THE RELATIVE ELECTRONEGATIVITY OF ORGANIC RADICALS

AND ITS USE IN INTERPRETING CERTAIN ORGANIC

REACTIONS

by

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OBJECT OF WORK

For some time the subject of the "electronegativity of organic radicals" has been very much confused in the minds of organic chemists. It is of the utmost importance, in order to help explain some of the baffling organic reactions, that a table somewhat corresponding to the electromotive series in inorganic chemistry be established for the different types of organic radicals.

To be entirely accurate, we should not speak of positive and negative radicals. The attraction of the radical for the pair of valence electrons is a function of the electronic structure of the molecule and the difference in electronegativity arises therefrom. The electronegativity of a radical is, therefore, the relative degree of attraction of the radical for the pair of valence electrons.

The method employed by me for determining the affinity of a radical for the pair of valence electrons was first reported by Kharasch and Grafflin[1]. The

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[1]
  J. Am. Chem. Soc. <u>47</u>, 1948, (1925).,Science,<u>58</u>,1510,(1923).

method depends upon the fact that when hydrogen chloride
is added to a mercury diaryl or dialkyl the correspond-
ing hydrocarbon and the aryl or alkyl mercuric chloride
are formed.

$$RHgR + HCl \rightarrow RHgCl + RH$$
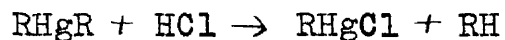
It was assumed that if one started with an unsymmetrical
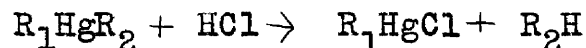mercury derivative, R_1HgR_2, and treated this with hydro-
gen chloride it should react, forming R_1HgCl and the
hydrocarbon, R_2H, when R_2 is the most electronegative
of the two radicals.

$$R_1HgR_2 + HCl \rightarrow R_1HgCl + R_2H$$

By varying the radicals, R_2 and R_1, it should thus be
possible to establish the order of the electronegativity
of most types of organic radicals.

The first record in literature on the preparation
of unsymmetrical organo-mercuri compounds is that by
Hilpert and Grüttner[2]. This method was to treat an
organo-mercuric halide with a Grignard reagent. Accord-
ing to their work, in order to prepare these unsym-
metrical molecules, it is necessary to proceed in a
definite way; thus, in order to prepare phenyl mercury
ethyl it is necessary to start with ethyl mercury
chloride and treat this with phenyl magnesium bromide.
If the order is reversed, the desired product is not
formed, according to these authors. In some cases they

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[2] Ber. 48, 908, (1915).

report that unsymmetrical molecules are so unstable
that they were unable to prepare them at all.

As Kharasch and Marker[3] pointed out, these limit-
ations, if true, would have defeated the object of this
work. However, by modifying the method of Hilpert and
Grüttner, these authors found it possible to prepare
the unsymmetrical molecules by attaching the radicals
to the mercury in any order desired.

PLAN OF PROCEDURE

The unsymmetrical compound was first prepared by
a method to be described in the experimental part.
After purification the unsymmetrical molecule was anal-
yzed for mercury. As a proof of the existence of the
unsymmetrical compound the analysis alone would not,
of course, suffice for it would not show whether the
substance was a pure unsymmetrical compound or a
mixture of two symmetrical molecules. To further
prove the existence of the unsymmetrical molecule,
two portions of it were taken and to the one, mercuric
chloride was added decomposing the compound into two
organo-mercuric chlorides:

$$R_1HgR_2 + HgCl_2 \longrightarrow R_1HgCl + R_2HgCl$$
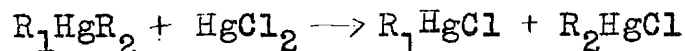
To the other was added hydrogen chloride decomposing
the compound into an organo-mercuric chloride and a
molecule of a hydrocarbon:

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[3] J. Am. Chem. Soc. **48**, 3130, (1926).

$$R_1HgR_2 + HCl \rightarrow R_2HgCl + R_1H$$
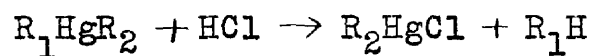
where R_1 is more electronegative than R_2. By the above procedure, Kharasch and Marker[4] determined the relative electronegativity of a number of organic radicals and established them in the following order, the most electronegative appearing at the top.

TABLE I

Order of Electronegativity of Some Common
Organic Radicals

4 loc. cit.

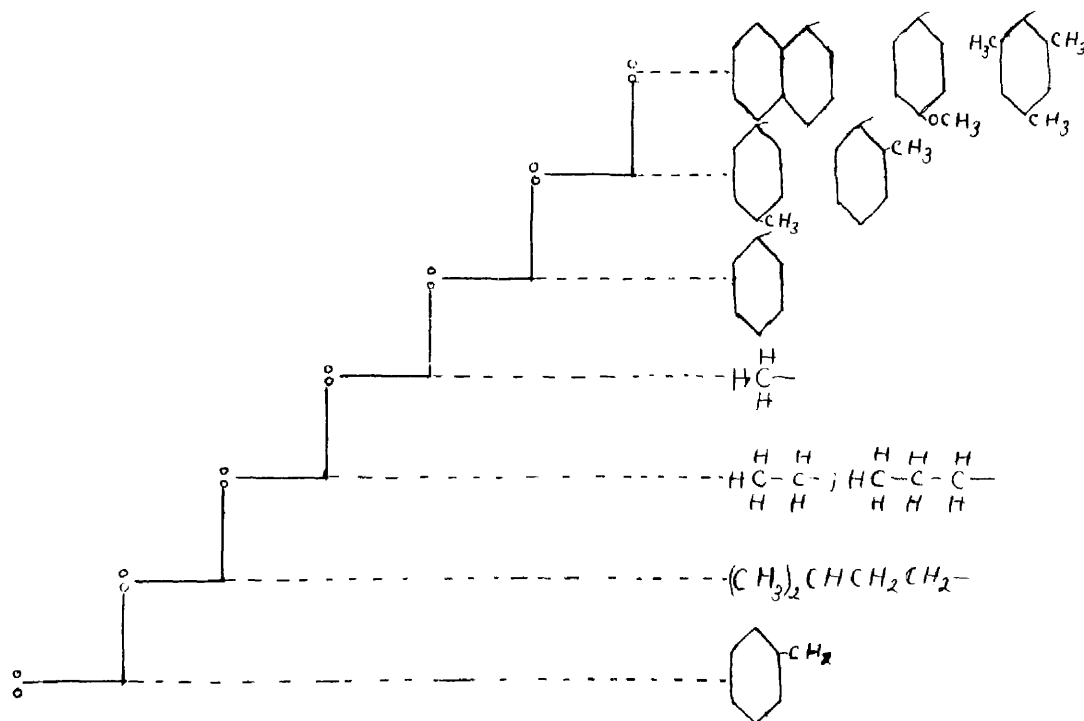When one considers the large number of organic radicals, it would seem like an endless task to establish the position of each one. But by collecting data on certain types of molecules it is hoped that certain laws may be deduced so that the relative electronegativity may be established therefrom. It has been my chief object to determine the effect on the electronegativity of increasing the carbon chain in both alkyl and aryl radicals and also the influence of substituents in the benzene ring in the ortho, meta and para positions.
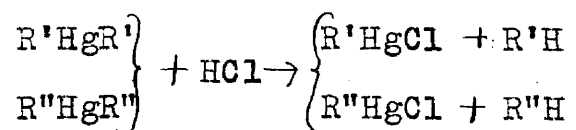
VALIDITY OF METHOD

In order to first test the validity of the method employed, equimolecular amounts of two symmetrical organo-mercuri compounds namely, mercury diphenyl and mercury diethyl, were mixed, then dissolved in alcohol and treated with alcohol saturated with hydrogen chloride. The mixture was warmed slightly to complete the reaction. Water was then added forming a heavy, white precipitate which was collected on a filter. This product was treated with boiling alcohol, part of the precipitate remaining undissolved in the hot alcohol. The precipitate was collected on a filter and washed with hot

alcohol. The melting point of this product was 245° which identifies the product as phenyl mercury chloride. Water was added to the alcohol filtrate forming a heavy, white precipitate which was crystallized from a small amount of hot alcohol. The melting point of this product was 185° which identifies the product as ethyl mercury chloride. This proves that when equimolecular quantities of mercury diphenyl and mercury diethyl are treated with hydrogen chloride reactions take place individually between the hydrogen chloride and mercury diphenyl in the one case and hydrogen chloride and mercury diethyl in the other, forming ethyl mercury chloride and phenyl mercury chloride, respectively. It also shows that there is no interchange of the phenyl and ethyl radicals.

The belief has been expressed that, if instead of having an unsymmetrical molecule of the type R'HgR" we had a mixture of R'HgR' and R"HgR", on treatment of this mixture with hydrogen chloride only one compound of the type RHgCl would be obtained. But the above experiment shows conclusively that on treatment of a mixture of two different symmetrical molecules with hydrogen chloride two distinct organo-mercuric chlorides would be obtained, the reaction taking place as follows:

$$\left.\begin{array}{c} R'HgR' \\ R"HgR" \end{array}\right\} + HCl \rightarrow \left\{\begin{array}{c} R'HgCl + R'H \\ R"HgCl + R"H \end{array}\right.$$

SIGNIFICANCE OF RESULTS

I. Arrangement of Radicals in Order of Electro-
        negativity.

As mentioned before the most important reaction
of the unsymmetrical organo-mercuri molecule is the
reaction with hydrogen chloride. It might be emphasized
once more that it is considered that the radical which
presumably is dissociated first from the mercury and
then combines with the hydrogen ion in solution to
yield the hydrocarbon is the more electronegative of
the two or the one having a greater attraction for
electrons. Using this criterion and incidentally the
results of Kharasch and Marker [5], the organic radicals
studied are arranged in Table II, the compounds above
resemble more the nonmetals while those below the metals.

II. Use of Table of Electronegativity of Organic
        Radicals in the Interpretation of Certain
        Organic Reactions.

As previously mentioned a complete list of organic
radicals arranged in the order of their relative electro-
negativity would be of great help in explaining many
baffling organic reactions. Already the list, incomplete
as it is, can be of great use in interpreting many
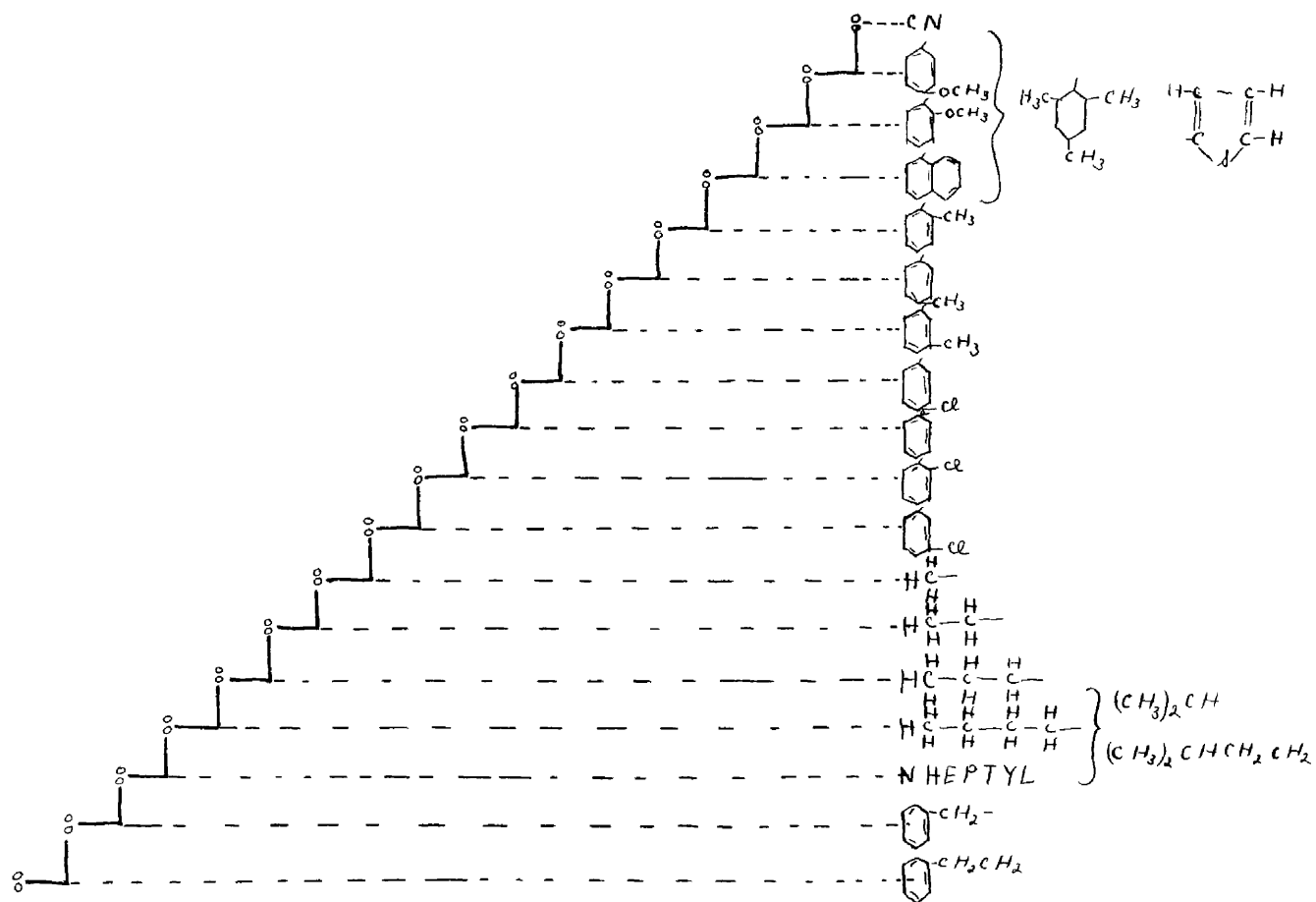organic reactions which previously we have not been able

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[5] loc. cit.

TABLE II.

Order of Electronegativity of Organic Radicals

to satisfactorily explain. These are: 1, the existence
of free radicals, 2, certain substitution reactions in
the benzene ring, 3, the influence of secondary radi-
cals and 4, the theory of alternate polarity which will
be discussed in the order mentioned.

1. The Existence of Free Radicals.

In order to help explain the possibility of the
existence of free radicals it is necessary to emphasize
how two carbon atoms can share a pair of valence elec-
trons to form what is ordinarily know as the valence
bond.

According to the Lewis[6] concept, two electrons
lying between two atomic nuclei constitute the chemical
bond and the pair of electrons may be between two atomic
nuclei in such a manner that there is no electrical
polarization, or the pair of 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. However, as pointed
out by Kharasch and Sher[7], from the standpoint of the
organic chemist another union is possible. This is
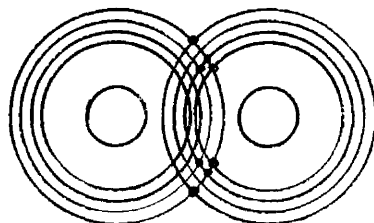best represented in Figure 1.

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[6]
"Valence and the Structure of Atoms and Molecules",
A. C. S. Monograph, The Chemical Catalog Co., New York
1923.
[7]
J. Phys. Chem. 29, 625, (1925).

FIGURE 1.

Concept of "Bond" between Two Carbon Atoms

and Variations thereof.

According to the Bohr theory, an atom is surrounded
by a finite number of shells corresponding to different
energy levels into which the electrons may fall. If
two carbon atoms would share their valence electrons in
their two inner orbits, this would presumably lead to
a strong bond. If two carbon atoms share a pair of
electrons in the inner shell of one and the outer shell
of the other or vice versa, this would lead to ionization.
If the two atoms would share the pair of electrons in
their outer shells or energy levels respectively, then
they would presumably 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.

By reference to the Table of Electronegativity
of Radicals, it will be seen 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. If all three hydrogen atoms in the methyl
radical are replaced by phenyl groups, the valence
electrons should be considerably displaced from the
methyl carbon atom, thus making the radical extremely
weak electronegatively. If two such triphenyl methyl
radicals were brought together they should not form
a stable compound for they may be assumed to share the
electrons in their outer shells and any supply of
energy would shift one or both of the electrons from
the sphere of the methyl carbon atom, thus rupturing
the bond. Thus, Table III represents the effect of
the replacement of hydrogen atoms by negative phenyl
radicals.

If we replace the hydrogen atoms of the methyl
group by radicals more electronegative than phenyl,
such as para chloro phenyl, tolyl, naphthyl and anisol,
then the electrons should be further displaced from
the methyl carbon atom than in triphenyl methyl. The
more negative the radicals substituted the less stable
and the more highly dissociated the double compound
should be.

TABLE III.

Effect of Groups upon the Electronegativity of the

Methyl Radical
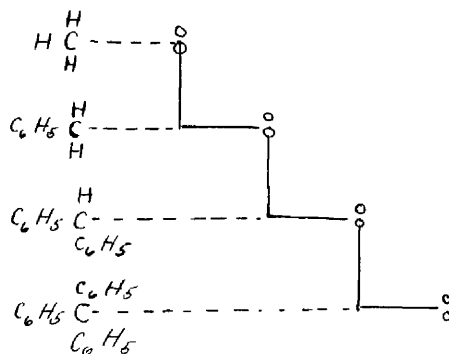
By reference to Gomberg's article on "Organic
Radicals"[8] , it will be seen that radicals which in the
Table of Electronegativity lie above the phenyl radi-
cal, increase dissociation. In this article Gomberg
reports the dissociation of certain aryl xanthyls in
the following order: α naphthyl xanthyl, tolyl,
xanthyl, para chloro phenyl xanthyl. This is in
exact agreement to what would be expected from refer-
ence to the Table of Electronegativity, the relative
order being shown in Table IV.

8
  Chem. Rev. 1, 91, (1924).

TABLE IV.
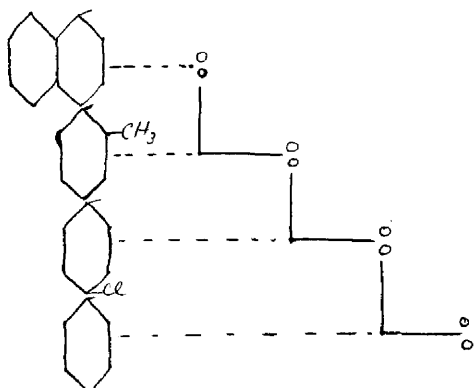
Gomberg also gives the dissociation of the double compound of triphenyl methyl as 28 per cent and of

∝ naphthyl diphenyl methyl as practically 100 per cent dissociated. This would also be predicted from the Table, ∝ naphthyl being much more electronegative than phenyl.

It would be interesting to test the dissociation of the double compound of ortho or meta chloro phenyl diphenyl methyl since ortho chloro phenyl and meta chloro phenyl both lie below phenyl in the Table. According to the concepts developed here these compounds should be less dissociated than triphenyl methyl. This would be a very excellent test of the general theory and will be undertaken in the near future in this laboratory.

Gomberg[9], in a later article on the dissociation

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[9] J. Am. Chem. Soc. **47**, 2376, (1925).

of triphenyl methyl, states that a methoxy group in either the ortho or para position of one of the phenyl groups in triphenyl methyl augments, to a large extent, the degree to which the free radical exists in the dissociated form. From the concepts of our theory it would be expected that, if two methoxy groups were substituted in the 2-5, 2-4 or 3-4 position, there might be some increase in the dissociation of the free radical but there would be a greater dissociation if the methoxy groups were distributed in separate phenyl nuclei. The introduction of a methoxy group into a phenyl nucleus should augment the electronegativity of the phenyl group much more than the introduction of a methoxy group in a methoxy phenyl nucleus.

Gomberg[10] further states that he found that the presence of two methoxy groups in the same nucleus alters but slightly the ratio of the free radical to the hexa-aryl ethane but when the methoxy groups are distributed in separate phenyl nuclei, the dissociation is greatly increased.

2. Substitution Reactions in the Benzene Ring.

The Table of Electronegativity helps to predict in advance the lability of the group in substitution reactions in the benzene ring. Not only can we predict the position of the entering group but also the relative

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[10]
    loc. cit.

ease of the reaction.

In the nitration of the substituted benzenes we would expect that the substitution of the nitro group would be favored in the position where the hydrogen atom is the most positive or has the greater tendency toward ionization. Considering chloro benzene, where we have the order of electronegativity as shown in Table V, the hydrogen in the para position would have the greater tendency to ionize, the ortho next and the meta the least.

TABLE V.
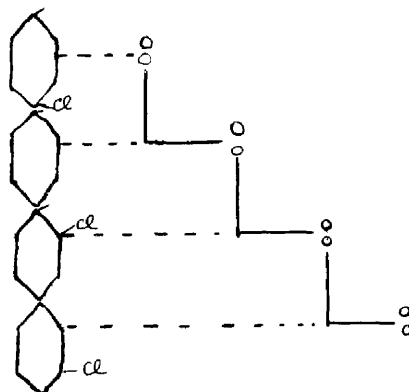
Therefore, in the nitration of chloro benzene, it would be expected that the nitro group would enter the para position more readily than the ortho and the ortho more readily than the meta. Holleman[11], in substantiation

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[11] Chem. Rev. 1, 187, (1924).

of this prediction has shown that in the nitration of
chloro benzene, 69.9 per cent of the para, 30.1 per cent
of the ortho and none of the meta compound are obtained.

From these concepts developed for the nitration of
the substituted benzenes we would expect in the case of
toluene, where the order of electronegativity is that
shown in Table VI, that the greater percentage of the
nitro group should enter the ortho position, the para
next and the meta the least.

TABLE VI.
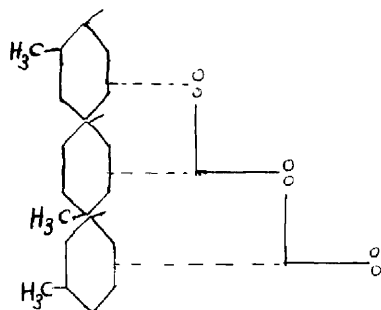
In the nitration of toluene, Holleman[12] obtained 58.8
per cent ortho, 36.8 per cent para and 4.4 per cent of
the meta compound, which is in agreement with the theory.

Furthermore, if a mixture of two substituted ben-
zenes were nitrated we would expect that the more electro-
negative radical would be nitrated in preference to the

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[12]
   loc. cit.

less electronegative. If a mixture of chloro benzene
and toluene were nitrated, since the tolyl radical is
more electronegative than the chloro phenyl, toluene
should be nitrated in preference to chloro benzene.
That such is the case is found in the results of Wilbaut[13]
who, on nitrating a mixture of toluene and chloro benzene,
found that toluene was nitrated in preference to chloro
benzene.

It would also be expected that on nitrating a
mixture of benzene and chloro benzene the nitro compound
of para chloro benzene should be obtained, since para
chloro phenyl has been found to lie above phenyl in the
Table while ortho and meta chloro phenyl lie below it.
While no work has been done to show this, it is hoped
that it may be carried out in the near future in this
laboratory.

Holleman's[14] complete results on the introduction
of the nitro group into compounds of C_6H_5X are given
in Table VII.

While no experiments have been tried to determine
the relative position of the fluoro benzenes or the nitro
benzenes, it would be predicted, since in the nitration
of the fluoro benzenes, 87.6 per cent of the para compound
and 12.4 per cent of the ortho compound is obtained, that
para fluoro phenyl would be much more electronegative than

13
  Rec. trav. chim. <u>34</u>, 241, (1915).
14
  loc. cit.

ortho fluoro phenyl. In nitro benzene the meta position should be found to be the most electronegative. It is contemplated to determine the position of these radicals in this table.

TABLE VII.

Introduction of a Nitro Group into Compounds
C_6H_5X

Substituent Present	Percentage of			Substituent Present	Percentage of		
	O	M	P		O	M	P
F	12.4		87.6	NO_2	6.4	93.2	0.25
Cl	30.1		69.9	CO_2H	18.5	80.2	1.3
Br	37.6		62.4	$CO_2C_2H_5$	28.3	68.4	3.3
I	41.1		58.7				
CH_3	58.8	4.4	36.8				
CH_2Cl	40.9	4.2	54.9				

Since nitration should be easiest in the position where the hydrogen has the greatest tendency to ionize and since the greater the electronegativity of the radical attached to the hydrogen the greater will be the tendency to ionize, then the ease of nitration should be a direct function of the electronegativity of the radical attached to the hydrogen. Thus, we would expect the ease of nitration to lie in the order given in Table VIII. Experimental facts show this to be the case.

TABLE VIII.
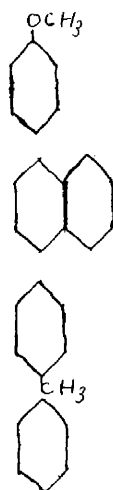
The thiophene radical has been found to lie above phenyl and, therefore, it should be much more reactive than benzene. It is a well-known fact that thiophene is much more easily nitrated or sulfonated than benzene.

There have been a large number of theories postulated for the mechanism of substitution in the benzene ring. One of the most recent is that of Francis[15], which can be considered as having been largely anticipated by many of the others, such as Flurscheim[16], Fry[17], Vorlander[18], Stieglitz[19], etc. However, we might state that all these theories exhibit a total

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[15] Chem. Rev. 3, 257, (1926).

[16] Ber. 39, 2015, (1906).

[17] J. Am. Chem. Soc. 36, 248, (1914).

[18] Ber. 52, 263, (1919).

[19] J. Am. Chem. Soc. 44, 729, (1922).

lack of experimental evidence as to the relative electro-
negativity of the ortho, meta and para positions, when
different radicals are introduced into the benzene
nucleus. All of these authors have more or less assigned
a difference in the electronegativity of the organic
radicals but have based their postulates on the experi-
mental facts of the nitration reactions which really
means a statement of facts in a different language.

The following are the postulates made by Francis[20] :

(1) Each nuclear bond of benzene consists of
three shared electrons. The aromatic character is due
to this. Each other single bond involves only two
shared electrons. A shared electron presumably revolves
around both atomic nuclei but in the figures to follow
it is represented by a dot between the atoms. This
may be considered the electron center of its orbit.

(2) Any substituent in benzene shifts the electrons
of all the bonds. The three electrons of the nuclear
bonds may not all shift together, two of them may shift
together and the third be free to move in response to
electrostatic influences and even shift in a direction
opposite to that of the pair. In most cases from lack
of data to decide the exact nature of the shifts, the
three are represented together in the drawings. The
direction and amount of the shift depend upon the sign
and degree of the polarity tendency of the substituent.

20
  loc. cit.

(3) A carbon atom toward which electrons have been shifted tends to attract its other electrons, forming a compact octet. A carbon atom away from which electrons have been shifted tends to repel its other electrons, forming an open octet. This is based upon considerations of symmetry.

(4) A bond is the more easily broken if the shift of its electrons is in such a direction as to accentuate the normal polarity of the atom or group to be displaced. Thus, hydrogen is easily displaced if electrons are shifted away from it while a halogen atom is labile if electrons are shifted toward it. The following figures illustrate the theory.

Benzene

Phenol

Toluene

Chlorobenzene

Nitrobenzene
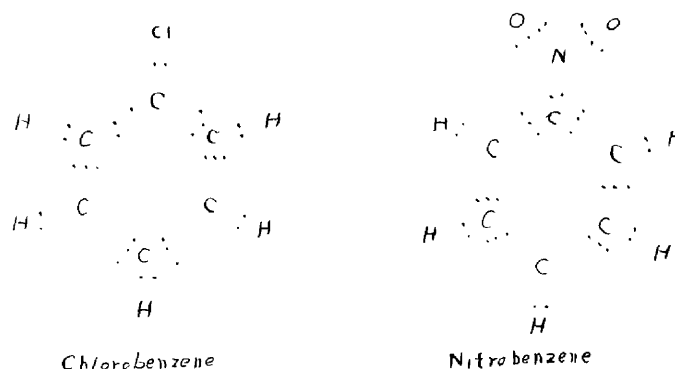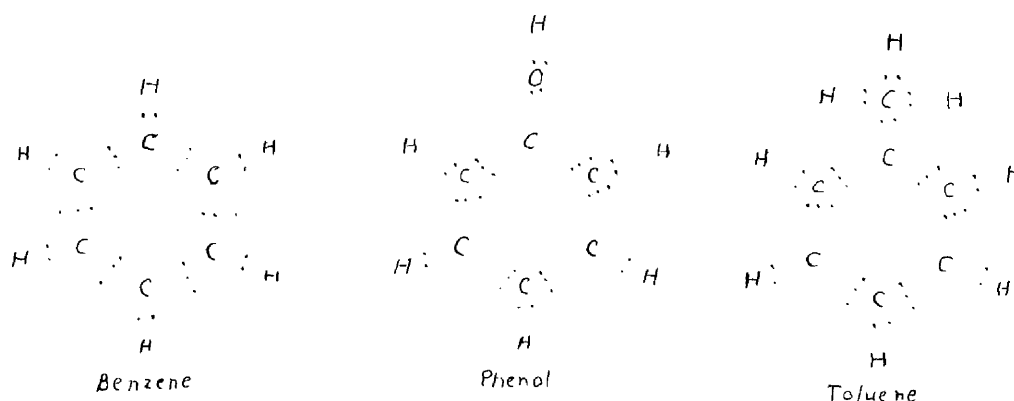
Hydroxyl tends to be negative and in order to acquire that polarity attracts the electrons which it shares with carbon. The latter then repels its other six electrons, forming an open octet. The two ortho carbon atoms then have compact octets, the two meta carbon atoms open ones and the para a compact one. The more positive hydrogen atoms are the ortho and para ones and these are the ones substituted. In toluene the arrangement of electrons is analogous to that of phenol but the shifts are much less extensive. In chloro benzene the shifts of the electron pairs are similar to those of toluene but the third electrons in the 1-2 and 1-6 bonds are attracted directly by the chlorine atom and so shift in the opposite direction to that of the pair. This distortion of the octet of the ortho carbon atoms greatly decreases the lability of the ortho hydrogen atoms so that there is a general decrease in reactivity and substitution is preferably in the para position. In nitro benzene the nitro groups tend as in nitric acid to be positive and the shifts are opposite to those in toluene, the meta hydrogen atoms being the more labile.

The above theory of Francis, though agreeing with some of the experimental facts, seems to be one deducted from these facts and not a theory from which the facts may be predicted. The following seem to be some of the

falacies in his theory:

(1) There is no experimental evidence to show that a carbon bond can consist of three shared electrons.

(2) If in chloro benzene the chlorine atom directly attracts the electrons in the 1-2 and 1-6 positions making the para position more labile, then why does not the same hold true with phenol where the hydroxyl is also an electronegative radical similar to chlorine?

(3) There is no possible explanation of why both ortho and meta chloro phenyl are less electronegative than phenyl.

(4) According to Francis' theory, ortho toluene and para toluene should be equally labile but in the work of Holleman[21] it is shown that the ortho position is much more labile than the para. Francis does not attempt to explain this difference.

If a theory is to be of any use in explaining the substitution reactions in the benzene ring, it must be one from which we can predict in advance the course of the reaction. It is believed that the use of the theory of electronegativity as outlined eliminates the uncertainty and enables one to explain all facts as far as the table goes.

<u>3</u>, The Influence of Secondary Radicals.

It has been shown that if one of the hydrogen atoms

21
    loc. cit.

in the methyl radical is replaced by a strongly electro-
negative group then the electronegativity of the entire
group will be decreased. In iso-propyl we have the
equivalent of substituting two methyl groups in place
of two hydrogen atoms of methyl and the arrangement of
electrons would be as shown in Table IX.

TABLE IX.
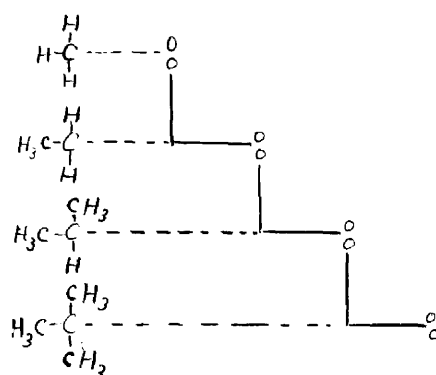
Thus, the iso-propyl radical should be less electro-
negative than the propyl. By the same analogy, a
tertiary radical should be less electronegative than
a secondary radical, although we have not carried out
this work as yet. By reference to the Table of Electro-
negativity it will be seen that the propyl radical lies
above iso-propyl, the propyl being the more electro-
negative.

In the reaction of water on the alkyl halides it
is a well-known fact that the tertiary halides react

readily, the secondary much less readily and the primary
with great difficulty. These reactions are due to the
difference in the electronegativity of the radicals.
Since the secondary radical is less electronegative than
the primary, the pair of electrons is pushed farther
toward the halogen in the case of the secondary. This
would make the halogen in the secondary radical the
more electronegative. The greater the difference in
polarity between the radical and the halogen the greater
will be the tendency for ionization and, therefore, the
greater would be the reactivity of the halogen with
water, forming the hydrogen halide and the corresponding
alcohol.

In the case of primary, secondary and tertiary
alcohols, since the hydroxyl group would be more electro-
negative in the tertiary than in the secondary and the
secondary more electronegative than the primary, it
would be expected that in the treatment of the three
alcohols with hydrogen chloride the chlorine would have
the greater tendency to enter the more electronegative
position. The above is found to oe the case, for only
tertiary alcohols react readily with hydrogen chloride[22]
to form water and the tertiary halide.

Another reaction which shows the difference in the
electronegativity of the radicals attached to the
hydroxyl in primary, secondary and tertiary alcohols

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[22] Rec. trav. chim. <u>76</u>, 89, (1907).

is the elimination of water from the alcohols by means
of a dehydrating agent.[23] When a tertiary alcohol is
heated, the following reaction takes place, water being
eliminated and an unsaturated compound formed:

$$
\begin{array}{c}
H \\
H-C-H \\
H \\
H-C-C-OH \\
H \\
H-C-H \\
H
\end{array}
+ \Delta \longrightarrow
\begin{array}{c}
H \\
H-C-H \\
H \\
H-C-C \\
H \\
H-C-H \\
H
\end{array}
+ H_2O
$$
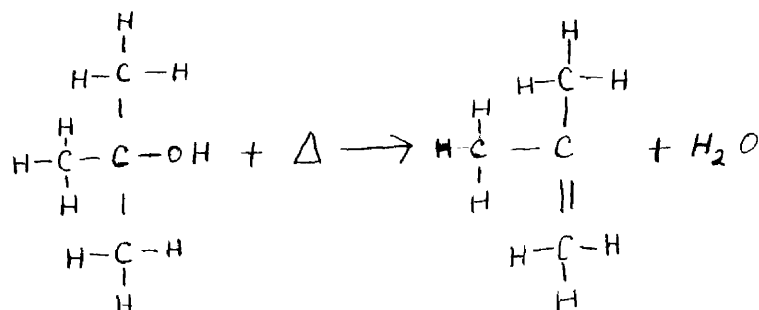
Iso-propyl alcohol is the only secondary alcohol that
will give this reaction and in this case the reaction
does not take place readily. Primary alcohols do not
react at all. The above reaction can be explained
from the fact that the pair of electrons in the case
of the tertiary alcohol are pushed farther toward the
hydroxyl group, thus giving the radical a tendency to
ionize. When a small amount of energy is applied, the
hydroxyl group being in an unstable condition unites
readily with one of the hydrogen atoms, forming an
unsaturated hydrocarbon and water.

 4. The Problem of Alternate Polarity in Chain
     Compounds.
Cuy[24] observed from the work of Hanke and Kossler[25]

23
  Compt. rend. 126, 1043, (1898).
24
  J. Am. Chem. Soc. 42, 503, (1920).
25
  J. Am. Chem. Soc. 40, 1726, (1918).

on "The Electronic Constitution of Acetoacetic Acid,
Citric Acid and Some of Their Derivatives" that their
formulas for these compounds made the carbon atoms
alternately positive and negative. Cuy[26] then en-
deavored to prove that the carbon atoms in a chain
tend to assume alternately positive and negative charges
by presenting evidence which may be summarized as
follows:

(a) The alternating character of the melting
point curves of homologous series.

(b) Addition of hydrogen halides to ethylene
homologs.

(c) Addition of hydrogen halides to allene
homologs.

(d) Rearrangement of alkyl bromides.

Lucas and Jameson[27] criticize the four postulates
of Cuy as follows:

(a) Alternating character of melting point curves.

If the alternation of melting points is a function
of the molecular structure, a similar alternation of
the boiling points should be manifest. The alternation
of the boiling points is of small magnitude and shows
little regularity outside of the fatty acid series.
Moreover, as Beutler[28] has pointed out, compounds con-

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[26] loc. cit.

[27] J. Am, Chem. Soc. 46, 2475, (1924).

[28] Z. anorg. allgem. Chem. 120, 24, (1922).

taining even numbers of carbon atoms possess a higher
symmetry and, therefore, higher melting points than the
compounds containing odd numbers of carbon atoms. The
alternation in melting points is, therefore, presumably
a function of the crystal lattice and not of the polar
condition within the molecule.

(b) Addition of hydrogen halides to ethylene

homologs.

The facts regarding the addition of hydrogen halides
to olefines cited by Cuy are: the action of hydrogen
bromide and of hydrogen iodide on 2 pentene to produce
2 bromo and 2 iodo pentane, respectively, and the
addition of hydrogen chloride to hexene to produce 2
chloro hexane. Yet the data of Wagner and Saytzeff[29]
on the action of hydrogen iodide on 2 pentene show that
their product was a mixture of isomeric iodides and
not 2 iodo pentane alone as Cuy assumes. Moreover, the
data of Morgan[30] on the action of hydrogen chloride
with hexene indicate that this hexene which he prepared
by the action of alcoholic potassium hydroxide on iso-
meric hexyl chlorides consisted largely of 1 hexene
and not 2 hexene as Cuy assumes. In a later communi-
cation Lucas[31] states that in the treatment of 2 pentene
with hydrogen bromide a mixture of isomeric bromides

[29]
  Ann. 179, 321, (1875).
[30]
  Ann. 177, 304, (1874).
[31]
  J. Am. Chem. Soc. 47, 1454, (1925).

was obtained consisting of 78 per cent of 3 bromo
pentane and 22 per cent of 2 bromo pentane.

(c) Addition of hydrogen chloride to allene
homologs.

Although Cuy interpreted successfully the addition
of hydrogen bromide to dimethyl and trimethyl allene,
the extention of the principle to diethyl allene fails
completely. According to him, the electronic formula
of diethyl allene should be:

$$-\overset{+}{\underset{-}{C}}- \quad +\overset{+}{\underset{+}{C}}+ \\ \overset{+}{\underset{+}{}} \quad \rangle = +\overset{+}{C}+ \ -C- \\ -\overset{-}{\underset{-}{C}}- \quad +\overset{+}{\underset{+}{C}}+$$
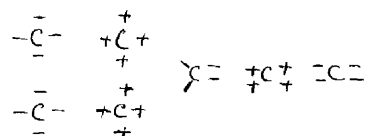
and the addition of hydrogen bromide should give
$(C_2H_5)_2CHBr_2CH_3$ exclusively whereas Cuy himself mentions
that $(C_2H_5)_2CBrCH_2CH_2Br$ is formed.

(d) Rearrangement of alkyl bromides.

Finally, Cuy finds additional support in the be-
havior of alkyl bromides when heated, in that 1 bromo
propane rearranges to 2 bromo propane, 1 bromo 2 methyl
propane rearranges to 2 bromo 2 methyl propane and
1 bromo butane does not rearrange. The rearrangement
of the latter substance at 248° has been studied in
Lucas' laboratory and found to proceed smoothly and
completely to 2 bromo butane. Moreover, when 2 bromo
butane was heated for 29 hours at 248° there was no
indication of 1 bromo butane being formed. This is
contrary to the alternate polarity idea which requires

that the secondary bromide should be transformed into
the primary. Thus, the results of Lucas and Jameson
seem to disprove the idea of alternate polarity as
advanced by Cuy.

In their paper on "The Relation between the
Structure of Organic Halides and the Speed of Their
Reactions with Inorganic Iodides", Conant and Kirner[32]
studied the reactions of certain organic halides with
potassium iodide in order to discover whether or not
the alternating polarity predicted by various electronic
theories of valence would manifest itself by alternations
in the reactivity of the halogen atom in the various
homologous series. They chose this reaction because
it gave the same type of product with a large variety
of halogen compounds and because they thought that it
was as far as possible free from side reactions and
other complicating possibilities so that their results
would be strictly comparable with one another. As a
solvent they used pure anhydrous acetone in which the
potassium chloride formed during the reaction is practi-
cally insoluble so that it crystallized from the
reaction mixture.

Three series of compounds were investigated. The
first consisted of substances containing the benzoyl
group, $C_6H_5CO(CH_2)_nCl$; the second was composed of the
esters, $C_2H_5OOCCH_2(CH_2)_nCl$; and the third series

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[32] J. Am. Chem. Soc. 46, 232, (1924).

consisted of compounds of the general formula $C_6H_5(CH_2)_nCl$. In a later paper, Conant and Hussey[33] gave the relative reactivity of a number of alkyl halides of the general formula, $C_nH_{2n+1}Cl$ and Kirner[34*] in a still latter communication gave additional results on compounds of the general types $HO(CH_2)_nCl$ and $C_6H_5O(CH_2)_nCl$. A summary of the results of these three papers is found in Table X.

The results as given in the following table seem to show an alternating reactivity in the aromatic series but in the aliphatic the relative reactivities are rather constant.

It has been found in determining the relative electronegativity of radicals that an increase in the carbon chain in both the aromatic and aliphatic series renders the radical less electronegative. The results of Conant and Kirner on the reactivity of the halides does not seem to be a measure of the electronegativity of the radical at all but of some other factor. According to our table the same difference in the reactivity of the halide in homologous series should be found in the aliphatic as in the aromatic series.

[33]
    J. Am. Chem. Soc. 47, 476, (1925).
[34*]
    J. Am. Chem. Soc. 48, 2746, (1926).

TABLE X.

Relative Reactivity of Chlorine in Groups.

Substance	Relative Reactivity
$CH_3(CH_2)_2Cl$	1.00
$CH_3(CH_2)_3Cl$	1.07
$C_6H_5(CH_2)Cl$	195.00
$C_6H_5(CH_2)_2Cl$	1.12
$C_6H_5(CH_2)_3Cl$	1.72
$C_6H_5(CH_2)_3Cl$	1.49
$C_6H_5(CH_2)_4Cl$	1.42
$C_6H_5(CH_2)_5Cl$	1.46
$C_6H_5(CH_2)_7Cl$	1.40
$C_2H_5OOCCH_2CH_2Cl$	1.61
$C_2H_5OOCCH_2(CH_2)_2Cl$	1.65
$C_2H_5OOCCH_2(CH_2)_3Cl$	1.35
$C_6H_5COCH_2Cl$	302,000.00
$C_6H_5CO(CH_2)_2Cl$	86.70
$C_6H_5CO(CH_2)_3Cl$	372.00
$HOCH_2CH_2Cl$	1.69
$HOCH_2(CH_2)_2Cl$	2.06
$C_6H_5OCH_2CH_2Cl$	.30
$C_6H_5OCH_2(CH_2)_2Cl$	1.67
$C_6H_5OCH_2(CH_2)_3Cl$	1.37
C_3H_7Cl	1.03
C_4H_9Cl	1.00
$C_5H_{11}Cl$	1.26
$C_6H_{13}Cl$	1.22
$C_7H_{15}Cl$	1.20
$C_8H_{17}Cl$	1.32
$C_{12}H_{25}Cl$	1.00
$C_{14}H_{29}Cl$	.97
$C_{16}H_{33}Cl$	.90
$C_{30}H_{61}Cl$	.88

The theory of alternate polarity is absolutely untenable when we consider that in the Table of Electronegativity we have the relative order given in Table XI.

TABLE XI.
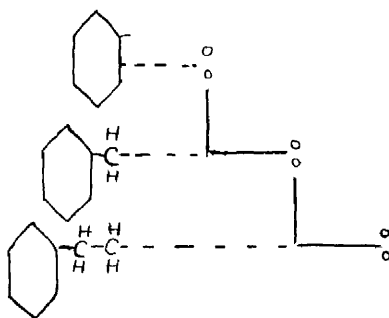
This indicates that the electronegativity of the radical is decreased with each increase in the carbon chain.

The same holds true in the aliphatic series. Methyl was found to be the most electronegative of the straight chain hydrocarbons and the electronegativity decreased with each increase in the carbon chain. Therefore, if the Table of Electronegativity is accepted, there can be no alternating polarity.

EXPERIMENTAL

I. Method of Analysis.

The method used was that of Rupp[34] as modified by

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[34] Chem. Ztg. 32, 1077, (1908).

Koten and Adams   for the volumetric determination of

mercury in organic compounds with certain additional

modifications by us.

In the Koten and Adams method, a sample of the

material is weighed into an Erlemeyer flask and decom-

posed by a mixture of fuming nitric and sulfuric acids.

Water is then added and an excess of potassium perman-

ganate so that all the mercury may be oxidized to the

mercuric state and to oxidize any nitrous acid that

may be present. The excess potassium permanganate is

neutralized by a solution of ferrous sulfate. About

5 cc. of a ten per cent solution of ferric alum indi-

cator is then added and the mercury titrated with

.1N KCNS.

The above method was found to work fairly well

with compounds of the type RHgR but with any type of

compounds containing halogen the method fails absolutely.

This was found to be due to the volatilization of the

mercury halide formed and also because it is impossible

to titrate with KCNS in the presence of halides.

After much experimenting with numerous methods

one was developed which w as very satisfactory for com-

pounds containing halogen. This method consists in

dissolving or suspending the compound to be analyzed

in glacial acetic acid and then decomposing it by

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    J. Am. Chem. Soc. 46, 2764, (1924).

adding a few cc. of bromine.

$$RHgCl + Br_2 \longrightarrow RBr + Hg\diagup^{Cl}_{\diagdown Br}$$
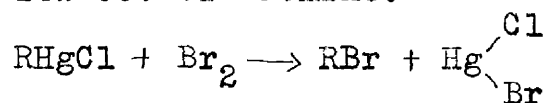
5 cc. of hydrochloric acid and a small amount of zinc
dust are added to the solution in order to reduce the
mercury compound to metallic mercury after which the
metallic mercury is filtered, washed and dissolved in
dilute nitric acid. Potassium permanganate is then
added for the reason explained above and, after re-
moving the excess with ferrous sulfate and adding the
ferric alum indicator, the mercury is titrated with KCNS.

The details of the method are as follows: About
.2 grams of sample are weighed into a 250 cc. Erlenmeyer
flask and 20 cc. of glacial acetic acid added and then
5 cc. of bromine. After standing for about 15 minutes,
5 cc. of hydrochloric acid are added and the zinc dust
in small amounts at a time, care being taken to add the
zinc slowly so that the temperature may not rise above
50°. As soon as all the color of bromine has dis-
appeared, 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 impregnated
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 KCNS until the pink color persists.

It has been found important not to titrate the excess potassium permanganate with ferrous sulfate until just ready to titrate with KCNS. Allowing the sample to stand with excess of potassium permanganate does not interfere.

When titrating with KCNS 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.

II. Preparation and Decomposition of Unsymmetrical

Compounds.

The method of preparation of the unsymmetrical organo-mercuri compounds is the method of Hilpert and Grüttner[36] as modified by Kharasch and Marker[37] and myself.

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[36] Ber. 48, 908, (1915).

[37] loc. cit.

About 8 grams of the organo-mercuri chloride are 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 it has gone into solution. The following reaction takes place:

$$2R'HgCl + 2R''MgBr \rightarrow 2R'HgR'' + MgBr_2 + MgCl_2$$
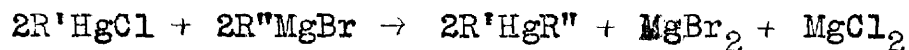
The excess Grignard reagent is then decomposed by ice and a 1 per cent solution of sulfuric acid, care being taken that the temperature does not rise above 10°. The unsymmetrical organo-mercuri compound is extracted with ether and dried with anhydrous sodium sulfate. It is then filtered and the ether evaporated off 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 grams of the above product, dissolved in ethyl ether, are added about 4 cc. of a saturated solution of hydrogen chloride in alcohol. The product is warmed slightly for about 5 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 grams of the unsymmetrical molecule
in ether a molecular equivalent of mercuric chloride
is added. The mixture is refluxed for about 10 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:

$$R'HgR" + HgCl_2 \rightarrow R'HgCl + R"HgCl$$
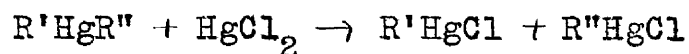
A third portion of the unsymmetrical compound is
dried to constant weight in vacuo and the percentage
of mercury determined by the method described above.

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 Table XII
with footnotes giving any modifications.

Phenyl Mercury Phenyl Ethyl, $C_6H_5HgCH_2CH_2C_6H_5$.

Phenyl ethyl mercury chloride was first prepared
by adding one molecular equivalent of mercuric chloride
to phenyl ethyl magnesium bromide. The mixture was
then decomposed by ice and 1 per cent sulfuric acid and
the compound isolated and purified. A small portion
of this compound was refluxed for about one hour in
alcohol 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°.

5 grams of phenyl mercury chloride were added to
the Grignard reagent of phenyl ethyl bromide. After
decomposition and purification a white crystalline
compound was obtained which was found not to have a
definite melting point but which softened at 120° and
melted slowly up to 170°. An analysis of this compound
gave the following results:

Subs., 0.1500, 0.1909: 7.5 cc., 9.5 cc.of KCNS

(1 cc. = 0.01049 g. of Hg).

Calculated for $C_{14}H_{14}Hg$: Hg, 52.35, found 52.4, 52.2

One gram of this compound was dissolved in alcohol
and 0.71 grams of mercuric chloride added. On warming
a heavy white precipitate formed which was filtered
while warm. After several recrystallizations 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 phenyl ethyl mercury

chloride, thus proving the substance to be phenyl
ethyl mercury chloride.

This shows that the unsymmetrical molecule was
decomposed as follows:

$$C_6H_5HgCH_2CH_2C_6H_5 + HgCl_2 \longrightarrow C_6H_5HgCl + C_6H_5CH_2CH_2HgCl$$

An additional 1 gram of the unsymmetrical compound was
treated with an alcoholic solution of hydrogen chloride.
Upon evaporation a white crystalline compound was ob-
tained which upon crystallization from alcohol melted
at 160° and weighed 0.8 grams. The melting point of
this compound was not lowered by the addition of pure
phenyl ethyl mercury chloride but when mixed with
phenyl mercury chloride was lowered to 145°, thus
proving the compound to be phenyl ethyl mercury chloride.
This shows that the unsymmetrical molecule was decom-
posed as follows:

$$C_6H_5HgCH_2CH_2C_6H_5 + HCl \longrightarrow C_6H_6 + C_6H_5CH_2CH_2HgCl$$
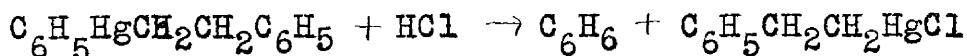
Thus it is shown that the phenyl radical has a greater
attraction for the pair of valence electrons than the
phenyl ethyl radical. Therefore, phenyl would be
placed above phenyl ethyl in the table.

On repeating the above experiment a compound
melting at 161° was obtained by treating the unsymmet-
rical molecule with hydrogen chloride and compounds
melting at 250° and 165° were obtained on treatment
with mercuric chloride. Thus the results were proved

to be correct.

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 will be found in Table XII. 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.

TABLE XII.

Summary of Experimental Work

Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	Cc. of KCNS 1cc = 0.01049g of Hg Cc.	Hg, % Found	Calcd.	$HgCl_2$	HCl
Phenyl Mercury Phenyl Ethyl	M.P. 120-170° $C_6H_5HgC^*_2H_4C_6H_5$ (a)	.1500 .1909	7.50 9.50	52.45 52.35	52.20	C_6H_5HgCl $C_6H_5C_2H_4HgCl$	M.P. 160°(b) $C_6H_5C_2H_4HgCl$
Benzyl Mercury Phenyl Ethyl	(liquid) $C_6H_5CH^*_2HgC_2H_4C_6H_5$	.3657 .3155	17.50 15.04	50.20 50.04	50.56	$C_6H_5CH_2HgCl$ $C_6H_5C_2H_4HgCl$	M.P. 163° $C_6H_5C_2H_4HgCl$
Benzyl Mercury Phenyl Ethyl	(liquid) $C_6H_5CH_2HgC^*_2H_4C_6H_5$	.4167 .3170	19.85 15.20	49.96 50.30	50.56	$C_6H_5CH_2HgCl$ $C_6H_5C_2H_4HgCl$	M.P. 160° $C_6H_5C_2H_4HgCl$
Benzyl Mercury Phenyl Ethyl	(liquid) $C_6H_5CH_2HgC^*_2H_4C_6H_5$					$C_6H_5CH_2HgCl$ $C_6H_5C_2H_4HgCl$	M.P. 160° $C_6H_5C_2H_4HgCl$
Thiophene Mercury Phenyl	M.P. 80-120° $C_4H_3SHgC^*_6H_5$	.2589 .1907	13.80 10.10	55.91 55.56	55.60	C_4H_3SHgCl C_6H_5HgCl	M.P. 250° C_6H_5HgCl
Heptyl Mercury Ethyl	(liquid) $C_7H_{15}HgC^*_2H_5$	.3420	19.85	60.88	61.02	(c)	M.P. 120° $C_7H_{15}HgCl$
Heptyl Mercury Ethyl	(liquid) $C_7H_{15}^*HgC_2H_5$	.3371	19.40	60.38	61.02	(c)	M.P. 120° $C_7H_{15}HgCl$

TABLE XII. Continued

Summary of Experimental Work

Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	CC. of KCNS / 1cc = 0.010499g of Hg / CC.	Hg, % Found	Hg, % Calcd.	$HgCl_2$	HCl
Heptyl Mercury Butyl	$C_7H_{15}HgC_4H_9$ (liquid)	.3511 .3605	18.75 19.20	56.18 55.87	56.25	(d)	M.P. 105° (e) $C_7H_{15}HgCl$ C_4H_9HgCl
Iso Butyl Mercury Butyl	(liquid) $C_4H_9^*HgC_4H_9$(Iso)	.3140 .3501	19.00 21.20	63.43 63.52	36.80	C_4H_9HgCl (Iso)C_4H_9HgCl	M.P. 122° (N)C_4H_9HgCl
Ethyl Mercury Cyanide (f)	M.P. 188° C_2H_5HgCN	.2235 .2608	16.60 19.25	77.91 77.42	78.40		M.P. 193° C_2H_5HgCl
Ortho Anisol (g) Mercury Cyanide	M. P. 175° $H_3COC_6H_4HgCN$	.2667 .	15.35	60.37	60.11		M. P. 179° $H_3COC_6H_4HgCl$
Iso Propyl Mercury Propyl	(liquid) $C_3H_7^*HgC_3H_7$(Iso)	.4375 .4082	28.95 26.95	69.41 69.25	69.97	(N)C_3H_7HgCl (Iso)C_3H_7HgCl	M.P. 119° (Iso)C_3H_7HgCl
Phenyl Mercury P Chloro Phenyl	M.P. 190-210° $C_6H_5HgC_6^*H_4Cl$	.2231 .2099	10.70 10.10	(h) 50.31 50.47	51.55	$C_6H_4ClHgCl$ $C_6H_5^*HgCl$	M.P. 248° C_6H_5HgCl

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TABLE XII. Continued

Summary of Experimental Work

Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	Cc. of KCNS 1cc = 0.01049 g of Hg Cc.	Hg, % Found	Calcd.	$HgCl_2$	HCl
Phenyl Mercury P Chloro Phenyl	M.P. 190-210° $C_6H_5^*HgC_6H_4Cl$	.2581 .2254	12.35 10.85	50.19 50.49	51.55	(h) $C_6H_4ClHgCl$ C_6H_5HgCl	M.P. 250° C_6H_5HgCl
Phenyl Mercury P Chloro Phenyl	M.P. 190-210° $C_6H_5HgC_6^*H_4Cl$	.2164 .2907	10.40 14.05	50.41 50.66	51.55	(h) $C_6H_4ClHgCl$ C_6H_5HgCl	M.P. 246° C_6H_5HgCl
Phenyl Mercury O Chloro Phenyl	M.P. 90° $C_6H_5^*HgC_6H_4Cl$	.2791	13.65	51.30	51.55	$C_6H_4ClHgCl$ C_6H_5HgCl	M.P. 143° $C_6H_4ClHgClo$
Phenyl Mercury O Chloro Phenyl	M.P. 89° $C_6H_5^*HgC_6H_4Cl$	.2171 .3756	10.65 18.45	51.46 51.53	51.55	$C_6H_4ClHgCl$ C_6H_5HgCl	M.P. 141° $C_6H_4ClHgCl$ o
Phenyl Mercury M Chloro Phenyl	M.P. 68° $C_6H_5^*HgC_6H_4Cl$	.2682	13.25	51.82	51.55	$C_6H_4ClHgCl$ C_6H_5HgCl	M.P. 203° m $C_6H_4ClHgCl$
O Chloro Phenyl Mercury P Chloro Phenyl	M.P. 165-200° $(o)C_6H_4ClHgC_6^*H_4Cl(p)$	.2137 .2419	9.55 11.00	46.88 47.70	47.36	(i)	M.P. 135° $oC_6H_4ClHgCl$

TABLE XII. Continued

Summary of Experimental Work

Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	CC. of KCNS / 1cc = 0.01099. of Hg / Cc.	Hg, % Found	Hg, % Calcd.	$HgCl_2$	HCl
Phenyl Mercury Ortho Tolyl	M.P. 65° / $C_6H_5^*HgC_6H_4CH_3$	.2175 / .4543	11.10 / 23.40	53.53 / 54.03	54.42	C_6H_5HgCl / $CH_3C_6H_4HgCl$	M.P. 250° / C_6H_5HgCl
Ortho Tolyl Mercury Para Tolyl	M.P. 195-205° / $p\ H_3CC_6H_4^*HgC_6H_4CH_3$	.2253 / .2104	11.20 / 10.50	52.15 / 52.35	52.43	$o\ H_3CC_6H_4HgCl$ / $p\ H_3CC_6H_4HgCl$	M.P. 228° / $pH_3CC_6H_4HgCl$
Ortho Tolyl Mercury Para Tolyl	M.P. 200-210° / $p\ H_3CC_6H_4^*HgC_6H_4CH_3$	.2165	10.75	52.09	52.43	$o\ H_3CC_6H_4HgCl$ / $p\ H_3CC_6H_4HgCl$	M.P. 230° / $pH_3CC_6H_4HgCl$
O Tolyl Mercury P Chloro Phenyl	M.P. 210-230° / $o\ H_3CC_6H_4HgC_6^*H_4Cl\ p$	.2218 / .2106	10.40 / 10.00	49.18 / 49.81	49.76	$o\ H_3CC_6H_4HgCl$ / $p\ ClC_6H_4HgCl$	M.P. 230° / $pClC_6H_4HgCl$
O Tolyl Mercury P Chloro Phenyl	M.P. 210-230° / $o\ H_3CC_6H_4HgC_6^*H_4Cl\ p$	.2207 / .3298	10.40 / 15.60	49.42 / 49.62	49.76	$o\ H_3CC_6H_4HgCl$ / $p\ ClC_6H_4HgCl$	M.P. 230° / $pClC_6H_4HgCl$
Para Tolyl Mercury Phenyl	M.P. 120-155° / $p\ H_3CC_6H_4HgC_6^*H_5$	.3686	19.10	54.35	54.41	$p\ H_3CC_6H_4HgCl$ / C_6H_5HgCl	M.P. 246° / C_6H_5HgCl

<div align="center">

TABLE XII. Continued

Summary of Experimental Work

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Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	$cc. of KCNS$ / $1 cc = 0.01049 g$ / $of Hg$ Cc.	Hg, % Found	Hg, % Calcd.	$HgCl_2$	HCl
Meta Tolyl Mercury Phenyl	M.P. 65-70° (j) $m\ H_3CC_6H_4HgC_6^*H_5$	.2235 .2022	11.50 10.40	53.97 53.95	54.41	$m\ H_3CC_6H_4HgCl$ C_6H_5HgCl	M.P. 250° C_6H_5HgCl
Meta Tolyl Mercury Para Tolyl	M.P. 180-205° $m\ H_3CC_6H_4HgC_6^*H_4CH_3$ p	.2036 .2315	10.20 11.50	52.55 52.11	52.43	$m\ H_3CC_6H_4HgCl$ $p\ H_3CC_6H_4HgCl$	M.P. 155° $m\ H_3CC_6H_4HgCl$
M Chloro Phenyl Mercury O Chloro Phenyl	M.P. 95-100° $m\ ClC_6H_4HgC_6^*H_4Cl$ o	.2276 .2113	10.20 9.55	47.01 47.40	47.36	$o\ ClC_6H_4HgCl$ $m\ ClC_6H_4HgCl$	M.P. 207° $m\ ClC_6H_4HgCl$
Meta Tolyl Mercury Para Chloro Phenyl	M.P. 165-220° $m\ H_3CC_6H_4HgC_6^*H_4Cl$ p	.2125 .2161	10.10 10.20	49.86 49.51	49.76	$mH_3CC_6H_4HgCl$ $p\ ClC_6H_4HgCl$	M.P. 230° $p\ ClC_6H_4HgCl$

TABLE XII. Continued.

Summary of Experimental Work

Compound	Formula	Anal. of Unsym. Molecule				Decomp. Unsym. Mols. with	
		Subs. grams	CC. of KCNS 1CC = 0.01049g. of Hg Cc.	Hg, % Found	Hg, % Calcd.	$HgCl_2$	HCl
O Tolyl Mercury Ortho Anisol	(liquid) $oH_3CC_6H_4HgC_6^*H_4OCH_3$ o	.2301 .2355	11.00 11.20	50.15 49.89	50.31	(k)	M.P. 143° $oH_3CC_6H_4HgCl$
Methyl Mercury M Chloro Phenyl	(liquid) $H_3CHgC_6^*H_4Cl$ m	.2143 .2285	12.00 12.70	58.86 58.29	58.82	H_3CHgCl $mClC_6H_4HgCl$	M.P. 168° H_3CHgCl
Para Anisol Mercury O Anisol	M.P. 102° $pH_3COC_6H_4HgC_6^*H_4OCH_3$ o	.2353 .2287	10.75 10.50	47.92 48.15	48.40	$oH_3COC_6H_4HgCl$ $pH_3COC_6H_4HgCl$	M.P. 175° $oH_3COC_6H_4HgCl$
Alpha Naphthyl Mercury P Anisol	M.P. 130-150° $C_{10}H_7HgC_6^*H_4OCH_3$ p	.2076 .2256	9.10 9.95	45.98 46.27	46.15	$C_{10}H_7HgCl$ $pH_3COC_6H_4HgCl$	M.P. 183° $C_{10}H_7HgCl$ (1)
Alpha Naphthyl Mercury O Anisol	M.P. 200-220° $C_{10}H_7HgC_6^*H_4OCH_3$ o						M.P. 188° $C_{10}H_7HgCl$ (m)

* 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

$$R_1{}^*MgCl + RHgCl \rightarrow R_1{}^*HgR + MgCl_2$$
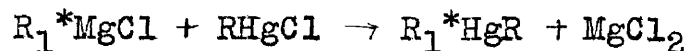
(a) The unsymmetrical radicals have no definite melting points. In this compound and in the unsymmetrical compounds to follow (M P) will indicate the decomposition temperature.

(b) The melting points given are a few degrees lower than the pure product. This is due probably to the presence of a small amount of the mercury halogen derivative of the other radical. But in every case before accepting the result the identity of the compound was proven by taking mixed melting points with some of the pure compound.

(c) 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 of the ethyl and in the other case the Grignard 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.

(d) The melting point of the decomposition pro-
duct with mercuric chloride was 110° and it was found
impossible to make any separation of products.

(e) The melting point of the decomposition pro-
duct 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: 12.35, 14.20 cc. of

KCNS (1cc. $=$ 0.01049 g. of Hg). Found: Hg 62.5, 62.25
Since butyl mercury chloride contains 68.45 per cent of
mercury, and heptyl mercury chloride contains 50.8
per cent of mercury, the mixture above contains 29.9
$\pm$1.0 per cent of butyl mercury chloride and 70.1$\pm$1.0
per cent of heptyl mercury chloride.

(f) Ethyl mercury cyanide was prepared by re-
fluxing 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.

(g) Ortho anisol mercury cyanide was prepared

similarly to ethyl mercury cyanide. After purification
this product gave no test for halogen but after decom-
position with hydrogen chloride and purification, gave
a strong test for halogen.

(h) The unsymmetrical molecule, phenyl mercury
para chloro phenyl,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 ortho chloro phenyl mercury para chloro phenyl with
mercuric chloride melted at 150° to 180° indicating
a mixture of the ortho and para chloro phenyl mercury
chlorides. But all attempts to separate the two pro-
ducts failed. Equal mixtures of ortho chloro phenyl
mercury chloride and para chloro phenyl mercury chloride
melted at 150° to 180° and likewise gave the same
difficulty in separation.

(j) The unsymmetrical molecule, meta tolyl mercury
phenyl, when first isolated was an oil which on treat-
ment 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 ortho tolyl mercury ortho anisol melted at 145°

which is similar to a mixture of ortho tolyl mercury chloride and ortho anisol mercury chloride. All attempts to separate these two products failed.

(1) The unsymmetrical compound α naphthyl mercury para anisol, 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 grams were, therefore, 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 naphthylene. This product also gave a strong odor of naphthylene. 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 grams of the unsymmetrical compound were 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 grams and its identity was further proved to be αnaphthyl mercury chloride by taking mixed melting points. With pure αnaphthyl mercury chloride the melting point was 184° . With pure para anisol mercury chloride the melting point was lowered to 161° .

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

(m) The decomposition of αnaphthyl mercury ortho anisol by hydrogen chloride was run in alcohol solution and gave results similar to αnaphthyl mercury para anisol, naphthylene and αnaphthyl mercury chloride being formed.

SUMMARY

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

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

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

4. A new table of electronegativity of organic radicals is given.

5. The table of electronegativity of organic radicals is used to :

    a. interpret the existence of free radicals,

    b. interpret certain substitution reactions in the benzene ring,

    c. to show the effect of a secondary radical,

    d. to show that the theory of alternating polarity is untenable.

APPROVED: _W. W. Kharasch_

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