Before the synthesis of 2-bromo-β-resorcylic acid was accomplished, indication that the position of its bromine atom was different from the position of the bromine atom in the substance described as 2- or 4-bromo-β-resorcylic acid was given by treating 3-bromo-5-nitro-2,4-dihydroxybenzoic acid, which is an intermediate product in the preparation of the 2-bromo-β-resorcylic acid, and the 2- or 4-bromo-β-resorcylic acid with nitric acid. A bromine atom protected by two *o*-hydroxyl groups is not replaced by a nitro group, while a bromine atom not so protected is replaced.

One g. of 3-bromo-5-nitro-2,4-dihydroxybenzoic acid was warmed on a water-bath for a few minutes with 15 g. of concd. nitric acid; the product was poured into ice water and the precipitated yellow solid recrystallized from alcohol; it separated in yellow needles, m. p. 189–191°, which gave no depression of the melting point of 2-bromo-4,6-dinitroresorcinol which was prepared from 2,4,6-tribromoresorcinol and nitric acid.[9] One g. of 4-bromo-β-resorcylic acid was warmed on a water-bath with an excess of concd. nitric acid until evolution of oxides of nitrogen ceased. The solid which separated when the product was poured into water was washed with water and recrystallized from methyl alcohol. It melts at 175° and was recovered unchanged after boiling for six hours with water and therefore cannot be 3,5-dinitro-β-resorcylic acid; it was shown to be 2,4,6-trinitroresorcinol by comparison with a specimen of this substance.

Summary

The position of the bromine atom in a bromo-dimethoxybenzoic acid obtained by oxidation of bromo-dimethoxybenzoylacrylic acid has been determined.

New York, N. Y.

[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

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Purpose of Work

A study of the electronegativity of organic radicals is of much importance from the standpoint of the electronic conception of valence. The information can also be used advantageously in the interpretation of a number of baffling organic reactions.

At the present time the words "positive" and "negative" with reference to organic radicals are used very loosely and there is no adequate method of determining directly which one of two radicals is more strongly electronegative. The classification of radicals as "positive" and "negative" is hardly necessary, for according to the modern conception of valence

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[9] Dahmer, *Ann.*, **333**, 362 (1904).

there is no such distinction. By "electronegativity" of a radical is meant the affinity of that radical for the pair of valence electrons. Naturally, the attraction of the radical for the pair of valence electrons is a function of the electronic structure of the molecule, and thus arises the difference of electronegativity of organic radicals.

The method we employ for establishing the relative electronegativity of organic radicals depends upon the fact that when hydrogen chloride is added to a mercury diaryl or dialkyl the corresponding hydrocarbon and the aryl or alkyl mercuric chloride are formed: $RHgR + HCl \longrightarrow RHgCl + RH$.[1] From this fact it was plausible to assume that if one started with an unsymmetrical mercury derivative R_1HgR_2 and treated that with hydrogen chloride it should lead directly to R_1HgCl and the hydrocarbon R_2H (when R_2 is the most electronegative of the two radicals): $R_1HgR_2 + HCl \longrightarrow R_1HgCl + R_2H$. By varying the radicals R_1 and R_2 it should thus be possible to establish the order of electronegativity of all types of organic radicals.[2]

It is of importance to point out here that the reaction of the unsymmetrical mercury compounds with hydrogen chloride is almost instantaneous. The possibility of side reactions taking place is thus practically eliminated. This point will be more fully discussed later in the paper.

Historical Part

The only unsymmetrical mercuri-organic compounds described in the literature are those recorded by Hilpert and Grüttner.[3] The method employed by these authors was to treat an organo-mercury halide with a Grignard reagent. However, they specifically state that in order to prepare these unsymmetrical molecules it is necessary to proceed in a definite way; thus, in order to prepare phenylmercury-ethyl it is necessary to start with ethylmercuric chloride and treat that with phenylmagnesium bromide.

According to these authors, if the order is reversed the desired product is not formed.[4] In some cases, the authors state the unsymmetrical molecules cannot be prepared at all, namely, when they treated ethylmagnesium bromide with naphthylmercuric chloride, mercury-diethyl was formed instead of the unsymmetrical molecule, ethylmercury-naphthyl.

These limitations, if true, would have defeated the object which we had

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[1] Thus, as given in the experimental part, mercury-diphenyl and mercury-dibenzyl when dissolved in alcohol and treated with alcohol saturated with hydrogen chloride gave at once phenylmercuric chloride and benzene, and benzylmercuric chloride and toluene, respectively.

[2] See discussion in paper of Kharasch and Grafflin, This Journal, **47**, 1948 (1925).

[3] Hilpert and Grüttner, *Ber.*, **48**, 908 (1915).

[4] This statement seemed to be corroborated by the work of Jones and Werner, [This Journal, **40**, 1268 (1918)]. They treated phenylmercuric chloride with benzylmagnesium chloride and obtained dibenzyl and therefore, presumably, first mercury-dibenzyl.

in mind and greatly limited the scope of our investigations. It was for this reason that the work of Hilpert and Grüttner was repeated and while their observations were found to be correct, by modifying the method we were able to prepare the unsymmetrical molecules by attaching the radicals to the mercury in any order we desired. The difference observed by Hilpert and Grüttner is thus not a real difference but only a limitation due to the experimental procedure employed. We were also able, by controlling the conditions (as described in the experimental part), to prepare unsymmetrical mercuri-organic compounds where other workers have obtained only their decomposition products.[3,4]

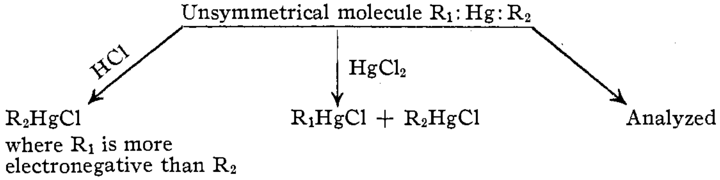
Another method of preparing unsymmetrical mercuri-organic derivatives applicable to compounds which cannot be used in the Grignard reaction, is the one described by one of us and Miss Grafflin[5] and depends upon the elimination of carbon dioxide from molecules R_1COOR_2, where R_1COOH represents an acid which loses carbon dioxide readily.

Proof of the Existence of Unsymmetrical Mercuri-Organic Molecules and Plan of Procedure

In the case of the four or five unsymmetrical compounds described by Hilpert and Grüttner, there is no direct evidence, except analysis, that the compounds are unsymmetrical molecules, and any of them could very well be a mixture of two symmetrical molecules. We used in conjunction with the analysis the following two criteria: (1) the decomposition of the unsymmetrical molecule with mercuric chloride to give two mercuri-organic molecules: $R_1HgR_2 + HgCl_2 \longrightarrow R_1HgCl + R_2HgCl$; (2) the splitting with hydrogen chloride whereby only one molecule of a mercuri-organic compound and one molecule of a hydrocarbon were formed: $R_1HgR_2 + HCl \longrightarrow R_1HgCl + R_2H$.

In cases where the difference of the electronegativity of the radicals R_1 and R_2 is large, the last two criteria in themselves are sufficient to establish whether the product of a reaction is an unsymmetrical molecule or a mixture of two symmetrical. Otherwise, the analysis of the compound must also be taken into account.

The method as employed by us was as follows. A quantity of the unsymmetrical mercury compound was prepared, purified and then immediately divided into three parts and the different portions treated as indicated below.



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[5] Kharasch and Grafflin, *Science*, **58**, 1510 (1923); THIS JOURNAL, **47**, 1948 (1925). See also Koten and Adams, *ibid.*, **46**, 2768 (1924).

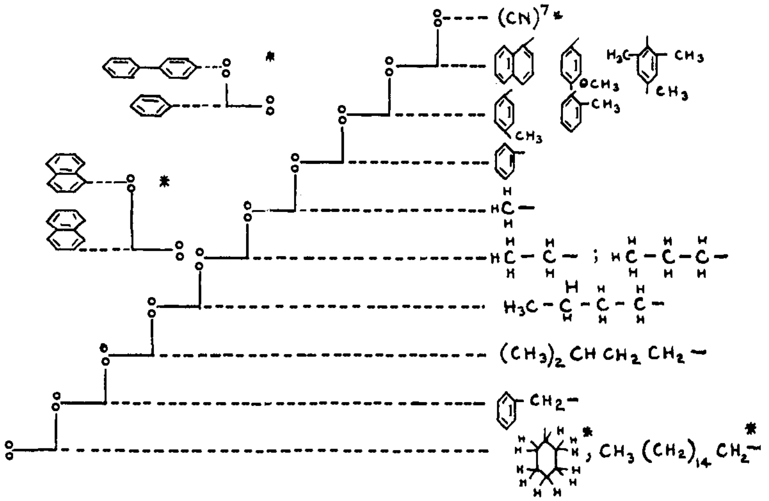
These criteria prove conclusively whether a compound is an unsymmetrical molecule or a mixture of two symmetrical compounds. No results were considered unless we had absolute concordance between these data.

Classification of Results

From our standpoint, the most important reaction of the unsymmetrical mercuri-organic molecules is the reaction with hydrogen chloride. It is particularly gratifying that all these decompositions were clean-cut and proceeded extremely rapidly, the reaction in most cases being carried to completion in one to two minutes. We might emphasize once more that we consider the radical which presumably is dissociated first from the mercury and then combines with the hydrogen ion in solution (to yield the hydrocarbon), as the more electronegative of the two, or the one having a greater attraction for electrons. Our results, then, are summarized in Table I.

Table I

Order of Electronegativity of Some Common Organic Radicals[a]



[a] The unsymmetrical molecules marked with an asterisk are not recorded in the experimental part of this paper. They were merely added to complete the list, and will be reported later in another investigation under way by one of us (Kh.).

In this table is indicated the decreasing tendency to hold the valence electrons, or decreasing electronegativity—the compounds above resemble more the non-metals, while those below, the metals.[6]

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[6] In an extensive investigation on gold carbon compounds which is being carried out by one of us (Kh.) and H. Isbell, this Table of Electronegativity of Organic Radicals was found to be of great service. It helped us predict in advance whether a certain gold compound could be prepared and the approximate stability of the molecule. At no time were we led to incongruous results.

It is also important to point out that in determining the position of *any one* radical in Table I, it was compared not only with the ones immediately above and below it, but with a large number of others in order to test the validity of the method. Thus, for instance, the phenyl radical was compared with the following in order to establish definitely the position of the "phenyl" group in the Table of Electronegativity of Radicals.

TABLE II

CRITERIA ESTABLISHING RELATIVE ELECTRONEGATIVITY OF "PHENYL" RADICAL

1. Phenyl Hg\Naphthyl
2. Phenyl/Hg Methyl
3. Phenyl Hg*p*-Tolyl
4. Phenyl/Hg Butyl
5. Phenyl Hg*o*-Anisyl
6. Phenyl/Hg Ethyl[7]
7. Phenyl Hg\CN
8. Phenyl/Hg Benzyl
9. Phenyl Hg\Mesityl
10. Phenyl/Hg Cyclohexyl

The lines merely indicate which radical was eliminated from the mercury. A brief reference to Table I also shows that the phenyl group was eliminated from the mercury with radicals below it but remained attached to those above it.

While establishing the position of other radicals in the Table of Electronegativity the number of unsymmetrical mercurial compounds prepared was not so large as with the phenyl radical yet, as can be seen from the experimental part, a sufficiently great number was used each time. It is particularly gratifying, and in some respects a check on the validity of the method employed, that in no case were any discrepancies observed—that is, at all times that radical lying above was eliminated from the mercury.

It is significant also that with radicals that lie very closely together, such as propyl and butyl, the decomposition with hydrogen chloride gave two products. This mixture, however, upon analysis was found to contain 74.2% ± 1.0% of butylmercuric chloride and 25.8% ± 1.0% of propylmercuric chloride. The unsymmetrical molecules were then prepared in two different ways, and altogether six different analyses were performed, but at no time did the composition of the mixture obtained by treating the unsymmetrical molecule with hydrogen chloride vary by more than the limit of experimental error. This proves that although propyl is more electronegative than butyl, it is so to only a slight extent. As compared with a methyl group, however, butyl is much less electronegative, for the unsymmetrical molecule butylmercury-methyl (prepared by the two methods mentioned—namely, starting with butylmercuric chloride and adding methylmagnesium iodide, or methylmercuric chloride and adding butyl-

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[7] This compound was prepared in two ways: first, from phenylmercuric chloride and ethylmagnesium bromide and second, from ethylmercuric chloride and phenylmagnesium bromide. The decomposition of the unsymmetrical molecule with hydrogen chloride, however, irrespective of the method of preparation, gave ethylmercuric chloride and benzene.

magnesium bromide) when treated with hydrogen chloride was decomposed quantitatively into methane and butylmercuric chloride.

Very similar results were obtained in the case of benzylmercuric ethyl. This product, upon decomposition with hydrogen chloride gave a mixture corresponding to 94.1% ± 1.0% of benzylmercuric chloride and 5.9% ± 1.0% of ethylmercuric chloride, indicating that the ethyl group is decidedly more negative than benzyl. Furthermore, the methyl radical, which is more negative than the ethyl radical, when balanced against the benzyl radical in methylmercury-benzyl, eliminated methane quantitatively when treated with hydrogen chloride. This result is entirely in accord with what we should expect from the position of the two radicals with respect to the ethyl radical.

The Table of Relative Electronegativity of organic radicals contains also some of the radicals in the same row—such as α-naphthyl, *p*-methoxyphenyl and mesityl. That, however, does not imply that these radicals are of the same order of electronegativity, but merely that, although their relationship to the radicals below and above them has been definitely determined, their individual relationships have not been as yet definitely established. We know, for instance, that α-naphthyl, *p*-methoxyphenyl and mesityl are more negative than phenyl or any radical occurring below it, but which one of these three radicals is the most electronegative has not been determined experimentally. The work is being continued by one of us (Kh.) and we hope in the near future to have established by this and similar methods the exact relative electronegativity of most of the simple organic groups.

Stability of the Unsymmetrical Mercuri-Organic Compounds

From the fact that a large number of futile attempts to prepare the unsymmetrical molecules have been recorded in the literature, it is evident that, if the molecules exist at all, they must be very unstable. This is completely borne out by our observations. Although we have been able to prepare all of the unsymmetrical molecules we started out to prepare, we had to work very rapidly in order to isolate them. The instability of these molecules, of course, is a direct function of their composition and the further apart the radicals are in the Table of Electronegativity, the less stable the unsymmetrical mercury molecule. They are all particularly unstable toward heat, decomposing into two symmetrical molecules. Even heating an ether or alcoholic solution of the unsymmetrical molecules produces that change. Thus, by warming an alcoholic solution of phenylmercury-*p*-tolyl (a solid which has a melting point of 120°) for 15 minutes, the melting point of the product rose to 145°, indicating considerable, if not complete, decomposition into mercury-diphenyl and mercury-di-*p*-tolyl. The unsymmetrical molecules must therefore be worked with great dispatch and heating completely avoided. The failure of Hilpert and Grüttner,[3] Jones and Werner[4] and others to obtain the unsymmetrical mercurial compounds is primarily due to the use of too large an excess of Grignard reagent and to warming the mixture after the addition of the Grignard reagent. It is undoubtedly at that time, as indicated by our own results when carried out under such conditions, that their unsymmetrical molecule decomposed into two symmetrical molecules.

When allowed to stand for any length of time the unsymmetrical molecules, whether solid or liquid or dissolved in a solvent, decompose into two symmetrical molecules.

The unsymmetrical mercuri-organic molecules have melting points much lower than those of the symmetrical molecules. They are very dangerous to work with, particularly the aliphatic unsymmetrical molecules which have stupefying odors even in minute concentration, and produce headache and nausea.

Discussion of the Significance of the Table of Electronegativity of Organic Radicals

Before we proceed with the discussion of the application of our results in the interpretation of organic reactions, we should like to emphasize what appears to us an important extension as to the manner in which two atoms, particularly two carbon atoms, can share a pair of valence electrons to form what is ordinarily known as the valence bond.

It is the basis of the Lewis[8] concept that two electrons lying between two atomic nuclei constitute the chemical bond, and that the pair of electrons may lie between two atomic nuclei in such a manner that there is no electrical polarization, or the pair of bonding electrons may be shifted in the direction of one atom or the other one in order to give to that atom a negative charge and consequently to the other a positive charge. Thus the various possibilities are denoted by Lewis in the manner indicated below, the circles merely denoting the relative positions of the pair of valence electrons.

A : B (1)   A :B (2)   A: B (3)

However, as pointed out by one of us and Sher,[9] from the standpoint of the organic chemist another union is possible. This is best represented in Fig. 1.[10] The two carbon atoms can share a pair of electrons at the intersection of their inner shells (corresponding presumably to Bond 1 of

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[8] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph, The Chemical Catalog Company, New York, **1923**.

[9] Kharasch and Sher, *J. Phys. Chem.*, **29**, 625 (1925).

[10] It is understood, of course, that the picture is merely an attempt to show the relative position that may be assumed by the electrons and not an attempt to indicate the actual positions assumed by electrons between two carbon atoms.

Lewis) or at the intersection of Inner Shell 1 and the outer fourth shell of the other, thus leading to polarization, or the reverse may be true. It is, however, also conceivable that the pair of valence electrons may be shared in the outer layers of the two carbon atoms, namely Shell 4 of one and Shell 4 of the other, as denoted by squares in Fig. 1.[11] (Furthermore, the number of possible degrees of polarity, that is, the number of possible energy levels in the Bohr sense is supposed to be finite, and not infinite as in the Lewis theory.)

Presumably, two atoms or radicals that would share a pair of valence electrons in their outer shells (4,4), respectively, have very slight attraction for the electrons and the addition of a slight amount of energy would displace the electrons beyond the attraction of the nucleus of one of the atoms, thus rupturing the bond.

If one bears this picture in mind and also the fact that a phenyl group replacing a hydrogen atom in a methyl radical decreases enormously the negativity of the radical, then the existence of free radicals follows as a consequence.

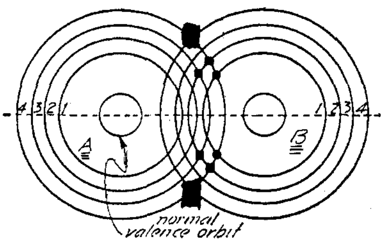
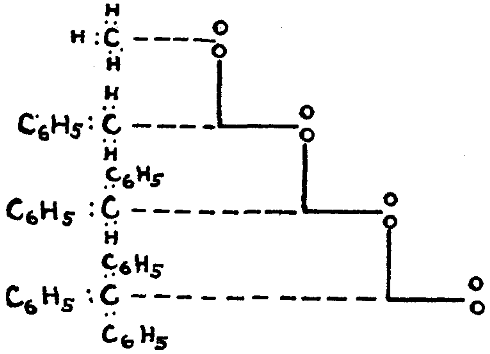


Fig. 1.—Concept of "bond" between two carbon atoms and variations thereof.

Thus, Table III represents the effect of the replacement of a hydrogen atom by a negative phenyl radical.

Table III

Effect of Groups upon the Negativity of the Methyl Radical



In the Table of Electronegativity of Radicals we have proved experimentally that the methyl radical is more electronegative than the benzyl, that is, the replacement of a hydrogen atom by an electronegative phenyl group repels the electrons from the methyl radical. This is in direct con-

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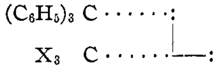
[11] For further elaboration of these concepts, consult Ref. 9.

tradiction to Lewis' idea as elaborated in his monograph,[12] a logical consequence of which is that the negative phenyl group should attract the electrons, making the benzyl radical more electronegative than the methyl radical. It seems to us, however, more logical that the phenyl radical would in virtue of its electronegativity attract the pair of electrons from the methyl carbon atom, become then negatively charged and repel other electrons from the methyl carbon atom, making the benzyl group much less electronegative than the methyl. It is also possible that the phenyl radical, displacing as it does the arrangement of the electrons around the methyl group and pulling the electrons into outer orbits, would have a tendency to displace the other electrons into outer shells as well. There is a great deal of evidence in favor of this hypothesis and it will be discussed more thoroughly in a publication by one of us (Kh.) and Starkey.

Irrespective of the mechanism of the action of the phenyl group, it is evident that an electronegative group has a tendency, when attached to a methyl carbon atom, to repel the valence electrons from that carbon atom. If all three hydrogen atoms are replaced by phenyl groups, the valence electrons should be considerably displaced from the methyl carbon atom, thus making the radical an extremely weak electronegative radical, one that begins to approach in reactions those of a metal. It is particularly instructive that the chemical reactions of the compounds of triphenylmethyl, for example, triphenylmethyl chloride, or triphenylmethane, bear out this conclusion most admirably.

It follows as a consequence that two such triphenylmethyl radicals should not form a stable compound, for they may be assumed to share the electrons in outer shells (4,4) (see Fig. 1) and any supply of energy will shift one or both of the electrons from the sphere of the methyl carbon atom, thus resulting in a break in the molecule, or what we may term ionization.

Pertinent to this is the idea that if we replace the hydrogen atoms of the methyl group by radicals more electronegative than phenyl, the radical X_3C (where X represents a group more electronegative than phenyl) should have the electrons further displaced from the methyl carbon atom than triphenylmethyl, that is



$$\begin{array}{l} (C_6H_5)_3\,C\cdots\cdots: \\ X_3\;\;C\cdots\cdots\cdots\text{—}: \end{array}$$

and therefore the double compound

$$X_3\,C\cdots\cdots:\cdots\cdots C\,X_3$$

should be less stable and dissociated to a greater extent. This can be

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[12] The organic chemist owes Lewis a tremendous debt for reviving and elaborating the Stark concept of valence. However, his speculations as to the mechanisms of organic reactions, addition reactions, etc., do not lend themselves to rigorous application.

shown to be in agreement with the facts by reference to Professor M. Gomberg's article on "Organic Radicals."[13]

Reference to the tables in the article mentioned will disclose the fact that radicals which in the Table of Electronegativity lie above the phenyl radical, increase dissociation, while those below the phenyl radical hinder, or stop it completely. It is also instructive to note that since the diphenyl radical is more electronegative than the phenyl radical, it increases the dissociation of the hexa-aryl ethane much more than the phenyl radical. The fact also that α-naphthyl radical is more electronegative than the β-naphthyl radical causes it to be more potent in causing dissociation of the hexa-aryl ethane molecule.[14]

These considerations we hope will help to clarify the confusion relative to influences causing dissociation in the hexa-aryl ethane series. Thus Gomberg writes, "From Schlenk's results with diphenyl-hexa-aryl ethanes one might infer that the dissociation of the hexa-aryl ethane into free radicals is greatly favored by the complexity or the weight of the aryl groups, the dissociation becoming apparently more manifest also in proportion to the number of such groups. Some support in favor of this inference is given by the α-naphthyl-diphenylmethyl, which was found to be monomolecular to the extent of 60%. But the hypothesis that the dissociation of the hexa-aryl ethane is proportional to the complexity of the aryl groups becomes wholly untenable when one compares triphenylmethyl with phenylxanthyl, $C_6H_5.C\overset{\cdot}{=}(C_6H_4)_2{=}O$, which is monomolecular to the extent of 75%. Is the union of two phenyl groups the paramount influence in this case?. . . .More facts are needed before we can hope to clarify this confusing interplay of various influences."

According to our hypothesis the weight or complexity of the radical is of no significance in this case and no logical deductions can be made from it; it is the electronegativity of the radical attached to the methyl carbon atom (with the consequent decrease in the electronegativity of the methyl group) that is of paramount importance. That is the reason the cyclohexyl radical decreases dissociation of the aryl ethane while the naphthyl radical increases it, although both of them are heavier than the phenyl radical, and the reason the α-naphthyl increases dissociation more than the β-naphthyl radical, for the former is the more negative radical.

The considerations developed here as to the importance of our knowledge of the relative electronegativity of organic radicals in the interpretation of organic reactions, apply equally forcibly to secondary and tertiary alkyl halides, the decomposition of organic acids into carbon dioxide or carbon monoxide and absorption reactions by a double bond. From the stand-

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[13] M. Gomberg, *Chem. Rev.*, **1**, 104 (1924).

[14] This difference in electronegativity between the α- and β-naphthyl radicals helps one to interpret a number of otherwise baffling reactions in the naphthalene series.

point of this theory these reactions can be treated as consequences of a general theory and not as so many isolated reactions. They will be dealt with in later papers by one of us (Kh.).

Experimental Part

The general method of preparation of the unsymmetrical mercuri-organic compounds is a modification of that used by Hilpert and Grüttner.[3] As stated in the theoretical part, the difficulty of these workers in obtaining the unsymmetrical molecules was due to their use of too large an excess of the Grignard reagent, and not controlling the temperature well enough. If these two factors are carefully controlled, but little difficulty will be experienced in preparing any unsymmetrical mercuri-organic compound by the use of the Grignard reaction.

As the general method employed in the preparation of these compounds is practically the same, only that for one, namely, *p*-tolylmercury-phenyl, will be described in detail and the modifications of the method whenever carried out will be noted under the individual compound.

***p*-Tolylmercury-phenyl,** *p*-$CH_3C_6H_4HgC_6H_5$.—To two molecular equivalents of phenylmagnesium bromide in absolute ether was added one molecular equivalent of finely pulverized *p*-tolylmercuric chloride. The latter product was introduced in very small portions with constant agitation of the flask. The temperature was kept at 5° so as to avoid the decomposition of the product into two symmetrical molecules. It was found experimentally that this decomposition took place almost quantitatively when the mixture was kept at the boiling point of ether for a half hour. The mixture was then shaken for a half hour, or until all of the *p*-tolylmercuric chloride dissolved. The excess of Grignard reagent was then decomposed by using a 0.1% solution of sulfuric acid. The flask during this operation was submerged in an ice-bath and at no time was the temperature allowed to rise above 10°. The unsymmetrical mercuri-organic compound was extracted with ether, the latter dried with anhydrous sodium sulfate, filtered off, and the ether evaporated in a vacuum, care being taken not to introduce any moisture. The product thus obtained was then washed thoroughly five times with alcohol to remove any of the mercuric chlorides or symmetrical compounds that might be present, and dried again in a vacuum.

At this point the product was divided into three portions. To the first portion was added an alcoholic solution of hydrogen chloride. A heavy white precipitate formed immediately. The product was warmed for ten minutes on the water-bath to insure complete reaction, then cooled and the total product precipitated by the addition of water. The solid was collected on a filter and dried. The melting point of this solid was 250° and it was not depressed by the addition of known phenylmercuric chloride. This proves that the decomposition of the unsymmetrical molecule took place as follows: $CH_3.C_6H_4.Hg.C_6H_5 + HCl \longrightarrow CH_3C_6H_5 + C_6H_5.HgCl$.

To the second portion, a molecular equivalent of mercuric chloride dissolved in alcohol was added. The mixture containing a large amount of solid material was then heated on the water-bath for ten minutes, and the solid that did not dissolve was collected on a filter (Filtrate 1). The precipitate was then treated again with alcohol, the latter heated and the precipitate again collected on a filter. The melting point of this solid was 252° and the melting point was not depressed by the addition of phenylmercuric chloride. However, when it was mixed with pure *p*-tolylmercuric chloride, the

TABLE IV

SUMMARY OF EXPERIMENTAL WORK

Analysis of Unsymmetrical Molecule.						Decomposition of Unsymmetrical Molecules with	
			Cc. of KNCS 1 cc. ≎ 0.01078 g. of Hg	Hg, %			
Compound	Formula	Subs., g.	Cc.	Found	Calcd.	$HgCl_2$	HCl
Mercurydiphenyl	$C_6H_6.Hg.C_6H_5$					$2C_6H_5.HgCl$	$C_6H_5.HgCl + C_6H_6$
Mercurydibenzyl	$C_6H_5.CH_2.Hg.CH_2.C_6H_5$					$2C_6H_5.CH_2.HgCl$	$C_6H_5.CH_2.HgCl + C_6H_5.CH_3$
Phenylmercury-methyl	$C_6H_5^*.Hg.CH_3^*$[a]	0.4142	26.20	68.19			
	(Liq.)	.4304	27.10	67.88	68.52	$C_6H_6.HgCl + CH_3.HgCl$	$CH_3.HgCl$[b] (M. p. 171°)[c]
Cyclohexylmercury-phenyl[d]	$C_6^*H_{11}Hg.C_6\overset{*}{H}_5$	1.3987	71.50	55.11			
	(Solid)	1.4329	73.20	55.07	55.64	$C_6H_5.HgCl + C_6H_{11}.HgCl$	$C_6H_{11}.HgCl$ (M. p. 155°)
Butylmercury-phenyl	$C_4H_9.Hg.C_6^*H_5$	0.6909	38.40	59.91			
	(Liq.)	.2476	13.70	59.69	59.93	$C_4H_9.HgCl + C_6H_5.HgCl$	$C_4H_9.HgCl$ (M. p. 129°)
Benzylmercury-methyl	$C_6H_5.C\overset{*}{H}_2.Hg.C\overset{*}{H}_3$	.2819	16.95	64.82			
	(Liq.)	.4869	29.41	65.09	65.40	$C_6H_5.CH_2.HgCl + CH_3.HgCl$	$C_6H_5.CH_2.HgCl$ (M. p. 102°)
Phenylmercury-naphthyl[e]	$C_6^*H_5.Hg.C_{10}H_7$	.4907	22.40	49.21			
	(Solid)	.4834	22.00	49.06	49.57	$C_{10}H_7.HgCl + C_6H_5.HgCl$	$C_6H_5.HgCl + C_{10}H_8$ (M. p. 256°)
Ethylmercury-naphthyl[f]	$C_2^*H_5.Hg.C_{10}H_7$	.1762	9.10	55.67			
	(Liq.)	.1696	8.80	55.93	56.24	$C_2H_5.HgCl + C_{10}H_7.HgCl$	$C_2H_5.HgCl + C_{10}H_8$ (M. p. 193°)
Butylmercury-methyl	$C_4^*H_9.Hg.CH_3$	.3875	26.30	73.17			
	(Liq.)	.6350	43.20	73.34	73.56	$C_4H_9.HgCl + CH_3.HgCl$	$C_4H_9.HgCl$ (M. p. 126°)
Ortho-anisolmercury-phenyl	*o*-$CH_3O.C_6H_4.Hg.C_6^*H_5$	.4436	21.30	51.76			
	(Solid)	.3811	18.30	51.76	52.14	*o*-CH_3.*O*-$C_6H_4.HgCl$ + $C_6H_5.HgCl$	$C_6H_5.HgCl$ (M. p. 249°)
Methylmercury-cyclo-hexyl	$CH_3.Hg.C_6H_{11}^*$	.3374	20.90	66.78			
	(Liq.)	.5754	35.70	66.88	67.13	$CH_3.HgCl + C_6H_{11}.HgCl$	$C_6H_{11}.HgCl$ (M. p. 159°)
Benzylmercury-ethyl	$C_6^*H_5.CH_2.Hg.C_2{}^*H_5$	1.2294	71.10	62.35			
	(Liq.)	1.2940	75.00	62.48	62.56	$C_6H_5.CH_2.HgCl + C_2H_5.HgCl$	$C_6H_5.CH_2.HgCl + C_2H_5.HgCl$ (M. p. 80–100°)[g]
Mesitylenemercury-phenyl[h]	$C_6\overset{*}{H}_5.Hg.C_6H_2(CH_3)_3$	0.3192	14.90	50.32	50.30	$C_6H_5.HgCl$ + $(CH_3)_3.C_6H_2.HgCl$	
	(Solid)						$C_6H_5.HgCl$ (M. p. 250°)
Mesitylenemercury-methyl	$CH_3.Hg.C_6H_2.(CH_3)_3$	.5025	27.80	59.64			
	(Solid)	.5571	39.90	59.79	59.93	$CH_3.HgCl + (C_6H_3)_3.C_6H_2.HgCl$	$CH_3.HgCl$ (M. p. 171°)
Propylmercury-butyl	$C_3H_7.Hg.\overset{*}{C}_4H_9$	.4742	29.20	66.38			
	(Liq.)	.4454	27.50	56.56	66.71	$C_3H_7.HgCl + C_4H_9.HgCl$	$C_4H_9.HgCl + C_3H_7.HgCl$[i] (M. p. 125–135°)
Propylmercury-butyl	$C_3^*H_7.Hg.C_4H_9$	.4628	28.50	66.38			
		.3924	24.25	66.62	66.71	$C_3H_7.HgCl + C_4H_9.HgCl$	
Propylmercury-butyl	$C_3H_7.Hg.C_4^*H_9$	.4502	27.90	66.80			
		.2494	15.40	66.56	66.71		
p-Tolylmercury-phenyl	$C_6^*H_5.Hg.C_6H_4.CH_3$[j]	.3492	17.61	54.36			
	(Solid)	.3657	18.40	54.24	54.41	$C_6H_5.HgCl + CH_3.C_6H_4.HgCl$	$C_6H_5.HgCl$ (M. p. 250°)
Butylmercury-*iso*-amyl	$\overset{*}{C}_4.H_9.Hg.C_5H_{11}^*$	.5548	31.20	60.62			
		.3041	17.10	60.62	61.01	$C_4H_9.HgCl + C_5H_{11}.HgCl$	$C_4H_9.HgCl + C_5H_{11}.HgCl$[k] (M. p. 100°)

[a] The asterisk on a radical indicates that in the preparation of the unsymmetrical molecule, the Grignard of the radical so marked was treated with the corresponding mercury halogen derivative of the other radical, thus: $R_1^*MgCl + RHgCl \longrightarrow R_1^*HgR + MgCl_2$. Where both of the radicals are marked with an asterisk it indicates that the unsymmetrical molecule was prepared also by attaching the radicals to the mercury in the reverse order.

[b] This product at times has a tendency to separate as an oil. If upon the addition of water the oil separates, it is best then to extract it with ether. Evaporation of the solvent in a vacuum usually leaves a solid.

[c] The melting points recorded in this column are those which were given by the materials without any purification, when the unsymmetrical compounds were treated with hydrogen chloride in alcohol and the whole precipitated with water. In case two solids precipitated, they were separated by fractional crystallization and are indicated in the table.

[d] The compound has no melting point, but decomposes within the range of 115–140°.

[e] Decomposition point, 110–115°.

[f] This compound is a yellow liquid, which upon standing decomposes rapidly into a liquid and a solid, which are presumably mercury-diethyl and mercury-di-α-naphthyl, respectively.

[g] The unsymmetrical molecule, benzylmercury-ethyl, was treated with hydrogen chloride dissolved in alcohol. To the solution water was added. A solid separated which melted between the temperature range of 80–100°, indicating that it was a mixture of benzylmercuric chloride and ethylmercuric chloride. It was, therefore, dried to constant weight in a vacuum over sulfuric acid and analyzed.

Anal. Subs., 0.3408, 0.3746: 19.7, 21.6 cc. of KNCS (1 cc. = 0.01078 g. of Hg). Found: Hg, 62.3, 62.2.

Since benzylmercuric chloride contains 61.4% of mercury and ethylmercuric chloride 75.7% of mercury, the mixture above contains 94.9% ± 1.0% of benzylmercuric chloride and 5.1% ± 1.0% of ethylmercuric chloride.

[h] The decomposition point of this compound is rather indefinite, 110–120°.

[i] The melting point of the decomposition product of the unsymmetrical molecule, butylmercury-benzyl with hydrogen chloride, indicates a mixture of the two mercury compounds. It was worked up essentially as described for benzylmercury-ethyl, except that six preparations in all were decomposed in that way and analyzed for mercury. The results were quite concordant, namely, 69.3, 69.3, 69.4, 69.2, 69.2, 69.05, an average of 69.2% of mercury. Since butylmercuric chloride contains 68.5% of mercury and propylmercuric chloride 71.6% of mercury, the mixture evidently contains 77.4% ± 1.0% of butylmercuric chloride and 22.6% ± 1.0% of propylmercuric chloride.

[j] This product decomposes at 120°. When boiled in alcoholic solution for a short time the melting point of the product isolated was 145°, indicating that the unsymmetrical molecule decomposed into two symmetrical molecules, mercury-diphenyl and mercury-di-*p*-tolyl, which melt at 120° and 238°, respectively.

[k] The melting point of the decomposition product of butylmercury-*iso*-amyl with hydrogen chloride indicates a mixture of two compounds. It was therefore worked up as described under benzylmercury-ethyl and analyzed for mercury.

Anal. Subs., 0.5414, 0.3996: 33.1, 24.4 cc. of KNCS (1 cc. = 0.01078 g. of Hg). Found: Hg, 65.9, 65.8.

Since *iso*-amylmercuric chloride contains 65.5% of mercury, and butylmercuric chloride, 68.5% of mercury, the mixture contains 88.3% ± 1.0% of *iso*-amylmercuric chloride and 11.7% ± 1.0% of butylmercuric chloride.

melting point was lowered to 225°. This proves that the product is pure phenylmercuric chloride.

Filtrate 1, obtained as described above, was cooled to 50° and the solid was collected on a filter. Water was added to the filtrate and a heavy precipitate separated. This precipitate was then dissolved in a small quantity of hot alcohol and allowed to cool to 50°. It was then again separated from a small amount of solid by collecting the latter on a filter. To the filtrate, water was added and the product that separated dried thoroughly. The melting point of this compound was 228° and it was not lowered by the addition of pure *p*-tolylmercuric chloride. However, the addition of phenylmercuric chloride lowered the melting point to 200°. This proves that the unsymmetrical molecule was decomposed by mercuric chloride as follows: $C_6H_5Hg{-}C_6H_4.CH_3(p) + HgCl_2 \longrightarrow C_6H_5.HgCl + Cl.Hg{-}C_6H_4CH_3(p)$.

The third portion of the above unsymmetrical mercuric compound was analyzed. It was brought to constant weight in a vacuum desiccator over phosphorus pentoxide. The analyses were carried out according to Rupp's method, modified by Koten and Adams.[15]

Anal. Subs., 0.3492, 0.3657: 17.6, 18.4 cc. of KNCS (1 cc. 0.01078 g. of Hg). Calcd. for $C_{13}H_{12}Hg$: Hg, 54.4. Found: 54.3, 54.1.

The unsymmetrical molecule *p*-tolylmercury-phenyl decomposes at around 120°, the melting point also of mercury-diphenyl. However, when the product is boiled with alcohol for ten minutes, the melting point is raised to 145°, indicating that the unsymmetrical molecule decomposes into two symmetrical molecules—namely, mercury-diphenyl and mercury-ditolyl which melt at 120° and 238°, respectively. The rise in the melting point of the unsymmetrical molecule upon boiling is thus easily accounted for.

For the sake of conservation of space, our results are shown in Table IV.

Summary

1. A method is described whereby the relative degree of electronegativity of organic radicals may be determined.

2. The order of electronegativity of a number of organic radicals is given.

3. An interpretation is offered of the existence of free radicals upon the basis of the electronegativity of radicals.

4. A method suitable for the preparation of unsymmetrical mercuric organic compounds is described.

5. The preparation of a number of new compounds is described.

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[15] Koten and Adams, THIS JOURNAL, **46**, 2768 (1924). Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).