true.

Buchner's discovery that alcoholic fermentation is a chemical and not a physiological process is too well known to require detailed presentation here. Suffice it to say that the numerous skeptics who assailed this discovery at its first appearance, have either been silenced or convinced. One recent interesting confirmation is worth nothing ; it is possible to kill the yeast cells completely, so that further growth and reproduction ceases ; these dead yeast cells still possess the power of fermentation.[5] Further proof of non-vital fermentation would seem to be unnecessary ; the fact being established, the mechanism now calls for careful study.

An observation that promises to be of much significance was recently made by Gomberg.[6] If triphenylchlormethane be treated with various metals, the halogen atom is removed, and a highly unsaturated hydrocarbon remains :

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[1] *Ber. d. chem. Ges.*, **32**, 2726 (1899).

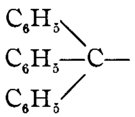
[2] *Am. Chem. J.*, **21**, 261 (1899).

[3] *Cf.* Micheal : *J. prakt. Chem.*, (2), **52**, 289 (1895).

[4] *Am. Chem. J.*, **24**, 289 (1900).

[5] *Cf.* Bokorny : *Chem. Centrbl.*, (1901), I, p. 1207.

[6] *Cf. Am. Chem. J.*, **25**, 315 (1901).



Gomberg assumes this hydrocarbon to be triphenylmethyl, and ascribes its unsaturated properties to the presence of a trivalent carbon atom. It is too early to dilate upon the consequences of this discovery ; but when the conditions which limit the existence of trivalent carbon are better known, a rather serious review of present conceptions will be inevitable.

The chemistry of naturally occurring substances, which engrosses the attention of a large number of the world's most skilful chemists, is of rather too detailed and complicated a character to be incorporated in a brief review like this. To be properly presented, the progress made in the study of the terpenes, of camphor, of caoutchouc, of starch, of cellulose, of the innumerable natural and artificial dye-stuffs, should in each case have a whole paper devoted to that one subject only ; and it seems better to omit their consideration altogether than to attempt a fragmentary and unsatisfactory jumble of facts.

The interests of the hour, however, permit of one exception to this sweeping exclusion. The chemical world has recently been stirred to the highest enthusiasm by the successful commercial synthesis of indigo. The laboratory synthesis of indigo was achieved long ago by Baeyer and others ; but the transfer of this laboratory process to the factory on a scale to permit of competition with natural indigo offered innumerable obstacles, and over twenty years of unexampled industry and intelligence were necessary before the problem was solved. Many a sermon can be preached upon this achievement as a text ; such as the examples set in patience, in foresight, in intelligent cooperation of the scientist and the technologist, in the expenditure of enormous sums for "scientific" work, etc. From the scientific side, it is a matter of chemical history that many of the modern problems and achievements took their rise in and around the investigations of indigo. H. Brunck, one of the directors of the "Badische Anilin und Soda Fabrik," has recently given an outline of the methods employed by his factory in the elaboration of their successful venture.[1] Permit me to outline the actual manufacture of indigo as it is carried out now by the Heumann process (D. R. P., 91202).

Starting with naphthalene, the cheapest and most abundant of the coal-tar ingredients, oxidation with highly concentrated sulphuric acid gives phthalic acid (and sulphur dioxide):

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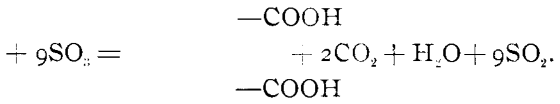
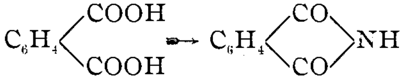
[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 71, (1900).



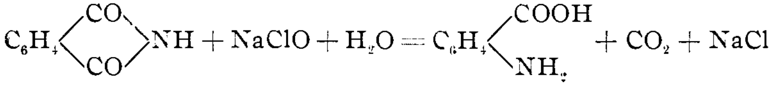
$$+ 9SO_3 = \begin{matrix}-COOH\\ \\ -COOH\end{matrix} + 2CO_2 + H_2O + 9SO_2.$$

10,000 tons of naphthalene are used annually.

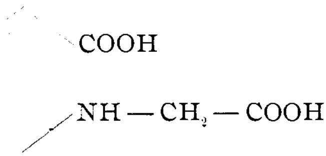
The recovery of this sulphur dioxide (some 40,000 tons annually) is an important matter; and it is interesting to note that the new "Badische" contact process is absolutely essential to the economical reconversion of sulphur dioxide into trioxide. This oxidation is accomplished by the air, so that at bottom it is the oxygen of the air that oxidizes naphthalene to phthalic acid. To give some idea of the immensity of this manufacture, even at this early stage of its development, a simple calculation shows that each year the oxygen standing over $1\frac{1}{4}$ acres of the earth's surface is completely exhausted. The phthalic acid thus obtained is converted into phthalimide by a process not given to the public:



Over 1,200,000 lbs. of ammonia are needed for the annual output. By means of sodium hypochlorite, phthalimide is converted into anthranilic acid:



The anthranilic acid thus obtained is united with chloracetic acid, forming phenylglycocollorthocarboxylic acid:



For this reaction, the "Badische" annually consumes 4,500,000 pounds of glacial acetic acid, requiring 26,000 cords of wood for their production. The chlorine needed for making chloracetic acid and anthranilic acid (above), is generated electrolytically,[1] and purified by liquefaction. 10,000,000 pounds of salt are consumed for this purpose (the contents of more than 37,000,000 gallons of sea-water, or of a cube of sea-water 368 feet on edge).

By fusing the last-named product (phenylglycocollcarboxylic acid) with caustic soda, two products may be obtained, according to conditions: indoxyl (I), or indoxylic acid (II):

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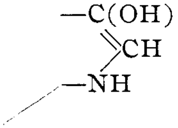
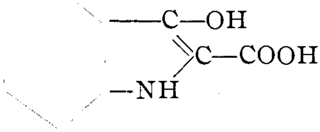
[1] Assuming an average current yield, 9,500,000 kilowatts or a steady consumption of 350 H. P., every second of the year are required for this process.

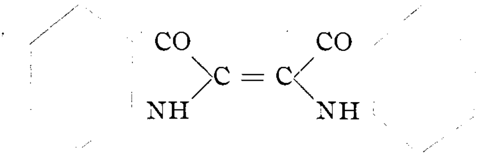


I.



II.

These, when oxidized by air in presence of alkalies, pass into indigo:



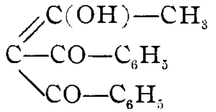
The present annual production of synthetic indigo has not been given to the public, but from the data obtainable it cannot be far from 3,000,000 pounds—about one-fourth of the world's supply. It is going to be a question of business rather than of manufacture when the indigo factories will have supplanted the indigo fields. Some of the above calculations will give a faint idea of the purely commercial side of this stupendous undertaking. The "Badische" has already invested over $4,500,000 in the plant and preliminary experiments.

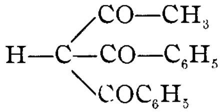
THE NEW ORGANIC CHEMISTRY.

The investigations we have just passed in rapid review have this in common, that they belong to the established order of things, and offer novelty chiefly in facts, hardly at all in principle. There is a newer organic chemistry in the air, however, just as there are a newer inorganic and a newer physical chemistry; and the developments of the newer organic chemistry are likely to be as startling as those of the older branches. The new organic chemistry at present tends in two directions, both of which shall engage our attention for a few minutes. The one is comprehended under the phenomena of tautomerism; the other deals with the chemistry of those elements other than carbon which enter into organic compounds.

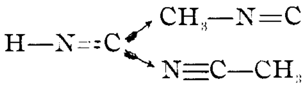
Tautomerism and its allied phenomena constitute one of the most difficult subjects of experimental science. Perhaps it will be best to give first of all a résumé of the nomenclature adopted by most of the investigators concerned in this work. By tautomerism in general, chemists have been accustomed to mean the ability of a single substance to behave as if it had two or more different structures, or to give derivatives belonging in two or more different classes. The closer investigation of these cases has shown that a much more careful method of classifying the facts is necessary.[1]

When two or more substances exist, so closely related that they pass into each other spontaneously, or upon very slight provocation (stereoisomerism being excluded), we speak of desmotropy; *e. g.*, dibenzoylacetyl methane, which forms the desmotropic isomers:[2]

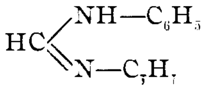


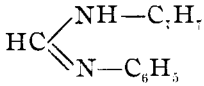


If we have two sets of derivatives, but only one mother-substance extant in the free state, we have a case of tautomerism proper; *e. g.*, hydrocyanic acid, from which we can obtain two distinct series of esters:



A similar tautomerism exists in the case of the amidines; *e. g.*, phenyltolyl formamidine, which behaves as if it possessed both of the following formulas:





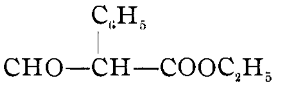
Such a case, where both tautomeric forms possess identical chemical character, is described as virtual tautomerism. Functional tautomerism exists where the (two) forms have different chemical character, as with acetoacetic ester; this reacts as a ketone,

$$CH_3—CO—CH_2—CO—OC_2H_5 \text{ keto form,}$$

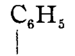
and as an unsaturated alcohol,

$$CH_3—C(OH)=CH—CO—OC_2H_5 \text{ enol form.}$$

Desmotropic isomers tend to change into each other upon fusion, upon solution, in various solvents, etc.; in nearly all instances, a condition of equilibrium is finally reached, when we have the isomers present at the same time. This condition is known as allelotropy. An example is found in Wislicenus' phenylformylacetic ether, which upon solution in alcohol or in chloroform forms an allelotropic mixture of the two forms:



$$CHO—\overset{\overset{\displaystyle C_6H_5}{|}}{C}H—COOC_2H_5$$



$$CH(OH)=\overset{\overset{\displaystyle C_6H_5}{|}}{C}—COOC_2H_5$$

It sometimes happens that of a pair of desmotropic substances, the conditions of equilibrium are such that one can exist only in

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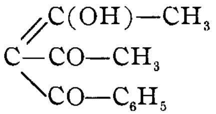
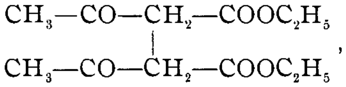
[1] *Cf.* Rabe: *Ann. Chem.* (Liebig), **313**, 129 (1900).

[2] *Cf.* Claisen: *Ibid.*, **291**, 25 (1896).

traces ; this limiting case of desmotropy is called pseudomerism ; *e. g.*, benzoyldiacetylmethane :[1]



The investigation and definition of substances in this category is an exceedingly tedious and difficult affair. Without going into details, one citation will suffice. Diacetosuccinic ester,



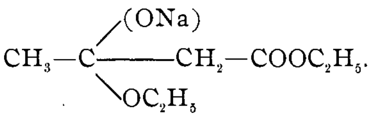
$$\begin{array}{l} CH_3-CO-CH_2-COOC_2H_5 \\ \qquad\qquad\quad | \\ CH_3-CO-CH_2-COOC_2H_5 \end{array},$$

can exist in no less than thirteen different forms, of which Knorr has already described five.[2]

The question of tautomerism calls to mind the old battle-ground of acetoacetic ether. I have no desire to open old wounds, and so will cite only one publication dealing with this vexed question. Michael disagrees with Claisen's commonly accepted theory of the synthesis of acetoacetic ether (the addition of sodium ethylate to acetic ether, with subsequent condensation and elimination of alcohol), because metallic sodium acts upon acetic ether so much better than sodium ethylate. Michael thinks the primary formation of sodium acetic ether much more probable,[3]

$$CH_2(Na)-COOC_2H_5.$$

This unsaturated compound then adds a molecule of unchanged acetic ester,



We cannot do more than refer to the tautomerism of the acid amides[4]

and to that of the oxyazo compounds, which seem to be either phenols or quinone-hydrazones according to circumstances.[5] In these cases, as in many others, two general rules must ever be kept in mind: One that generalizations are misleading, and that each case must be investigated upon its own merits,[6] the

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[1] *Cf.* Knorr : *Ann. Chem.* (Liebig), **306**, 350 (1899).

[2] *Ibid.*, **306**, 332 (1899).

[3] *Cf. Ber. d. chem. Ges.*, **33**, 3731 (1900).

[4] *Cf.* Titherley : *J. Chem. Soc.*, **79**, 391 (1901).

[5] *Cf.* McPherson: *Am. Chem. J.*, **25**, 485 (1901).

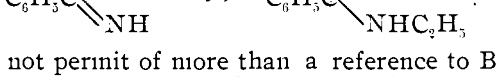
[6] *Cf.* Claisen: *Ann. Chem.* (Liebig), **291**, 45 (1896).

other that the metal derivatives (salts) of tautomeric and desmotropic forms are almost always constituted with their metal attached to oxygen when that is possible. This latter rule, laid down by Michael, was formally approved by no less an authority than Baeyer a short time ago.[1]

This theory of Michael's was recently elaborated and developed by Hantzsch, in connection with the latter's investigation of the diazo compounds.[2] In order to determine which of the two possible structures a tautomeric compound may have, Hantzsch shows that if one form may be acid in character the diagnosis is easy. If the given substance have the acid formula, it will be an electrolyte, and will form salts instantaneously; if it possess the neutral formula, it will (usually) be a non-conductor, and it forms salts with measurable velocity. It was this theory that led Hantzsch to revise his erstwhile views of the isodiazo compounds.[3]

Differing from tautomerism in outward appearance, yet closely related in their internal mechanism, are those reactions for which we possess no good English name. The Germans call them "Umlagerungen;" we are obliged to use the much more awkward term "molecular rearrangements." Fittig has long been engaged in studying the rearrangements occurring in unsaturated acids. The double bond in these acids seems to migrate from one part of the molecule under conditions that do not admit of prophecy,[4] so that in spite of the enormous amount of labor devoted to this investigation by Fittig and his pupils, no reliable generalizations can be drawn of the behavior of these substances.

Interesting rearrangements have been studied by H. L. Wheeler and his pupils.[5] These deal with the changes occurring in various acid amide derivatives. To cite only one example, phenylformimido ether is easily isomerized into ethyl benzamide,



$$C_6H_5C\begin{matrix}\diagup OC_2H_5\\ \diagdown NH\end{matrix} \rightarrow C_6H_5C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NHC_2H_5\end{matrix}.$$

Time will not permit of more than a reference to Bamberger's study of the rearrangements of aromatic nitrogen compounds; *e. g.*, phenylhydroxylamine[6] forms a complex mixture of products on treatment with acids or alkalies. Bamberger assumes the intermediate existence of compounds with univalent nitrogen.

The second phase of the new organic chemistry is still in its beginnings. While the chemistry of carbon in its organic derivatives is by no means exhausted, an ever-increasing army of in-

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[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 64 (1900).

[2] *Cf.* above.

[3] *Cf. Ber. d. chem. Ges.*, **32**, 575 (1899).

[4] *Ann. Chem.* (Liebig), **304**, 117 (1899).

[5] *Am. Chem. J.*, **23**, 135 (1900).

[6] *Ber. d. chem. Ges.*, **33**, 3600 (1900).

REVIEW

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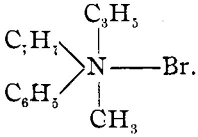
vestigators is devoting itself to the study of the other elements which enter into organic compounds. To be sure, we have long been aware of the development of "nitrogen chemistry;" but the peculiarities of nitrogen in its numerous compounds have been so intimately bound up with the history and progress of carbon chemistry proper, that we have not been conscious of any sharp line of demarcation. But now that we are beginning to be interested in the welfare of the carbon derivatives of other elements, the time seems ripe for a systematic attempt to "organize" inorganic chemistry; *i. e.*, to study the inorganic elements as carbon has been studied. Much valuable material has already been collected for this purpose.

During the past year or two, much interest has been accorded the stereochemistry of other elements. It is hardly necessary to recall the tremendous influence that the theories of van't Hoff and LeBel have had on the growth of carbon chemistry during the past twenty years. LeBel himself extended his studies to nitrogen, and had succeeded in obtaining an asymmetric nitrogen compound possessing optical activity.[1] To be sure, there was considerable skepticism about LeBel's results, until he showed that the greatest care is necessary in separating the optical isomers by fermentation, the method he had adopted. How quickly our views on such things change! Only two years ago Marckwald published some work to prove conclusively that these so-called isomers could not be separated.[2] To-day a dozen groups of isomers have been carefully studied. There was needed only the proper reagent. This was found by W. J. Pope in camphor sulphonic acid, $C_{10}H_{15}O.SO_3H$.[3] A short time before, Wedekind[4] had prepared two isomeric forms of a substituted ammonium salt; *viz.*, benzylphenylallylmethyl ammonium bromide (and iodide),

α- and β-



$$\alpha\text{- and }\beta\text{-}\ (C_7H_7)(C_6H_5)N(C_3H_5)(CH_3)\text{—}Br.$$

These isomers were inactive. Pope succeeded in separating the α-form into two optically active modifications, turning polarized light to the right and to the left almost equally ($[\alpha]_D + 68.6°$ and $-67.3°$). Pope has since then prepared numerous other active ammonium compounds.

The sulphur atom also has the power of becoming asymmetric. Pope and Peachey[5] have isolated an optically active *d*-methyl-

[1] *Compt. rend.*, **112**, 724 (1891).

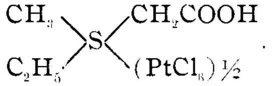
[2] *Ber. d. chem. Ges.*, **32**, 560 (1899).

[3] *J. Chem. Soc.*, **75**, 1127 (1900).

[4] *Ber. d. chem. Ges.*, **32**, 517 (1899).

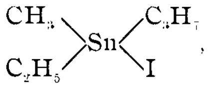
[5] *Loc. cit.*, p. 1072.

ethylthetin chlorplatinate,



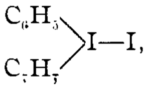
The asymmetric sulphur atom is easily racemized ; *i. e.*, rendered inactive by isomerization of half the molecules present.

Tin, an element resembling carbon and sulphur in that it can become quadrivalent, may also be rendered asymmetric and optically active.[1] Methylethylpropyl stannic iodide,



is an oil, and is dextrorotatory. The chief peculiarity of this asymmetric tin atom, however, is that no laevorotatory modification exists. As fast as the dextro form separates, the remaining laevo racemizes itself, thus forming fresh dextro, which alone separates. By completely evaporating the solution to dryness, the whole of the previously inactive salt is converted into its dextrorotatory isomer. This fact is of great significance for the future of stereochemistry.

Efforts to render the iodine atom in iodonium compounds asymmetric have proved abortive so far.[2] Phenyltolyliodonium iodide,



could not be rendered optically active.

It is to be expected that molecular asymmetry will be discovered in a great many other elements. Numerous elements are capable of combining with carbon radicals, and many curious compounds have resulted. We cannot do more at this time than refer to the extensive studies that Michaelis has been carrying on for years with the organic derivatives of selenium, tellurium, phosphorus, boron, silicon, etc. Michaelis has recently told us his motive in this work. He points out[3] that the type theory, to which organic chemistry has owed so much of her early progress, has been deserted by the modern "organiker." His own work has been carried on for the express purpose of developing this theory, which he hopes will eventually lead to an insight into the real laws of combination.

Quite a number of new mercury compounds of organic radicals have been prepared recently, a number of investigators apparently stumbling upon them at about the same time. Thus, Dimroth[4] has found that aromatic compounds generally easily replace

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[1] *Proc. Chem. Soc.*, **16**, 42 (1900).

[2] Kipping and Peters : *Proc. Chem. Soc.*, **16**, 62 (1900).

[3] *Ann. Chem.* (Liebig), **314**, 276 (1901).

[4] *Ber. d. chem. Ges.*, **31**, 2154 (1898); **32**, 758 (1899).

one or more hydrogen atoms by univalent mercury radicals; a different class of aromatic quicksilver compounds related to benzoic acid are described by Pesci;[1] whereas Hofmann and his pupils[2] have found that in the fatty series four different types of substitution of mercury for hydrogen can be distinguished.

Even the chemistry of so well-known an element as oxygen has been greatly extended by the organic chemist within the last few years. One important topic, though outside the lines of organic chemistry proper, may be alluded to. The phenomena of auto-oxidation have excited much interest. Many substances which are absolutely indifferent towards free oxygen (moist or dry) are easily oxidized in the presence of certain other substances. In many instances, these "contact-substances" or catalyzers are themselves oxidized at the same time. In other cases, they remain unchanged. The exact mechanism of auto-oxidation still needs very careful study, in which Manchot[3] has made an excellent beginning. Hydrogen peroxide often plays an important part in these reactions as an intermediate product. In other cases, again, Baeyer and Villiger have been able to demonstrate the intermediate formation of complex organic hyperoxides;[4] thus benzaldehyde, which in moist air is oxidized to benzoic acid, first takes up a molecule of oxygen, forming benzoyl hydroperoxide,

$$C_6H_5CHO + O = C_6H_5CO - O - OH.$$

This will oxidize a second molecule of benzaldehyde,

$$\begin{array}{l} C_6H_5CO\text{—}O\text{—}OH \\ C_6H_5CHO \end{array} + = \begin{array}{l} C_6H_5CO\text{—}OH \\ C_6H_5CO\text{—}OH \end{array} + H_2O,$$

but other substances are usually oxidized first if they are present.

Baeyer and Villiger have also prepared mono- and diethylhydrogen peroxide. The former, preferably called ethyl hydroperoxide, is easily prepared by action of hydrogen peroxide upon ethyl sulphate. It has the formula $C_2H_5\text{—}O\text{—}OH$, is fairly stable, and differs from its mother-substance hydrogen peroxide (now called hydroperoxide) in possessing no reducing properties whatever; it is merely an oxidizing agent.[2]

The same chemists obtained diethyl-peroxide from the same reagents in different proportions. It has the formula $C_2H_5\text{—}O\text{—}O\text{—}C_2H_5$; it has neither oxidizing nor reducing properties. Reducing agents convert it into alcohol. From the behavior of these two compounds Baeyer thinks that hydrogen peroxide itself has the old formula HO—OH; the existence of

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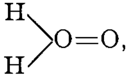
[1] *Atti dei Lincei Roma.* (5), **9**, 255 (1900).

[2] *Cf. Ber. d. chem. Ges.*, **33**, 1328-1364.

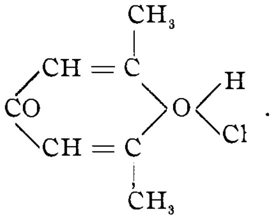
Cf. Ztschr. anorg. Chem., **27**, 397 (1901).

[4] *Ber. d. chem. Ges.*, **33**, 1581 (1900).

[5] *Ibid.*, **34**, 738 (1901).

quadrivalent oxygen in its molecule, as in the suggested formula  $\begin{matrix}H\\H\end{matrix}\!\!>O=O$, appears to be excluded.[1]

But although hydroperoxide may not contain quadrivalent oxygen, the fact that oxygen does become quadrivalent in some of its compounds has been established by Collie and Tickle.[2] Dimethyl-pyrone forms salts with various hal-hydric acids; *e. g.*, the hydrochlorate



These salts behave like the salts of a very weak base, and are completely hydrolyzed in dilute aqueous solution. If the addition of hydrochloric acid had occurred within the carbon ring, this hydrolysis would not manifest itself.

Oxygen owes its name to its strong acid-forming tendencies. We should expect that as we increase the amount of oxygen in a given molecule, the acid properties of that molecule would show a proportional augmentation. But such does not seem to be the case. If in benzoic acid, $C_6H_5CO—OH$, we introduce a third oxygen atom in the place where it ought to have the greatest acidifying influence (*viz.*, in the carboxyl group itself, $C_6H_5CO—O—OH$), the resulting compound (benzoyl hydroperoxide) is not only less acid than benzoic acid, but is actually weaker than carbonic acid.[3] It would have been difficult to foresee this.

SOME NEW ORGANIC THEORIES.

Time and space will not permit more than a brief reference to the recent endeavors to extend our fundamental conceptions of organic processes. For many years, chemists have been content to study organic chemistry with attention fixed chiefly upon matters of detail. The larger aspects of the subject have lain dormant until quite recently. During the last few years, however, an effort has been made on several sides to replace some of our theoretical views by others better suited to present conditions. For it must not be concealed that many investigators are dissatisfied with structural and with stereochemical methods of explana-

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[1] *Ber. d. chem. Ges.*, **33**, 3392 (1900).

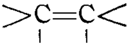
[2] *J. Chem. Soc.*, **75**, 710 (1899).

[3] Baeyer-Villiger: *Ber. d. chem. Ges.*, **33**, 1569 (1900).

tion, dissatisfied with the idea of valence, aye, even with the atomic theory itself.[1]

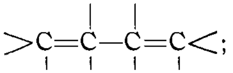
In the nature of things, all recent and untried theories meet with opposition ; they are often crude in detail, sometimes in error as to facts ; and for our present purposes it will be better to sketch in a few words what the theorists are hoping to achieve rather than attempt to weigh what they have actually accomplished. Organic chemistry is in no urgent need of new guide-posts (witness the mass of new material each year), so that our caution is at least pardonable.

A comprehensive theory of unsaturated compounds has been attempted by Thiele.[2] His fundamental idea is that in the so-called double bond the carbon atoms are really united by two valence units each, but that a small amount of "residual affinity" is left :



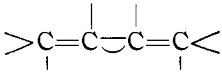
$$>\underset{|}{C}=\underset{|}{C}<$$

It is this residual affinity that gives to the double bond its additive power ; as addition occurs, more residual affinity is liberated, owing to a sort of equilibrium condition. In the case of two adjacent double bonds, two pairs of residual affinities would exist,



$$>\underset{|}{C}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=\underset{|}{C}<;$$

but the central pair neutralize each other, just as two magnet bars would, and we have residual affinity left only at the extreme ends of such a "conjugated system of double bonds" as Thiele calls it :

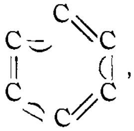


$$>\underset{|}{C}=\overset{|}{C}\smile\overset{|}{C}=\underset{|}{C}<$$

In this way he seeks to explain the actual fact that where such a pair of double bonds occurs within a molecule, addition takes place only at the outer ends, with the establishment of a new double bond :

$$H_2C=CH-CH=CH_2+Br_2=BrH_2C-CH=CH-CH_2Br.$$

Applied to benzene, this theory shows us three conjugated double bonds,



and many of the peculiarities of benzene can be brought into rela-

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[1] *Cf.* Ostwald's "Text-book of Inorganic Chemistry."

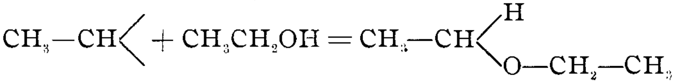
[2] *Ann. Chem.* (Liebig), **306**, 87 (1899).

tion to the properties of other unsaturated compounds. Thiele has found a supporter in Baeyer,[1] who declares that here we have the "final expression" of thirty years of discussion. As we owe the bulk of our knowledge of the benzene ring to Baeyer, this sounds encouraging.

An entirely different method of explaining organic reactions and additions has been elaborated by Nef;[2] according to him, organic compounds have an irresistible tendency to become strongly unsaturated, with formation of bivalent carbon; *e. g.*,

$$CH_3CH_2OH \rightarrow CH_3{-}CH\langle + H_2O,$$

and an equally irresistible tendency to pass back again to the saturated, quadrivalent condition by adding on any molecules that may be within reach; *e. g.*,



$$CH_3{-}CH\langle + CH_3CH_2OH = CH_3{-}CH\left\langle\begin{array}{l}H\\ O{-}CH_2{-}CH_3\end{array}\right.$$

What is missed in Nef's theory is the motive; it is often difficult to see why some other form of addition does not occur when a number of different, available molecules are present. Nef's views have not found the support that has been accorded to Thiele's theory.

Finally, a third course of reasoning has been developed by Michael.[3] Michael's theory is too recent, too complicated and too extensive to permit of any properly comprehensive summary. In its essence, it ascribes to every atom in the molecule a polarity (which is expressed in electric terms); addition reactions are caused by attempts to neutralize this polarity; and the polarity of each atom is modified more or less profoundly by the presence and polarity of all the other atoms in the molecule. With reference to the theories of Thiele and Nef, Michael endeavors to show that Nef's views do not agree with the facts, whereas all of Thiele's deductions can be drawn from his own,—these being more general and more fundamental. If I may append my personal opinion of these three theories, I should venture the prediction that Michael's is more likely to grow into the needs of organic chemistry than either of the others.

CONCLUSION.

It will be seen that the prospects of organic chemistry are as bright as ever. At each of the older problems hosts of busy workers are successfully laboring. New problems are constantly arising, and new methods of experimentation are being as steadily devised for their study. A healthy and skeptical criticism is being accorded our present theories; and from the constructive side

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[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 63 (1900).

[2] *Ann. Chem.* (Liebig), **298**, 202 (1897).

[3] *J. prakt. Chem.*, **60**, pp. 1-178 (1899).

efforts are not lacking to provide us with more accurate and more comprehensive generalizations. From within and without, the organic chemist is stimulated to his best endeavors; his efforts are encouraged, and his achievements are appreciated. The scientist can ask no more.

To him, however, busy with other work, who gazes occasionally on organic chemistry, it may often seem to lack coherence of effort, to waste its strength burrowing for details, and to owe many of its successes to mere chance. If such a one there be, I recommend to his attention a notable address by Baeyer last year.[1] From this address he will learn of the unity of research work—that nearly all of this master's brilliant discoveries were due not to luck or chance, but to the consistent prosecution of a logical train of ideas. Baeyer's first extensive research work dealt with uric acid. The similarity of alloxan and isatin led him to the indigo group. From this sprang the tension theory, the quinoline synthesis, and tautomerism. The tension theory led to the curious tetra-acetylene dicarboxylic acid; this to the benzene ring studies. The investigation of terpenes and related substances took its rise from their similarity to reduction products of benzene. During the terpene researches some curious peroxides were obtained, and the work described above (on ethyl hydroperoxide, etc.) resulted from following up these latter. Thus we can trace Baeyer's research work—than whom no single man has contributed more to the stupendous growth of organic chemistry—back in an unbroken logical chain extending over forty years.

There lies here a world of thought for him who cares to find it.

ARTHUR LACHMAN.

NOTE.

A Gravimetric Method for the Estimation of Hydrogen Dioxide. —All the methods thus far described for the estimation of hydrogen dioxide are volumetric, which may be divided into the three following classes: first, gasometry, by the use of Lunge's nitrometer, or some modification of it; second, iodometry, originated by Kingzett, and depends upon the liberation of iodine from potassium iodide in the presence of sulphuric acid; and, third, oxidimetry, the mutual decomposition of potassium permanganate and hydrogen dioxide in the presence of sulphuric acid. Of these three methods, the latter is preferred and most frequently used. The author has obtained good results by estimating the hydrogen dioxide as water. For the purpose a "Schrötter" apparatus (with tube and glass stoppers), such as used for carbon

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[1] *Ber. d. chem. Ges.*, **33**, Sonderheft, p. 52ff. (1900).