States,"[1] classifies the solid native bitumens, excluding the melaterite and wurtzelite for some remarkable reason and giving no place whatever to asphalt, as asphaltite and coal, the former including albertite, impsonite, grahamite, nigrite and uintaite (gilsonite). Hofer has recently proposed to the writer that the solid native bitumens which are not asphalt shall be so denominated. It seems, however, that all these materials are so entirely different in character that we are hardly justified in putting them in one class, except for the fact that they are not asphalt, and the proposition does not, at present, commend itself.

In conclusion, the writer must acknowledge his indebtedness to the several assistants who have engaged in the investigation of the various grahamites and especially Mr. Kenneth Gerard Mackenzie, and Mr. J. S. Miller, Jr., for the study of the action of turpentine and tetrachloride of carbon on this bitumen. Prof. Jamieson and Mr. Ralph Langhy, of New Haven, have contributed ultimate analyses of several of the specimens, and have determined the presence of nitrogen, by the absolute method, in the Trinidad grahamite, Mr. Mackenzie has also aided in assembling the data and examining the cross references.

30 CHURCH ST., NEW YORK CITY.

PROGRESS IN SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS.[2]

BY S. P. MULLIKEN.

Received June 29, 1910.

A general procedure in organic qualitative analysis that may be trusted to lead to the discovery of the proximate composition of any unknown organic substance whatever, whether this be a simple compound or a mixture, is demonstrably incapable of practical realization. Before proceeding to the discussion of the main subject of this paper, it therefore behooves us to pause for a moment to note certain limits which Nature seems to have set against the too curious advances of the analyst.

The most clearly insuperable of these limitations are associated with high molecular weight. If a paraffin hydrocarbon of the formula $C_{35}H_{72}$ were to be isolated in a state of perfect purity and in large quantity from some natural product, it would be impossible to absolutely identify it as a compound corresponding to any particular structural formula by any combination of methods of investigation now known, or whose future discovery appears probable. Such a hydrocarbon would not differ by one one-hundredth of one per cent. in its hydrogen or its carbon content from its adjoining homologues, while in chemical and physical properties there would be no measurable differences between it and

---

[1] 22nd Annual Report U. S. Geological Survey, Part I, 209–452.

[2] An address delivered at the Second Decennial Celebration of Clark University, Worcester, Mass., Sept. 16, 1909.

thousands of its four million undiscovered structural isomers, which, according to the calculations of Cayley, are theoretically possible. Indeed, in the case of the discovery of such a high hydrocarbon by any process other than one of simple synthesis, no proof could be contrived which would show that the substance might not well be a mixture of many isomers and neighboring homologues; for all finite methods of purification by fractional separation based on differences in properties must inevitably fail when the numerical odds against them are so great, and we have no choice in such a case but to resign ourselves with the best grace possible to an inevitably partial solution of our problem.

But without having ascended to such an altitude in the homologous scale as in the instance just cited, it is often necessary or expedient to accept incomplete answers in qualitative inquiries because of our thralldom to the rule that unknown compounds in mixtures cannot in general be fully identified without previous isolation in a state of purity. It is for this reason that it is so common a practice in technical analysis to express the quantitative composition of familiar and important products in conventional or collective terms. Long and thoroughly as the animal fats have been studied, for example, there is probably no instance on record of a quantitative examination of any natural fat in which it could be safely claimed that the structural identity of all its fatty acids containing less than eighteen carbon atoms had been irrefutably established. Nor would it be surprising under the circumstances if such a result were never accomplished.

Thus handicapped, systematic qualitative organic analysis has developed slowly when compared with the simpler qualitative analysis of the inorganic elements and salts. Yet, if we contrast the difficulties to be overcome in constructing an orderly scheme for the separation and identification of the list of less than one hundred elements with the difficulties to be met in any corresponding scheme for the organic compounds, and then recall what has already been accomplished in overcoming them, and also the imperfections which present-day inorganic qualitative schemes still exhibit when the rarer elements are included, the organic chemist will find little cause for pessimism. The greater part of the contributions to organic qualitative analysis have been made, however, without much thought of the part which they might be made to play in any comprehensive scheme of procedure, and have often owed their origin to incidental observations made during the execution of investigations of broader scope and different purpose. Fischer's numerous characterizations of compounds in the sugar, purine and protein groups, by well chosen reactions and derivatives, and his ingenious separations for the amino acids formed in proteolysis are illustrations of this fact. Among the rather numerous handbooks of organic analysis, although many devote much space to qualitative testing, the speaker recalls only one whose author (Barfoed, 1878) has been sufficiently venturesome to incorporate the phrase "Organic Qualitative Analysis" in its title. Of the many commendable partial schemes for the isolation and identification, or the detection in certain classes of mixtures, of carbon compounds belonging to restricted groups, we owe the origin of a large proportion to an acute need of special analytical assistance in some department of industry, research, or governmental control. To such cause we owe much of what is most valuable in "Allen's Commercial Organic Analysis," Posts's "Chemisch-technische Analyse," and the works of Vortmann, Dragendorff, Hoppe-Seyler, König, Leach, Sherman, and others. The investigation of methods for the detection and determination of constituent radicals has also proved a fruitful source of valuable material, much of which has been made accessible for ready reference in H. Meyer's "Analyse und Konstitutionermittelung organischer Verbindungen."

The resolution of mixtures is usually the first, and often the most difficult part of a qualitative analysis. Definite plans for correlation in a broad general procedure of the methods of separation that have proved effective in the study of restricted classes of mixtures have yet to be proposed. The speaker is not in accord with the rather prevalent view that it is useless to strive for broader and more systematic separation procedures. But, on the other hand, as he is unprepared to play the prophet's rôle, it may be more profitable for him to confine the following discussion to the topic of systematic procedures for the identification of pure compounds, this being an important division of the qualitative problem whose solution seems nearer accomplishment.

Prior to 1831, the date of the inauguration of those revolutionary improvements in organic combustion methods by Liebig, which rendered it possible to determine the percentage composition of any carbon compound with considerable accuracy and comparative convenience, it does not appear that any comprehensive systematic methods for identifying previously described organic compounds had been formulated, or that the lack of them had been felt as a serious inconvenience. The number of pure compounds that had been described was comparatively small, the possibility of laboratory syntheses for organic compounds having only just become recognized, and the descriptions of such compounds as were known were not scattered as to-day through an almost endless list of special journals and treatises. A chemist of this earlier period, if a man of extended practical experience, well read, and having access to a good library, rested more or less content in the knowledge that he could probably accomplish by a purely eclectic procedure based on his miscellaneous sources of information, ingenuity, and common sense, all that was then analytically possible.

Thanks to Liebig's writings and the influence of the students who passed from his Giessen laboratory, his simplified methods of ultimate analysis were not long in becoming widely known. In scientific laboratories they were everywhere welcomed and adopted. This welcome was richly deserved; for, besides serving as a means to determine percentage composition values—which will perhaps always remain the most fundamental of chemical constants—their use, in connection with the later widely adopted vapor density molecular weight determination methods, furnished all information required for the calculation of empirical formulas. These, if we add knowledge of genetic relations and chemical behavior, become structural formulas with all the added information as to chemical characteristics and individuality which are inherent in the latter. The vapor density molecular weight determination methods reached their climax for the organic chemist in the air displacement form proposed by Victor Meyer in 1878. The prestige of the empirical formula as an aid in compound identification was soon still further enhanced by the discovery of Raoult's principle, followed by the invention of the Beckmann thermometer in 1888, these aids to molecular weight determination finally enabling the inclusion among the compounds of directly determined empirical formulas of a large share of the non-volatile compounds. Other causes about to be mentioned also conspired to bring the analytical importance of the empirical formula to extreme prominence.

During the two decades closing in 1880, the unprecedented increase in newly described organic compounds had already begun to assume the dimensions of a threatening deluge. The synthesist responsible for the creation of a new species, being aware of its genetic relations, and having determined its empirical formula, was usually in a position to correctly interpret the chemical identity of his progeny; though to prove that his discovery was really an original one by a search through the swollen literature had become a task to be undertaken with fear and trembling. The time rapidly approached when the healthy future development of organic research seemed likely to receive a serious check from the confusion and discouragement in store for investigators who could only hope to escape plagiarism in recounting their alleged discoveries by well-nigh interminable bibliographical delvings. Those of us in the younger generation of organic chemists are not in a position to even faintly appreciate the sigh of relief that must have been breathed by hundreds of workers in many lands when these chaotic conditions were ameliorated in 1882 by the completion of the first edition of Friedrick Beilstein's great handbook of organic chemistry. With rare foresight Beilstein had in season anticipated the mission which this remarkable work had to fulfil, and its publication after twenty years of incessant labor, occurring as it did at this critical period in the development of organic chemistry, is of epoch-making importance to organic qualitative analysis as well as to all other departments of the science.

Beilstein's "Handbuch" was a digest of the complete literature of the modes of formations, properties and reactions of all the analyzed compounds of carbon. It did not purport to be an analytical guide, and in its introduction the possibility of a qualitative organic analysis at all comparable to the inorganic is categorically denied. Nevertheless, because of the completeness and orderly arrangement of its concise descriptions, its importance as an aid in the identification of organic compounds may be fairly estimated as greater than that of all the special analytical treatises which have ever been issued. Its general classification for the compounds has some times been criticized as clumsy and confusing, but the division of species according to chemical function, saturation, and in homologous series, has, on the whole, served the interests of the analyst well; and the invention of a simple device for locating in its pages the description of any desired compound of known empirical formula, which has been more recently made available through the ingenuity and coöperation of M. M. Richter, the manager of the Prinz Dye Works in Carlsruhe, has now long served in case of compounds of this class to greatly facilitate their identification.

Richter's "Tabellen der Kohlenstoff-Verbindungen" with its 20,000 brief references to the literature and properties of the analyzed organic compounds was issued in 1884. The first volume of the second edition appeared in 1900 under the altered title of "Lexikon der Kohlenstoff-Verbindungen." In its present completed form this edition registers more than one hundred thousand compounds of determined empirical formulas, and gives direct access to the full description and literature of each by citation of the proper volume and page number of Beilstein. As a bibliographical index for compounds of known empirical formula it is hard to imagine anything simpler or more complete than the Richterian classification. The exact position of every possible compound (if we exclude the arrangement of isomers with reference to one another) is automatically fixed by its formula alone, and is as easily found, and in much the same manner, as a word in a dictionary through a knowledge of the relative positions of its letters in the alphabet. The completeness of the tabulation is suggestively indicated by the author's remark that his guiding thought during its preparation was "Das Unwesentliche, d. h. die weniger bekannten Verbindungen, stets in erster Linie und vollstandig hervorzuheben." On the other hand, its use as the basis for a method of identification for unknown organic compounds is often attended with serious or prohibitive difficulties.

It has been already pointed out that an absolute determination of species among the carbon compounds is theoretically impossible by any combination of tests in the case of compounds of extremely high molecular weight, and that the unavoidable errors of ultimate organic analysis with such substances are large enough to prevent analysts from making any selection between a large number of seemingly possible and equally probable empirical formulas. This unfortunate circumstance prohibits the use of the Richterian system in large and important fields where quantitative investigation by other methods may be conducted with good prospect of success. For example, the dyestuff tables of Schultz and Julius describe a hundred distinct tetra-azo dyestuffs having molecular weights above 500, and some of them exceeding 1000. These colors are many of them important, their constitutions well established by synthesis, and their identification through their physical and chemical properties, or at least their approximate identification—which is often all that is required—is not especially troublesome. The absurdity of an attempt to identify an unknown color of this class through its empirical formula—which would usually involve the quantitative determination of at least six elements with an impossible degree of precision—is so patent from the mere mention of the stoichiometric conditions that it may be hoped it has never been made by any rational being.

A second defect in the method of the empirical formula, which in the ordinary laboratory curtails its actual application even more than the absolute limitation just mentioned, is the fact that much special manipulation, skill and apparatus are necessary to ensure trustworthy results in elementary organic analysis, and that so much time is always consumed in the preliminary arrangements for a combustion and in its conduct. In the larger organic laboratories where the combustion of new synthetic products is an almost daily incident of the routine of investigation, and the equipment of the combustion room is maintained at all times in a state of perfect preparedness for emergency calls, so that no time need ever be lost in the mobilization for an analysis, the organic combustion is not formidable to the initiated. But under other circumstances—and they are the prevalent ones—chemists do not resort to the method of the empirical formula except under rather strong compulsion, and many identifications which ought to be made are not even attempted.

In view of these defects and inconveniences, it is natural to inquire whether there is hope of securing in the future any scientific substitute for the method of the empirical formula. In the comprehensiveness and simplicity of its classification of compounds, it must be admitted that it will be vain to expect anything but loss from radical changes in the Richterian arrangement; but, if we accept the logician's definition of a scientific classification as "Nothing more than a system of division carried out in such a way as to best serve a given purpose," and if our purpose is convenience and effectiveness in general qualitative investigation, the possibility of other and more scientific classifications is not to be denied; and it has seemed to the speaker that the discovery of such methods of classification is at present one of the important and attractive fields for organic chemical research. What the final outcome of this quest will be—if we have the right to speak of a final outcome in a problem which from its nature permits of only progressive partial solution—no one can as yet speak with full authority. Some of the general considerations bearing on the subject may, however, be brought to your attention.

Scientific classifications are chiefly concerned with relations of resemblance and contrast. To answer the question what points of resemblance and contrast must be regarded, and in what order, if we are to make a classification scientific, is to say that no basis of classification ("*fundamentum divisionsis*") is *per se* better than any other. All depends on the ultimate object. If the object of a classification is ready diagnosis of natural objects, it is evident that the characteristics used as *differentiae* for distinguishing between groups should permit of easy as well as certain determination; and it is also a good quality in such a division to collect individuals in the lowest group for comparison which are on the whole most alike. Methods of subdivision which aim at discovering something without regard to whether the resemblances of adjacent species are fundamental or accidental, like the classification of words in a dictionary according to the accidental alphabetical sequence of their letters, are called artificial systems. The Linnæan and Richterean systems belong to this category. No comprehensive system of division in natural science is free from many artificial features. But these are more likely to be prominent in the early than in the later stages of the development of a classification; the pioneer in such work having to first bridge his rivers with such structural materials as lie nearest at hand.

To the observant mind the discovery of possible *differentiae* for the classification of natural objects is an easy and fascinating pastime, though to make a wise selection may often be quite the reverse. Thus we read in the quaint diary of the botanist Linnaeus under the date of June 12, 1632, in his "*Lapland Observations*": "Close to the road hung the under jaw of a horse, having six front teeth, much worn and blunted, two canines, and at a distance from the latter twelve grinders, six on each side. If I knew how many teeth and what peculiar form, as well as how many udders, and where situated, each animal has, I should perhaps be able to contrive a most natural methodical arrangement of quadrupeds." As with Linnaeus' quadrupeds, so with organic compounds—we find a multitude of easily determined properties from which we may choose the *differentiae* for our classification, and by the exact coincidence of a sufficient number of these characteristics of different orders with those of an unknown compound, the identity of the latter may be proved. Qualitative elementary composition, color, melting and boiling point, specific gravity, odor, taste, solubility, refractive index, specific optical rotation, electrical conductivity, absorption spectra, color reactions, precipitations, and general chemical behavior—especially simple chemical reactions that throw light on the nature of dominant atomic groups and structural peculiarities—may all be thus used.

Regarding the chemical compound, or individual, as the *species* of a chemical system, it appears most natural to group these species in such a way as to make the next higher unit or *genus* contain species which are most similar in general chemical behavior. This would, for example, tend to make congeners of members of all homologous series containing the aldehyde radical, provided we could find sufficiently reliable and simple chemical tests for showing the presence of the CHO group. Recent chemical literature abounds in suggestions for tests suitable for generic *differentiae*, though much additional work will be required in every instance to determine the real value and exact boundaries of the genera that their employment would create, there being ever-present danger that overconfidence in the constancy of behavior of a reagent towards a given radical in different structural environments may lead to false conclusions. Thus, it is not safe to assume that under certain specified conditions all ketones will form oximes; all acids and phenols will dissolve in alkali; all esters will be saponified; or all unsaturated compounds will add bromine. In first delimiting a genus such assumptions may be adopted, after preliminary experiments, as tentative working hypotheses; but the contents and existence of the genus must be held to be strictly provisional and dependent on the positive outcome of the proposed genetic reaction when applied to a larger number of its carefully selected species, and to its negative outcome when tried with numerous members of all genera of higher numerical designation in the same classificatory *order*. It will also be the duty of the classifier to indicate, in a manner that will leave no doubt in the minds of readers, all descriptions, or parts of descriptions, for which he is personally responsible; for unless some means is given for distinguishing between data which he has verified, and others which he has not, the authority is liable to be more or less implicated in the mistakes of others for which he need have assumed no responsibility, but which will now tend to vitiate the value of his classification as a whole.

It would be premature at this time to present in all its minutiae any plan for such a classification as has just been suggested in its outlines. Details in illustration of the speaker's original conception and partial execution of such a plan are to be found in the already published first and third volumes of his "*Method for the Identification of Pure Organic Compounds.*" All that is desired here is to lead to a discussion of the advantages in the plan for Chemistry; and, if it is sound, to arouse interest with a view to eventually bringing about a wider coöperation for furthering its future development. The difficulties to be overcome are considerable. Recorded descriptions of organic compounds, while frequently very complete for a few properties like melting and boiling points, are commonly equally deficient concerning others—especially in exact data showing the extent of the influence of slight variations in chemical constitution on the results of the selected differential tests. The occasion hence arises for an investigation or partial reexamination of a considerable proportion of the species receiving locations. If one has the pure compounds with which to experiment, the tests are easily made. But as only a few thousand pure compounds can be procured through commercial channels, and most of these require some purification, success in the construction of a comprehensive diagnostic classification implies assistance from private collections throughout the world; for to synthesize any considerable part of the rarer species would overtax the facilities of the largest and best equipped of laboratories.

To bring a majority of the carbon compounds referred to in Richter's Lexikon into an essentially "natural" classification of the kind suggested would, assuming the study of tests and revision of constants to be thoroughly done, perhaps involve a labor as great as the transformation of the "artificial" botanical classification of Linnaeus into the modern "natural" system as it was left by de Candolle. An undertaking of this magnitude and character might presumably in the present century be accomplished with greater benefit to science under the direction of some such organization as the committee entrusted with the periodical revision of Beilstein's "Handbuch" and the Richter "Lexikon" than under private auspices.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

[CONTRIBUTION FOR THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESIS OF THE α,α'-DIMETHYLADIPIC ACIDS, AND SEPARATION OF THE RACEMIC ACID INTO OPTICAL ISOMERS.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

Received June 24, 1910.

The α-α'-dialkyl-dicarboxylic acids are described in the literature as existing in two stereomeric forms—known as maleinoid and fumaroid. As far as we know none of these acids have been resolved into optical isomers. Bischoff and Walden[1] have failed in the resolution of the suc-

---

[1] *Ber.*, 22, 1814.