[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

THE DECOMPOSITION OF UNSYMMETRICAL MERCURI-ORGANIC COMPOUNDS: A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF ELECTRONEGATIVITY OF ORGANIC RADICALS. II[1]

BY M. S. KHARASCH AND A. L. FLENNER[1]

RECEIVED AUGUST 22, 1931 PUBLISHED FEBRUARY 5, 1932

Introduction

In previous publications of this series,[2] the view has been expressed that the terms "positive" and "negative" as applied to organic radicals are too indefinite to be of much use. The methods which have been used to establish the line of demarcation between the two classes of substituents are frequently unsatisfactory and sometimes even ambiguous;[3] hence contradictory results are obtained when these terms are employed. A single new term "relative electronegativity" has therefore been carefully defined with the intention of avoiding the difficulties apparently inherent in the use of the older nomenclature. That such an idea will prove to be adequate appears probable, since the users of the older terminology, when they speak of any particular pair of radicals, usually have in mind only the difference between the groups in question with respect to their attraction for electrons.

But the concept of relative electronegativity may be expected to go further and to yield results which are semi-quantitative. For example, the old classification placed phenyl, tolyl and *p*-chlorophenyl among the negative radicals, but failed to arrange them in any particular order. By use of the concept of relative electronegativity ordered series may be established, and the information thus obtained is of considerable importance in the interpretation and prediction of reactions involving the radicals in question.

In view of the large number of organic radicals, the task of arranging them in order might seem to be endless. It is hoped, however, that from data on radicals of certain important types, some broad generalizations may be drawn. The object of the work recorded in the present paper is to determine: (a) How the electronegativity of an aliphatic radical is affected by a lengthening of the carbon chain. (b) How the electro-

---

[1] The material presented in this paper formed part of a dissertation submitted in 1927 by A. L. Flenner to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the Ph.D. degree.

[2] Kharasch and Grafflin, THIS JOURNAL, **47**, 1948 (1925); *Science*, **58**, 1510 (1923); Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926).

[3] See chapter on "Negative Nature of Atomic Groups," by Henrich translated by Johnson and Hahn, John Wiley and Sons, Inc., New York, 1922.

negativity of the phenyl radical is affected by the introduction of various ortho, meta and para substituents.

Validity of the Method for Determining Relative Electronegativity of Organic Radicals.—The method of establishing the relative electronegativity of organic radicals has been described by Kharasch and Marker.[2] This method depends only upon the fact that when hydrogen chloride is added to an unsymmetrical mercury compound, the following reaction takes place.

$$R_1HgR + HCl \longrightarrow R_1H + ClHgR$$

The group R_1 which presumably first dissociates from the mercury and then combines with the hydrogen ion in solution to form the hydrocarbon R_1H is defined as the more electronegative of the two radicals; that is, it has the greater attraction for electrons.

Data thus obtained have no validity whatever unless it can be shown beyond doubt that the mercurial used is really unsymmetrical. We have based our conclusions to this effect on the analysis of the substance in question and on the nature of its reactions with both hydrogen chloride and mercuric chloride. No results have been considered save in those cases where all lines of investigation led to concordant results. Certain investigators[4] have expressed the opinion, however, that, where analysis shows the presence of two different radicals, to obtain by the use of hydrogen chloride a single reaction product (R_1H) is not conclusive proof that the reacting substance is an unsymmetrical mercurial R_1HgR. This same result, they suggest, might be obtained from an equimolecular mixture of R_1HgR_1 and RHgR if the rate of reaction of the former compound were much greater than that of the latter compound. However, the decomposition by hydrogen chloride of an equimolecular mixture of mercury diethyl and mercury diphenyl has shown the objection to be unfounded. The mixture in question gives nearly equimolecular amounts of phenyl mercuric chloride and ethyl mercuric chloride in sharp contrast to the unsymmetrical phenyl mercury ethyl which yields ethyl mercuric chloride alone.

Furthermore, if the series of radicals obtained by this reaction is to find any sort of general applicability, it must be shown that the order of the groups is not usually affected by variations in any of the following factors: (1) the temperature at which the reaction is carried out; (2) the solvent used; (3) the concentration of the reaction mixture; (4) the relative solubility of the possible reaction products; (5) the purely hydrolytic agent used to accomplish the reaction; (6) the atom connecting the two organic radicals in question.

The effects of variations in temperature, concentration, solvent and hydrolytic agent used have been investigated by Kharasch and Pines[5]

---

[4] Private communication.

[5] Kharasch and Pines, unpublished work.

and within the range of their researches, no change in the order of the organic radicals has been found. Moreover, it has also been shown[2,5] that phenyl mercury ethyl, when dissolved in ether, is instantly decomposed by hydrogen chloride to form benzene and ethyl mercuric chloride in spite of the fact that phenyl mercuric chloride is much less soluble in ether than ethyl mercuric chloride, and hence would be the expected reaction product if relative solubility rather than relative electronegativity were the important influence guiding the course of the reaction. These results very nearly dispose of the criticisms of Wooster and Mitchell.[6]

In connection with the question as to the effect of variations in the hydrolytic agent used and the atom connecting the two organic radicals, the work and conclusions of Bullard[7] must be considered. Here it should be stated at once that since the arrangement of organic radicals in order of their relative electronegativity depends only upon the cleavage of the carbon to metal union it is best to employ a reagent which accomplishes selectively that type of reaction. As soon as reagents such as the halogens or mercuric salts are employed, a complication is introduced—that is, the possibility that the organic molecule may be attacked and altered before the cleavage occurs. For example, the reaction

$$R_2MCH_2R + Cl_2 \longrightarrow RMCl + ClCH_2R$$

---

[6] Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930). In our opinion the other objections of Wooster and Mitchell may also be readily answered. These authors, after attempting to apply our hypothesis to triphenylmethane and similar hydrocarbons, state that the experimental facts are inconsistent with our views. The difference of opinion arises because Wooster and Mitchell make an assumption which seems to us of doubtful validity. They assume implicitly that when triphenylmethane and similar hydrocarbons react in liquid ammonia with alkali metals, the hydrocarbons ionize into a hydrogen ion and an organic ion, and that only the hydrogen ion reacts with the metal. Our view is that such reactions are reductions involving first the weakly electronegative carbon atom.

The ability to receive electrons is common to carbon atoms the valence electrons of which are shared with comparatively electronegative radicals and thus drawn into higher energy levels. When this occurs, hydrogen is not always the group eliminated in a subsequent splitting of the molecule. If a group less electronegative than hydrogen is present, it may be split off instead. For example, *sym.*-tetraphenylethane reacts with sodium–potassium alloy in dry benzene or ether to form potassium (sodium) diphenylmethyl [Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923)].

The idea that the hydrides of the most weakly electronegative radicals react most readily with metals is also supported by the behavior of the hydrides of carbon, silicon and germanium toward alkali metals, for the hydride of the most weakly electronegative element (germanium) is the one which reacts most readily with the metal.

In certain other arguments, Wooster and Mitchell have interpreted our theory peculiarly. Some of their predictions (*e. g.*, on the addition of bromine and sodium to phenylated unsaturated hydrocarbons) are contrary to the ones which we would make in the same instances. The facts, so far as we know, support our own predictions in all cases.

[7] Bullard, THIS JOURNAL, **51**, 3065 (1929).

might run directly as indicated. But on the other hand it might proceed in steps as

$$R_2MCH_2R + Cl_2 \longrightarrow R_1MCHClR + HCl$$
$$R_1MCHClR + HCl \longrightarrow R_1MCl + ClCH_2R$$

In this case it would not be the radical $—CH_2R$ but the radical $—CHClR$ which was being cloven from the metal and consequently the reduction could throw no light on the position of the radical $—CH_2R$ in the table. In order to be sure what radical is being split off, it is necessary to use a cleavage agent which can react with the molecule in only one way; and among such agents are the acids which we have always employed.

Certain of Bullard's experiments with tetravalent tin derivatives, R_3SnR_1, probably suffered from complications of the kind indicated for some of them have been repeated[8] with the sole difference that halogen acids were used in place of chlorine, and in all cases the results have been found to be in agreement with our original table. Moreover, Kipping[9] has reported the splitting of tribenzylethylstannane by hydrochloric acid. He finds that the ethyl group is removed and tribenzyl tin chloride formed—a result in complete accord with our predictions.

Differences between the results obtained by the use of halogens and those obtained by the use of halogen acids would be expected to occur most strikingly when weakly electronegative radicals are involved. Thus Kraus and Bullard[10] have found that trimethylbenzylstannane and bromine yield trimethyl tin bromide and benzyl bromide

$$(CH_3)_3SnC_7H_7 + Br_2 \longrightarrow (CH_3)_3SnBr + BrC_7H_7$$

and Kipping and Smith[11] have reported that tribenzylethylstannane when treated with iodine gives dibenzyl ethyl tin iodide and benzyl iodide. On the basis of these and similar results Bullard[7] arrived at the order phenyl, benzyl, methyl, ethyl in contrast to our order phenyl, methyl, ethyl, benzyl. Whether by the use of halogens alone a self-consistent ordered series of radicals can be established seems rather doubtful in view of the complexity of the reactions involved. One thing, however, appears certain. If an ordered series can be thus obtained, it should not be expected to coincide at all points with the series obtained by the use of non-oxidizing cleavage agents.

Assuming that only purely hydrolytic agents are used, whether or not the order of relative electronegativity of organic radicals varies with the nature of the central atom becomes at once a clear cut and an important question. As far as we are aware, all known cases of the cleavage of unsymmetrical compounds support the table we have published. On

---

[8] Sher and Kharasch, unpublished work.

[9] Kipping, *J. Chem. Soc.*, 2366 (1928).

[10] Kraus and Bullard, THIS JOURNAL, **48**, 2135 (1926).

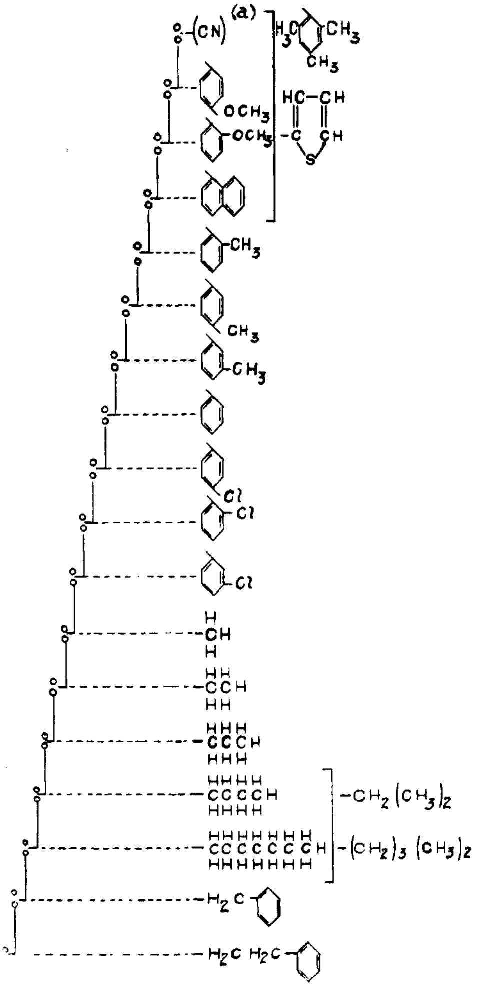
[11] Kipping and Smith, *J. Chem. Soc.*, **101**, 2553 (1912).

the other hand, our choice of the mercury organic compounds as a starting point was not a matter of chance.[12] It is desirable to use a metal (that is, a very weakly electronegative atom) so that the organic radical may readily capture the bonding electrons and split off at ordinary temperatures; and among organo-metallic compounds the unsymmetrical mercurials are peculiarly easy to isolate and identify. Moreover, when mercurials are used, since mercury is bivalent, it is unnecessary to consider questions of statistical probability such as might arise with a compound like RRRSnR.[2]

Table I

Relative Order of Electronegativity of Organic Radicals

The radicals to the right of the brackets have not been precisely placed as yet. It is known that they fall within the respective ranges indicated by the brackets.



(*a*) From silver cyanide.

Arrangement of Radicals in the Order of Their Relative Electronegativity.—The most important reaction of the unsymmetrical organo-mercuri molecules is their decomposition with hydrogen chloride. It should be emphasized once more that we consider the radical which dissociates more readily from the mercury and then combines with the hydrogen ion in solution to be the more electronegative of the two radicals. Using this criterion (and incidentally the results of Kharasch and Marker) the organic radicals studied are arranged in Table I. The compounds at the top of the table have a greater resemblance to the non-metals while those below resemble the metals.

Use of the Table of Relative Electronegativity of Radicals in the Interpretation of Organic Reactions.—Although Table I is far from

---

[12] Kharasch and Reinmuth, *J. Chem. Ed.*, **5**, 407 (1928).

complete, it may be used in certain interesting ways to elucidate the properties of organic molecules. Some of these applications will be discussed briefly under the following heads: (1) the existence of free radicals, (2) the relative electronegativity of aliphatic radicals, (3) substitution reactions in the benzene ring.

(1) **The Existence of Free Radicals.**—The relation between the electronegativity of organic radicals and the degree of dissociation of the respective hexa-arylethane derivatives has been fully discussed by Kharasch and Marker. An hypothesis was presented for critical analysis rather than as a basis for any contention and conclusion.[13]

The failure of compounds such as dichlorotetraphenylethane to dissociate into free radicals (cited in refutation of our theory by Wooster and Mitchell)[6] was well known to us, but was not considered to be a discrepancy. We suggested that the dissociation of a hexa-substituted ethane would be promoted by any radical lying above phenyl in our Table of Relative Electronegativity. The well-established facts we believe are in harmony with our views. But since the positions of the halogens in the table have not yet been determined, it is premature to draw conclusions as to the dissociability of ethane derivatives loaded with halogens attached directly to the central carbon atoms.

The necessity for caution is illustrated by reference to Table I. The introduction of a chlorine atom into the benzene nucleus decreases the electronegativity of the radical no matter whether the entering chlorine be ortho, meta or para to the point of attachment. On the other hand, methyl and methoxy groups whether ortho, meta or para increase the electronegativity of the phenyl. Such facts are not readily inferred from a superficial examination of structural formulas; neither can they be obtained by simply applying the laws of electrostatic attraction. Moreover, it is an important (and in this case a very pertinent) fact that a molecule may relieve its internal stress in various ways other than by the formation of free radicals. Dissociation of the very labile halogen atoms in dichlorotetraphenylethane provides a second possible method of relief, and the decomposition of the molecule might take place in this manner. In conformity with our views, Schlenk and Racky[14] record that the halogens in dichlorotetrabiphenylethane are much more labile than those in di-

---

[13] Much attention has been paid to the substance prepared by Ziegler and Boye and called by them trinitrotriphenylmethyl [*Ann.*, **458**, 254 (1927)]. In view of the fact that these authors report neither the molecular weight of this compound nor the preparation of a peroxide from it, we cannot share their confidence that it is extensively dissociated. That a hexanitro compound should be strongly colored is scarcely surprising, and many substances for which dissociation into free radicals has not been suggested show when treated with bromine a rupture of the carbon to carbon bond. Ziegler and Boye's compound seems to us a questionable choice for a test case.

[14] Schlenk and Racky, *Ann.*, **394**, 211 (1912).

chlorotetraphenylethane, as regards both hydrolysis and liberation of chlorine.

Recently Ziegler and Mathes[15] have determined the dissociation constants of various para-substituted triphenylmethyl chlorides in liquid sulfur dioxide. Their results are in full agreement with the positions of these radicals in our table, and with the influence on the dissociation of the chloride ion which we have ascribed to them.

At this point it is necessary to call attention to another factor besides the relative electronegativity of radicals which very probably influences the course of reactions. In the valence bond R—X, if the radical X is joined to the organic radical through an atom of the elements B, C, N, O or F, then the valence electrons involved in the bond form part of the L shell of the elements in question. If the radical X is joined to the organic radical through an atom of Si, P, S or Cl, the valence electrons are part of the M shell. When the linkage is through Ge, As, Se or Br, the valence electrons are in the N shell, and when the linkage is through Sn, Sb, Te or I, they are in the O shell. In our opinion it is very doubtful whether linkages involving electrons from different shells can be directly compared with one another. A single ordered series containing radicals which involve linkages of the various sorts mentioned might very well prove misleading as a basis for the prediction of reactions.

Thus far, our own work on the electronegativity of organic radicals has involved only linkages through the carbon atom, and so the difficulty mentioned has not yet arisen for us. We have some confidence that the series we have begun can be extended to include linkages of metal to nitrogen, oxygen and fluorine; and similarly we hope that three other series involving, respectively, linkages to Si, P, S and Cl, to Ge, As, Se and Br and to Sn, Sb, Te and I may also be established. But whether, after these four series have been worked out, they can be usefully combined into a single series is a question which we wish to leave entirely open.

With regard to the halogens, in particular, great caution should be used. We believe that the fluorine atom can be included in the table containing carbon radicals and many of the properties of fluorine compounds are in harmony with this view. But the case of chlorine is quite different. It may well be that the stability of a bond involving electrons in the L shell differs widely from that of a bond involving electrons in the M shell, and if this is true, then in order to predict reactions where one of the radicals is a chlorine atom and another a carbon radical, a new factor (the shell of the valence electrons involved in the bond) in addition to relative electronegativity must be taken into account. (The same argument of course applies *a fortiori* to the halogens bromine and iodine.) For this reason we doubt the validity of arguments based on the behavior of such a compound

---

[15] Ziegler and Mathes, *Ann.*, **479**, 11 (1930).

as α,β-dichlorotetraphenylethane. A far better substance for comparison would be α,β-difluorotetraphenylethane and attempts to synthesize this compound are now under way.

(2) **The Relative Electronegativity of Aliphatic Radicals.**—As already stated by Kharasch and Marker,[2] if the radicals R and R_1 are widely separated in the Table of Relative Electronegativity, the decomposition of R_1HgR proceeds quantitatively in one direction. If R and R_1 lie close together in the table, the decomposition with hydrogen chloride gives two products, but the substance containing the less electronegative radical always constitutes the greater proportion of the mixture of RHgCl and R_1HgCl. In conformity with these views, we can report the following findings.

(*a*) Six repetitions of the cleavage of *n*-butyl mercury *n*-propyl showed the reaction product to consist of a mixture of 74.2 ± 1% of butyl mercuric chloride and 25.8 ± 1% of propyl mercuric chloride.

(*b*) Ethyl is much more strongly electronegative than *n*-heptyl for *n*-heptyl mercury ethyl is decomposed by hydrogen chloride to give nearly pure heptyl mercuric chloride and ethane.

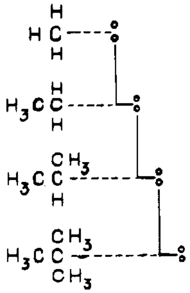
(*c*) The *n*-butyl radical however falls closer to *n*-heptyl, for *n*-butyl mercury *n*-heptyl gives a mixture of 70% of *n*-heptyl mercuric chloride and 30% of *n*-butyl mercuric chloride.

(*d*) By similar methods *n*-propyl has been shown to be more electronegative than isopropyl.

Judging by these data, the following conclusions appear to be justified: (1) In the straight chain aliphatic series, increase in the carbon chain leads to decrease in the electronegativity of the radical. No alternation in electronegativity has been observed. (2) Iso radicals are less electronegative than straight chain radicals and recent work with tertiary radicals indicates that their electronegativity is smaller still.

TABLE II

EFFECT OF SUBSTITUENT METHYLS ON THE ELECTRONEGATIVITY OF THE METHYL RADICAL



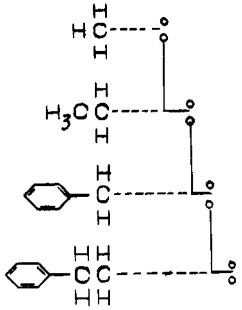
The order of arrangement is given in Table II.

As to the effect of introducing a phenyl radical into an aliphatic chain, we can cite the following facts: (*a*) Kharasch and Marker[2] showed that ethyl is decidedly more electronegative than benzyl, for benzyl mercury ethyl is decomposed by hydrogen chloride to give 94% of benzyl mercuric chloride and 6% of ethyl mercuric chloride. (*b*) We now find that the β-phenylethyl radical is decidedly less electronegative than the benzyl radical, since the decomposition of benzyl mercury β-phenylethyl with hydrogen chloride yields 10% of benzyl mercuric chloride and 90% of phenylethyl mercuric chloride.

Our conclusion is that the introduction of a phenyl group on the β-carbon atom of the ethyl radical must lower the electronegative character of that radical tremendously. That the *n*-butyl radical is more electronegative than the isobutyl radical appears to be in harmony with this view, but general conclusions must be postponed until further experimental work has been done. Table III summarizes the results so far obtained.

TABLE III

EFFECT OF A PHENYL GROUP ON THE ELECTRONEGATIVITY OF THE METHYL AND ETHYL RADICAL



(3) Application of the Data on Relative Electronegativity to the Problem of Substitution in the Benzene Ring.—No attempt will be made here to discuss the general merits and demerits of the various theories proposed to account for substitution in the benzene ring, since such a review would be beyond the scope of this article. It is our impression, however, that most of these theories have been built up *a posteriori* by inspecting the well-known data and then fitting the hypothesis to the facts. In contrast to such procedure, our treatment of the benzene substitution problem from the standpoint of relative electronegativity is based upon an experimental method which demands no knowledge of the position taken by an entering group when that group is substituted for one of the hydrogen atoms in a benzene derivative.

The data so far collected may be most conveniently treated by considering the following phases of the problem: (*a*) the effect of substituents on the electronegativity of the phenyl radical; (*b*) interpretation of the substitution reactions of aromatic substances in terms of the concept of electronegativity.

(*a*) Substituents introduced into the benzene ring may be divided into two classes according to whether they increase or decrease the electronegativity of the phenyl radical. The most remarkable feature of Table I is that when the substituents are thus divided, the methyl and methoxy radicals on the one hand, the chlorine atom[16] on the other hand, fall into different classes. All the tolyl and all the methoxyphenyl radicals are *more* electronegative than phenyl, while all the chlorophenyl radicals are *less* so. Yet all three of these substituents are ordinarily said to be nega-

---

[16] One of us and Pines (unpublished work) have extended this study to other (Br) halogen substituted phenyl radicals. The effect of this halogen on the electronegativity of the phenyl radical is quite similar to that observed with chlorine.

tive, and a close similarity between them is usually assumed on the ground that when attached to phenyl all three direct further substitution into the ortho and para positions. Clearly the classification of substituents according to their effect in raising or lowering the electronegativity of the phenyl radical leads to distinctions which are sharply at variance with current ideas.

If only a single substituent be considered, examination of Table I reveals the effect of altering the position of the group in question. Thus the lowering effect of the chlorine atom is greatest in the meta and least in the para position, from which it follows that the order of electronegativity of the three chlorophenyl radicals is $p > o > m$. It is perhaps worth noting that, so far as may be concluded from data now available, the effect of altering the position of a substituent seems to be much smaller than the effect of altering the substituent. For this reason the three radicals involving the same substituent occupy adjacent places in the table; no radical intervenes between the members of the different triads.

Considering first only those substituents which increase the electronegativity of the phenyl, certain interesting differences may be observed. The methyl radical exerts its maximum influence in the ortho position and gives the order $o > p > m$ for the tolyl radicals. The methoxyl radical on the other hand is most effective in the para position and gives for the methoxyphenyl radicals the order $p > o > m$. A finer subdivision of substituents into various sub-classes is thus indicated, but more data are needed before this idea can be developed.

Among the substituents which lower the electronegativity of phenyl, similar and even more striking differences may be noted. The radicals so far studied are —Cl, —Br, $—NO_2$ and —CN. Of these, the halogens have the greatest effect in lowering the electronegativity of the radical in the meta and a less effect in the ortho and para positions. Hence the order (o and p) $> m$. But preliminary experiments on —CN indicate that with this substituent the order is reversed. The radical —CN has least lowering effect when it is in the meta position, which leads to the order of electronegativity $m >$ (o and p).

The only conclusion which can at present be drawn from these curiously divergent effects is the necessity for great caution in making predictions.

(*b*) Independent of any particular mechanism of substitution in the benzene ring, it is evident from Table I that there is a relation between electronegativity and ease of substitution. Thus anisole, the hydride of the most electronegative radical investigated, is much more easily substituted than benzene, the hydride of the less electronegative phenyl radical. It is also well known that naphthalene and thiophene are much more reactive than benzene—facts which agree with the positions of their respective radicals in the table. Greater electronegativity, therefore, seems to imply a higher rate of reaction.

The first and most obvious application of this idea is to the triads of radicals containing a common single substituent. If the order of such a triad is (o and p) $> m$, the substituent in question is an ortho–para directing group; if the order is $m >$ (o and p), the substituent is meta directing.

This generalization moreover suggests that in competitive reactions a larger quantity of the substitution product of the more electronegative radical should be formed. Thus the positions of the chlorophenyl radicals in the table indicate that chlorobenzene should be less readily attacked by reagents than benzene, and that the products of substitution should be mainly para and ortho. The facts substantiate these predictions.[17] Similarly, since all the tolyl radicals lie above benzene in the table while all the chlorophenyl radicals lie below it, toluene should be attacked before chlorobenzene. This prediction accords with the observation of Wibaut,[18] who demonstrated that the velocity of nitration of toluene is greater than that of chlorobenzene.[19]

Another proposed rule which seems important may be drawn from the following facts. The substituents chlorine, bromine and the nitro radical may all be attached to the benzene ring by a process of direct substitution, and all of them lower the electronegativity of phenyl. Not a single group which can be thus directly introduced into benzene is to be found among those substituents which increase the electronegativity of phenyl. It would thus seem that *direct substitution by its very nature reduces the electronegativity of phenyl, and if this is the case all compounds formed from benzene by direct substitution will be less reactive toward new substituents than benzene itself.* The work of Kharasch and Legault[20] on mono and di-substituted phenyl radicals bears out this idea.

When two substituents both of which shift the electronegativity of phenyl in the same direction are introduced together into the benzene ring, it is reasonable to predict that the electronegativity of the resulting radical should be shifted even further from that of phenyl. For example, hydroxy and methyl radicals both increase the electronegativity of phenyl, and so the cresyls should be even more electronegative than the tolyl and hydroxy-

---

[17] Note the rather unsatisfactory reply of Holleman to the objections raised by Van der Linden relative to the difference in the speed of bromination of chlorobenzene and benzene [Holleman, "Some Factors Influencing Substitution in the Benzene Ring," *Chem. Reviews,* **1,** 195 (1924–1925)]. Van der Linden's objection is readily answered from the standpoint of difference in the relative electronegativity of the radicals.

[18] Wibaut, *Rec. trav. chim.,* **34,** 241 (1915).

[19] Holleman,[17] page 204, remarks with reference to these findings. "It was evident that toluene nitrated much more rapidly than chlorobenzene, just the reverse of what had been expected. This result was corroborated further by the nitration of chlorobenzene and of toluene separately in acetic anhydride solution."

[20] Kharasch and Legault, Master's dissertation, University of Maryland, unpublished work.

phenyl radicals; on the other hand, since both chlorine and the nitro groups decrease the electronegativity of phenyl, the chloronitrophenyls should be less electronegative than the chlorophenyl and nitrophenyl radicals. Furthermore, direct substitution should exert its lowering effect not only on phenyl but also on substituted phenyl radicals; for instance, the chlorotolyls should be less electronegative than the tolyl radicals.

In radicals such as the chlorotolyls, the effects of the two substituents are opposed and a complex interplay of forces results. Thus methyl increases the electronegativity of phenyl in the order $o > p > m$, while chlorine decreases the electronegativity and gives rise to the order $p > o > m$. Under these circumstances it is not surprising that Wibaut[21] when he nitrated orthochlorotoluene should have observed the formation of all four possible isomers.

Summing up, we believe we have shown that the idea of relative electronegativity distinguishes as effectively as other schemes between ortho–para and meta directing groups. In addition it accounts successfully for the lowered reactivity of the chlorinated and brominated benzenes. And finally it shows for the first time experimentally that the effect of methyl as a ring substituent is antagonistic to that of chlorine and hence that the ortho–para directing substituents are really of two distinct types. A quantitative measure of the effect of any given substituent in altering the electronegativity of the phenyl radical is, of course, still lacking, and therefore when various substitution products are formed at the same time, the ratios of the amounts produced cannot be exactly foretold. When the forces are very evenly balanced, secondary effects such as those of the solvent and of the temperature probably come into play, and may even in borderline cases alter the order of electronegativity of radicals which lie very close to one another in the Table. But in spite of such uncertainties, we believe that the concept of relative electronegativity throws more light on the problem of substitution in the benzene ring than any other theory now in the field.

Experimental Part

Method of Analysis for Mercury.—A volumetric method of analysis for mercury is described by Rupp.[22] Koten and Adams[23] modified this method for the volumetric determination of mercury in organic compounds. In the Koten and Adams method a sample of the material is weighed into an Erlenmeyer flask and decomposed by a mixture of fuming nitric and sulfuric acids. Water is then added and a solution of potassium permanganate until a definite color persists. The excess of potassium permanganate is then destroyed by the addition of ferrous sulfate. Ferric alum is added as an indicator and the mercury titrated with potassium thiocyanate.

The above method is quite satisfactory for mercury compounds of the type $RHgR_1$,

---

[21] Wibaut, *Rec. trav. chim.*, **32**, 244 (1913).

[22] Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

[23] Koten and Adams, This Journal, **46**, 2764 (1924).

but with any type of compounds containing halogen the method for obvious reasons fails absolutely.

After much experimentation the following volumetric method of analysis of mercuri-organic substances including those containing halogens was developed.

The procedure of analysis is as follows. About 0.2 g. of sample is weighed into a 250-cc. Erlenmeyer flask, 20 cc. of glacial acetic acid added and then 3 cc. of bromine. After standing for about twelve to twenty-four hours, 5 cc. of hydrochloric acid is added and then zinc dust, in small amounts at a time, care being taken to add the zinc slowly so that the temperature may not rise above 40°. As soon as all the color of bromine has disappeared, a slight excess of zinc is added and the mixture allowed to react for about two hours or longer. A small amount of finely powdered silica gel (the silica gel is added to retain any colloidal mercury that may be present) is then added to the mixture and the supernatant liquid filtered through a Gooch crucible, the asbestos pad of which has been previously covered with silica gel. The residue remaining in the flask is washed by decantation until free from halogen, the washings being poured through the Gooch crucible. The asbestos pad is then removed from the crucible and added to the residue in the flask and any mercury adhering on the walls of the crucible is washed into the flask by dilute nitric acid. The combined residue is dissolved in 1–1 nitric acid and when completely dissolved, the potassium permanganate, ferrous sulfate and ferric alum are added in the above order. The mercury is then titrated with potassium thiocyanate until the pink color persists.

It has been found important not to destroy the excess potassium permanganate with ferrous sulfate until just before the titration with potassium thiocyanate. Allowing the sample to stand with excess of potassium permanganate does not interfere with the analysis.

When titrating with potassium thiocyanate it was found necessary in order to insure the obtaining of the proper end-point that a blank be run and the colors made to check. Due to the tendency of the color to fade, this blank must be made just at the time of titration.

The Decomposition of a Mixture of Mercury Diethyl and Mercury Diphenyl with Hydrogen Chloride.—One gram of mercury diethyl was dissolved in 25 cc. of alcohol and 1.4 g. of mercury diphenyl added to it. Three cc. of alcohol saturated with hydrogen chloride was then added and the whole warmed to about 30° for two minutes. A precipitate separated. Water was then added and the solid collected on a filter. The solid was boiled with a small amount of alcohol and the residue collected on a filter. The melting point of the alcohol insoluble material was 248° and it was proved to be phenyl mercuric chloride. The weight was 1.10 g. Upon cooling the filtrate a product was obtained which melted at 185°. It was ethyl mercuric chloride mixed with a very small quantity of phenyl mercuric chloride. The weight of the ethyl mercuric chloride was 0.95 g.

Preparation and Decomposition of Unsymmetrical Mercury Compounds.—The method of preparation of the unsymmetrical organo-mercury compounds of Kharasch and Marker[2] was further modified. A complete description of the method follows.

About 8 g. of the organo-mercuri chloride is added in small portions at a time to about two molecular equivalents of the Grignard reagent of the other radical in anhydrous ether. The mixture is shaken constantly and kept immersed in ice water during the addition. After the addition of all the mercury compound the mixture is shaken until all of the solid has gone into solution.

$$R'HgCl + R''MgBr \longrightarrow R'HgR'' + MgBrCl$$

The excess Grignard reagent is then decomposed by ice and a 1% solution of sulfuric acid, care being taken that the temperature does not rise above 10°. The unsymmetrical organo-mercuri compound is extracted with ether and dried with anhydrous sodium sulfate. It is then filtered, and the ether evaporated *in vacuo,* care being taken not to introduce any moisture. The product thus obtained is washed several times with anhydrous alcohol and dried *in vacuo.*

To about 1.2 g. of the above product, dissolved in ethyl ether, about 4 cc. of a saturated solution of hydrogen chloride in alcohol is added. The product is warmed slightly for about five minutes and the solution evaporated. The solid product obtained is then crystallized from a small amount of alcohol. The melting point of this compound is determined and mixed melting points taken with pure organo-mercuri chlorides of R′ and R″.

To another 1.2 g. of the unsymmetrical molecule in ether a molecular equivalent of mercuric chloride is added. The mixture is refluxed for about ten minutes, evaporated and the products separated and purified by the use of suitable solvents. The melting points of the products obtained are determined and the identity of the compounds further proved by taking mixed melting points with R′HgCl and R″HgCl. The following reaction takes place

$$R'HgR'' + HgCl_2 \longrightarrow R'HgCl + R''HgCl$$

A third portion of the unsymmetrical compound is dried to constant weight *in vacuo* and the percentage of mercury determined by the method described above.

The above procedure was carried out in a general way for each compound prepared and split, but certain modifications had to be made to suit the properties of the different compounds. One example will be given in detail while all others are listed in the summary, with footnotes giving any modifications.

Preparation of Phenyl Mercury Phenylethyl, $C_6H_5HgCH_2CH_2C_6H_5$.—Phenylethyl mercury chloride was first prepared by adding one molecular equivalent of mercuric chloride to phenylethylmagnesium bromide. The mixture was then decomposed by ice and 1% sulfuric acid and the compound isolated and purified. A small portion of this compound in alcohol was refluxed for about one hour with an excess of silver chloride in order to change any organo-mercuric bromide to the chloride. The pure compound was then isolated and the melting point determined, which was found to be 165°.

Five grams of phenyl mercury chloride was added to the Grignard reagent of phenylethyl bromide. After decomposition and purification a white crystalline compound was obtained which was found to have no definite melting point but which softened at 120° and melted slowly up to 170°.

Anal. Subs., 0.1500, 0.1909; 7.5, 9.5 cc. of KCNS (1 cc. $\Bumpeq$ 0.01049 g. of Hg). Calcd. for $C_{14}H_{14}Hg$: Hg, 52.35. Found: Hg, 52.4, 52.2.

One gram of this compound was dissolved in alcohol and 0.71 g. of mercuric chloride added. On warming a heavy white precipitate formed which was collected on a filter. After several crystallizations from alcohol the insoluble portion melted at 250° and weighed 0.7 g. The melting point of the compound was not lowered by the addition of a small amount of pure phenyl mercury chloride, thus proving the substance to be phenyl mercury chloride.

The portion soluble in hot alcohol upon purification was found to have a melting point of 158° and weighed 0.8 g. The melting point of this product was not lowered by the addition of pure phenylethyl mercury chloride, thus proving the substance to be phenylethyl mercury chloride.

This shows that the unsymmetrical molecule was decomposed as follows

$$C_6H_5HgCH_2C_6H_5 + HgCl_2 \longrightarrow C_6H_5HgCl + C_6H_5CH_2CH_2HgCl$$

An additional one gram of the unsymmetrical compound was treated with an alcoholic solution of hydrogen chloride. Upon evaporation a white crystalline compound

SUMMARY OF EXPERIMENTAL WORK

The asterisk on a radical indicates that in the preparation of the unsymmetrical molecule the Grignard reagent of the radical so marked was treated with the organo mercury halogen derivative of the other radical, thus, $R_1{*}MgCl + RHgCl \longrightarrow R_1{*}HgR + MgCl_2$.

		Anal. of unsym. molecule				Decomp. unsym. molecules with	
Compound	M. p., °C.	Subs., g.	Cc. of KCNS 1 cc. ≈ 0.01049 g. of Hg	Hg, % Found	Hg, % Calcd.	$HgCl_2$	HCl
Phenyl mercury	120–170	0.1500	7.50	52.45	52.20	C_6H_5HgCl +	M. p. 163° [b] $C_6H_5C_2H_4HgCl$
*Phenyl ethyl	Dec.	.1909	9.50	52.35		$C_6H_5C_2H_4HgCl$	
*Benzyl mercury	Liq.	.3657	17.50	50.20	50.56	$C_6H_5CH_2HgCl$ +	M. p. 160° [a] $C_6H_5CH_2CH_2HgCl$ (90% ± 10%) + $C_6H_5CH_2HgCl$ (10% ± 10%)
Phenyl ethyl		.3156	15.04	50.04		$C_6H_5C_2H_4HgCl$	
Benzyl mercury							
*Phenyl ethyl	Liq.	.4167	19.85	49.96	50.56	$C_6H_5CH_2HgCl$ +	Same
		.3170	13.20	50.30		$C_6H_5C_2H_4HgCl$	
Benzyl mercury							
*Phenyl ethyl	Liq.					$C_6H_5CH_2HgCl$ + $C_6H_5C_2H_4HgCl$	Same
Thiophene	80–120	.2589	13.80	55.91	55.60	C_4H_3SHgCl +	M. p. 250° C_6H_5HgCl
Mercury *phenyl	Dec.	.1907	10.10	55.56		C_6H_5HgCl	
Heptyl mercury *ethyl	Liq.	.3420	19.85	60.88	61.02	[b]	M. p. 120° $C_7H_{15}HgCl$
*Heptyl mercury ethyl	Liq.	.3371	19.40	60.38	61.02	[b]	M. p. 120° $C_7H_{15}HgCl$
Heptyl mercury *butyl	Liq.	.3511	18.75	56.18	56.25	[c]	M. p. 105° [d] $C_7H_{15}HgCl$ (70% ± 10%) C_4H_9HgCl (30% ± 10%)
		.3605	19.20	55.87			
Isobutyl mercury *butyl	Liq.	.3140	19.00	63.43	63.80	C_4H_9HgCl +	M. p. 122°, main prod. (N)C_4H_9HgCl + small amounts of iso-C_4H_9HgCl
		.3501	21.20	63.52		Iso-C_4H_9HgCl	
Ethyl mercury	188	.2235	16.60	77.91	78.40		M. p. 193° C_2H_5HgCl
Cyanide[e]	Dec.	.2608	19.25	77.42			
o-Anisole	175	.2667	15.35	60.37	60.11		M. p. 179° $H_3COC_6H_4HgCl$
Mercury cyanide[f]	Dec.						
Isopropyl	Liq.	.4375	28.95	69.41	69.97	(N)C_3H_7HgCl +	M. p. 119° Iso-C_3H_7HgCl (85% ± 10%) *n*-C_3H_7HgCl (15% ± 10%)
Mercury *propyl		.4082	26.95	69.25		Iso-C_3H_7HgCl	
Phenyl mercury	190–210	.2231	10.70	50.31	51.55	$C_6H_4ClHgCl$ +	M. p. 246° [c] [g] *p*-ClC_6H_4HgCl (80% ± 10%) C_6H_5HgCl (20% ± 10%)
**p*-Chlorophenyl[h]	Dec.	.2099	10.10	50.47		C_6H_5HgCl	

SUMMARY OF EXPERIMENTAL WORK (*Continued*)

Compound	M. p., °C.	Subs., g.	Anal. of unsym. molecule Cc. of KCNS 1 cc. = 0.01049 g. of Hg	Hg, % Found	Hg, % Calcd.	$HgCl_2$	Decomp. unsym. molecules with HCl
*Phenyl mercury	190–210	0.2581	12.35	50.19	51.55	$C_6H_4ClHgCl$	M. p. 246°.[g] p-ClC_6H_4HgCl (70% ± 10%) + C_6H_5HgCl (30% ± 10%)
p-Chlorophenyl[h]	Dec.	.2254	10.85	50.49		C_6H_5HgCl	
Phenyl mercury	190–210	.2164	10.40	50.41	51.55	$C_6H_4ClHgCl$	M. p. 248°.[g] p-ClC_6H_4HgCl (80% ± 10%) + C_6H_5HgCl (20% ± 10%)
*p-Chlorophenyl[h]	Dec.	.2907	14.05	50.66		C_6H_5HgCl	
*Phenyl mercury	90	.2791	13.65	51.30	51.55	$C_6H_4ClHgCl$	M. p. 143°. o-ClC_6H_4HgCl (95% ± 5%) + C_6H_5HgCl (5% ± 5%)
o-Chlorophenyl	Dec.					C_6H_5HgCl	
*Phenyl mercury	89	.2171	10.65	51.46	51.55	$C_6H_4ClHgCl$	M. p. 141°. o-ClC_6H_4HgCl (90% ± 5%) + C_6H_5HgCl (10% ± 5%)
o-Chlorophenyl	Dec.	.3756	18.45	51.53		C_6H_5HgCl	
*Phenyl mercury	68	.2682	13.25	51.82	51.55	$C_6H_4ClHgCl$	M. p. 203°. m-ClC_6H_4HgCl
m-Chlorophenyl	Dec.					C_6H_5HgCl	
o-Chlorophenyl	165–200	.2137	9.55	46.88	47.36		M. p. 135°. Mostly o-ClC_6H_4HgCl (70%+)
Mercury *p-chlorophenyl	Dec.	.2419	11.00	47.70			
*Phenyl mercury	65	.2175	11.10	53.53	54.42	C_6H_5HgCl +	M. p. 250°. C_6H_5HgCl
o-Tolyl	Dec.	.4543	23.40	54.03		$CH_3C_6H_4HgCl$	
*o-Tolyl mercury	195–205	.2253	11.20	52.15	52.43	o-$H_3CC_6H_4HgCl$ +	M. p. 228°. p-$H_3CC_6H_4HgCl$ (80% ± 10%) + o-$CH_3C_6H_4HgCl$ (10% ± 5%)
p-Tolyl	Dec.	.2104	10.50	52.35		p-$H_3C_6H_4HgCl$	
o-Tolyl mercury	200–210	.2165	10.75	52.09	52.43	o-$H_3CC_6H_4HgCl$ +	M. p. 230°. p-$H_3CC_6H_4HgCl$ (80% ± 10%) + o-$CH_3C_6H_4HgCl$ (20% ± 10%)
*p-Tolyl	Dec.					p-$H_3CC_6H_4HgCl$	
o-Tolyl mercury	210–230	.2218	10.40	49.18	49.76	o-$H_3CC_6H_4HgCl$ +	M. p. 236°. p-ClC_6H_4HgCl (95%)
*p-Chlorophenyl	Dec	.2106	10.00	49.81		p-ClC_6H_4HgCl	
o-Tolyl mercury	210–230	.2207	10.40	49.42	49.76	o-$H_3CC_6H_4HgCl$ +	M. p. 230°. p-ClC_6H_4HgCl (95% ± 3%)
*p-Chlorophenyl	Dec.	.3298	15.60	49.62		p-ClC_6H_4HgCl	
p-Tolyl	120–155	.3686	19.10	54.35	54.41	p-$H_3CC_6H_4HgCl$ +	M. p. 246°. C_6H_5HgCl (90% ± 10%) + p-$CH_3C_6H_4HgCl$ (10% ± 5%)
Mercury *phenyl	Dec					C_6H_5HgCl	
m-Tolyl	65–70	.2235	11.50	53.97	54.41	m-$H_3CC_6H_4HgCl$ +	M. p. 250°. C_6H_5HgCl (80% ± 10%) + m-$CH_3C_6H_4HgCl$ (20% ± 10%)
Mercury *phenyl[j]	Dec.	.2022	10.40	53.95		C_6H_5HgCl	

SUMMARY OF EXPERIMENTAL WORK (*Concluded*)

Compound	M. p., °C.	Subs., g.	Anal. of unsym. molecule Cc. of KCNS 1 cc. ≈ 0 01049 g. of Hg	Hg, % Found	Hg, % Calcd.	Decomp. unsym. molecules with HgCl$_2$	Decomp. unsym. molecules with HCl
m-Tolyl mercury	180–205	0.2036	10.20	52.55	52.43	*m*-$H_3CC_6H_4HgCl$ + *p*-$H_3CC_6H_4HgCl$	M. p. 155°. *m*-$H_3CC_6H_4HgCl$ (90% ± 10%) + *p*-$CH_3C_6H_4HgCl$ (10% ± 10%)
**p*-Tolyl	Dec.	.2315	11.50	52.11			
m-Chlorophenyl	95–100	.2276	10.20	47.01	47.36	*o*-ClC_6H_4HgCl + *m*-ClC_6H_4HgCl	M. p. 207°. *m*-ClC_6H_4HgCl (80% ± 10%) + *o*-ClC_6H_4HgCl (20% ± 10%)
Mercury **o*-chlorophenyl	Dec.	.2113	9.55	47.40			
m-Tolyl mercury	165–220	.2125	10.10	49.86	49.76	*m*-$H_3CC_6H_4HgCl$	M. p. 230°. *p*-ClC_6H_4HgCl (90% ± 10%) + *m*-$CH_3C_6H_4HgCl$(10% ± 10%)
**p*-Chlorophenyl	Dec.	.2161	10.20	49.51		*p*-ClC_6H_4HgCl	
o-Tolyl mercury	Liq.	.2301	11.00	50.15	50.31	[k]	M. p. 143°. *o*-$H_3CC_6H_4HgCl$
**o*-Anisole		.2355	11.20	49.89			
Methyl mercury	Liq.	.2143	12.00	58.86	58.82	H_3CHgCl	M. p. 168°. H_3CHgCl
**m*-Chlorophenyl		.2285	12.70	58.29		*m*-ClC_6H_4HgCl	
p-Anisole	102	.2353	10.75	47.92	48.40	*o*-$H_3COC_6H_4HgCl$	M. p. 175°. *o*-$H_3COC_6H_4HgCl$
Mercury **o*-anisole	Dec.	.2287	10.50	48.15		*p*-$H_3COC_6H_4HgCl$	
α-Naphthyl	130–150	.2076	9.10	45.98	46.15	$C_{10}H_7HgCl$	M. p. 183°. $C_{10}H_7HgCl$[l]
Mercury **p*-anisole	Dec.	.2256	9.95	46.27		*p*-$H_3COC_6H_4HgCl$	
α-Naphthyl	200–220						M. p. 188°. $C_{10}H_7gCl$[m]
Mercury **o*-anisole	Dec.						

[a] The separation of the two compounds was attained by fractional crystallization from alcohol. The amount of each component was determined by weight and the identity was confirmed by the fact that neither of them lowered the melting point of the corresponding pure material.

[b] The entire product resulting from the decomposition with mercuric chloride melted at 125°. It was found impossible to make any separation of the two compounds. An equal mixture of heptyl mercury chloride and ethyl mercury was prepared and this melted at 125° and was likewise found to be impossible to separate. The fact that the same result was obtained by preparing the compound in one case by using the Grignard reagent of the ethyl and in the other case the Grignard reagent of the heptyl offers sufficient evidence that the unsymmetrical compound was obtained. It will be noted that in each case the compound gave the correct analysis.

[c] The melting point of the decomposition product with mercuric chloride was 110° and it was found impossible to make any separation of products.

[d] The melting point of the decomposition product of the unsymmetrical molecule, heptyl mercury butyl, with hydrogen chloride indicates a mixture of the two mercury chlorides. The product was dried in a vacuum over sulfuric acid and analyzed. *Anal.* Subs., 0.2069, 0.2399: 12.55, 14.20 cc. of KCNS (1 cc. ≎ 0.01049 g. Hg). Found: Hg, 62.5, 62.25. Since butyl mercury chloride contains 68.45% of mercury, and heptyl mercury chloride contains 50.8% of mercury, the mixture above contains 29.9 ± 1.0% of butyl mercury chloride and 70.1 ± 1.0% of heptyl mercury chloride.

[e] Ethyl mercury cyanide was prepared by refluxing one mole of ethyl mercury chloride with one and one-half moles of silver cyanide in benzene for one hour. The solution was then filtered and the benzene evaporated, leaving a white crystalline product which was crystallized from alcohol in white flakes. This last product gave no test for halogen.

[f] *o*-Anisole mercury cyanide was prepared similarly to ethyl mercury cyanide. After purification this product gave no test for halogen but after decomposition with hydrogen chloride and purification, gave a strong test for halogen.

[g] The percentage composition of the two components was estimated by analysis for mercury of the substance which resulted from the decomposition of the unsymmetrical molecule with hydrogen chloride. The results consistently indicated that about 80% of the solid was *p*-chlorophenyl mercury chloride. In view of the fact that a very small error in the mercury analysis affects appreciably the percentage composition of the solid, we have indicated what in our estimation constitutes the maximum error in the determination of the composition of the sample. (The authors are indebted to Mr. Pines for many of these analyses.)

[h] The unsymmetrical molecule phenyl mercury *p*-chlorophenyl was washed numerous times with petroleum ether but it was found difficult to obtain it in an absolutely pure state. It always retained a slightly brown color.

[i] The product obtained from the decomposition of *o*-chlorophenyl mercury *p*-chlorophenyl with mercuric chloride melted at 150 to 180°, indicating a mixture of the *o*- and *p*-chlorophenyl mercury chlorides, but all attempts to separate the two products failed. Equal mixtures of *o*-chlorophenyl mercury chloride and *p*-chlorophenyl mercury chloride melted at 150 to 180° and likewise gave the same difficulty in separation.

[j] The unsymmetrical molecule, *m*-tolyl mercury phenyl when first isolated was an oil which on treatment with petroleum ether in the cold immediately changed to a crystalline product. This compound was much more soluble in ethyl ether than the corresponding para compound.

[k] The product resulting from the decomposition of *o*-tolyl mercury *o*-anisole melted at 145°, which is similar to a mixture of *o*-tolyl mercury chloride and *o*-anisole mercury chloride. All attempts to separate these two products failed.

[l] The unsymmetrical compound α-naphthyl mercury *p*-anisole, being but slightly soluble in alcohol and ether and soluble in chloroform, it was thought best to decompose this molecule with hydrogen chloride in chloroform solution; 1.2 g., therefore, was treated with hydrogen chloride in chloroform. The solution was evaporated to dryness and the white residue dissolved in alcohol. Water was then added to the alcohol solution, forming a heavy white precipitate which was filtered and dried. The melting point of this product was found to be 80°, the melting point of naphthalene. This product also gave a strong odor of naphthalene. It is probable that the α-naphthyl mercury chloride was first formed and that this product was reacted upon by the excess hydrogen chloride forming naphthalene and mercuric chloride. An additional 1.2 g. of the unsymmetrical compound was then treated with hydrogen chloride in alcohol solution and after warming for about three minutes water was added, forming a heavy white precipitate which melted at 153°. The product melting at 153° was treated

with a small amount of hot alcohol, filtered and washed with a little cold alcohol. The residue gave a melting point of 183°. The weight of this product was 0.6 g. and its identity was confirmed by the fact that the melting point of the material was not depressed by admixture with pure α-naphthyl mercury chloride. With pure *p*-anisole mercury chloride the melting point was lowered to 161°.

To the alcohol filtrate and washings of the above, water was added and the precipitate which formed was filtered. The melting point of this product, about 0.1 g., was 80°, which is the melting point of naphthalene.

[m] The decomposition of naphthyl mercury *o*-anisole by hydrogen chloride was run in alcohol solution and gave results similar to naphthyl mercury *p*-anisole, naphthalene and naphthyl mercury chloride being formed.

was obtained which upon crystallization from alcohol melted at 160° and weighed 0.8 g. The melting point of this compound was not lowered by the addition of pure phenylethyl mercury chloride but when mixed with phenyl mercury chloride was lowered to 145°, thus proving the compound to be phenylethyl mercury chloride. This shows that the unsymmetrical molecule was decomposed as follows

$$C_6H_5HgCH_2CH_2C_6H_5 + HCl \longrightarrow C_6H_6 + C_6H_5CH_2CH_2HgCl$$

Upon repeating the above experiment a compound melting at 161° was obtained by treating the unsymmetrical molecule with hydrogen chloride and compounds melting at 250 and 165° were obtained on treatment with mercuric chloride.

The general method described with one specific example in detail gives an idea of the procedure employed in the experimental work, a summary of which follows. Any modification of the method is noted in footnotes under the designating symbol.

In each case all decomposition products isolated were weighed and no results considered unless quantitative yields were obtained.

The authors wish to acknowledge their indebtedness to Dr. James K. Senior for much help in connection with the preparation of this manuscript.

Summary

1. The validity of the method of establishing experimentally the relative electronegativity of organic radicals is discussed.

2. An enlarged table of the order of electronegativity of organic radicals is given.

3. The Table of Electronegativity of Organic Radicals is employed in the study of the following topics: (*a*) the interpretation of the existence of free radicals; (*b*) the study of the effect of various substituents upon the electronegativity of the phenyl radical; (*c*) the study of substitution in the benzene ring.

4. The preparation and properties of a number of unsymmetrical organo-mercuri compounds are described.

5. A method is given for the analysis of compounds of the type RHgCl.

6. Various criticisms of the writers' views are shown to be untenable.

CHICAGO, ILLINOIS