A MOLECULAR ORBITAL CORRELATION OF REACTIVITIES
OF SUBSTITUTED 9-PHENYLFLUORENYL SYSTEMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
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By

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* * * * * *

The Ohio State University
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STATEMENT OF PROBLEM

The properties and reactivities of many π-electron systems have been interpreted and correlated by use of molecular orbital calculations. Although this approach has met with considerable success when applied to all carbon systems, the results have been less than satisfactory when heteroatoms were involved. In treating molecules containing heteroatoms, it is usual to choose certain parameters (the resonance and Coulomb integrals of the heteroatom and sometimes of other atoms) to give the best fit of the experimental data on which the calculation rests. This has resulted in a wide range of these parameters being reported in the literature.

The present research was undertaken to determine whether a single set of parameters for a heteroatom could be used for interpreting reactions which varied widely in charge type. 3,6-Disubstituted 9-phenyl-9-fluorenyl systems were chosen for this purpose because the planarity of the fluorene system would avoid complications in the theoretical treatment.

Quantitative measures of the effect of four very different substituents (excluding hydrogen) on the π-electron energy levels of the 9-phenyl-9-fluorenyl
cation and anion were made. (Inclusion of the 9-phenyl-9-fluorenyl free radicals in the study was not possible because of difficulties in the preparation of the required molecules.) Using these data it was hoped that such Coulomb integrals could be selected for the substituent atoms so that these Coulomb integrals would reproduce quantitatively the variations of the \( \pi \)-electron energy levels reflected by the data, when employed in the molecular orbital treatment of the substituted 9-phenyl-9-fluorenyl ions.

The reactions selected for study were the ionization of the substituted 9-phenyl-9-fluorenols in acid to give the corresponding cations and the rate of tritium exchange in the 9-position of substituted 9-phenyl-9-fluorenes. (This latter involves the anion as an intermediate.) Ten compounds were prepared for this study. They were 3,6-dimethoxy-9-phenyl-9-fluorenone, 3,6-dimethyl-9-phenyl-9-fluorenone, 9-phenyl-9-fluorenone, 3,6-dibromo-9-phenyl-9-fluorenone, 3,6-dicyano-9-phenyl-9-fluorenone, 3,6-dimethoxy-9-phenylfluorene, 3,6-dimethyl-9-phenylfluorene, 9-phenylfluorene, 3,6-dibromo-9-phenylfluorene, and 3,6-dicyano-9-phenylfluorene. Substituents at positions 3 and 6 of the fluorene nucleus are para to the methylene bridge carbon at which the ion-generating reactions take place. Therefore, the substituents are placed for maximum demonstration of their effect on the \( \pi \)-electrons.
INTRODUCTION

For the last three decades two theories of molecular bonding have shared the attention of chemists. They are the Valence Bond Theory and the Molecular Orbital Theory. They complement each other in several important respects, and the chemist finds it convenient to use the terms of one or the other, depending on which one most satisfactorily describes the laboratory phenomenon. The Valence Bond Theory is used in the qualitative description of molecules and is of great aid in visualizing the cause of stabilization in molecules, metal chelates, metal-to-metal bonds, and explaining the energies which give the great variety of ionic and mixed ionic and covalent crystal structures. However, quantitative treatments of all but very simple molecules are prohibitively complex. The description of molecules given by the Molecular Orbital Theory is more difficult to grasp, since it lacks the simple pictorial nature of the Valence Bond Theory. Its prime asset is that quantitative application to molecules containing many atoms is possible.
The application of Molecular Orbital Theory to organic chemistry is described in detail by A. Streitwieser, Jr.\textsuperscript{1}

\textsuperscript{1} A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemistry, John Wiley and Sons, New York, 1961.

What is presented in this section is a simple outline of the theory with definitions of its terms and symbols and how they arise. As its name implies, the theory postulates that molecules have associated with them molecular orbitals just as atoms have atomic orbitals. These have definite shapes and orientation in space and correspond to discrete electron energy levels, and each may be occupied by two electrons with opposed spins. If the orbital energy level is such that by placing an electron in that orbital, the stability of the molecules is increased, it is said to be a bonding orbital. If the stability of the molecule is thereby decreased, the orbital is anti-bonding. Electrons placed in the third type, non-bonding orbitals, have no effect on the stability of the molecule. In molecular orbital terminology, a bond is formed between two atoms by the overlap of an atomic orbital of one atom with an atomic orbital of the other atom. The strength of the bond is proportional to the extent of atomic orbital overlap. It also depends on the relative energy levels, of the two atomic orbitals, since there is no covalent bonding action between two atomic orbitals of very different energies.
The limitations of mathematics make it impossible to
develop the exact molecular orbital wave functions for com­
plex molecules. A common approximation is to form each
molecular orbital by making a linear combination of the
atomic orbitals of the atoms in the molecule (the LCAO
method). Designating the atomic orbital wave function for
atom \( i \) by \( \phi_i \) and each molecular orbital wave function by
\( \Psi_j \), for a molecule composed of \( N \) atoms
\[
\Psi_j = \sum_{i=1}^{N} c_{ji} \phi_i , \quad j = 1, 2, \ldots, N.
\]

There would be \( N \Psi_j \)'s of this form because there may be
\( N \) linear, independent combinations of \( N \) independent func­
tions. These are generated from the linear variation
function
\[
\Psi = \sum_{i=1}^{N} c_i \phi_i
\]
by application of the variation method.\(^2\) For example,

\(^{2}\) L. Pauling and E. B. Wilson, Introduction to
The energy $E$ of a particle whose position and motion are described by the wave function $\phi$ is

$$E = \int \phi^* H \phi \, d\tau / \int \phi^* \phi \, d\tau$$

The complex conjugate of $\phi$ is $\phi^*$, $H$ is the exact Hamiltonian operator for the electronic system, and $d\tau$ refers to all coordinates. The approximate energy given by the linear variation function is $E = \int \psi H \psi \, d\tau / \int \psi \psi \, d\tau$, in which $H$ is the Self Consistent Field Hamiltonian operator for the entire molecule. (The designation of the complex conjugate wave function has been dropped because these functions are real.) The condition that the approximate energy $E$ be a minimum, giving the closest approximation to the energy of the molecule, requires that the $N$ partial derivatives $\frac{\partial E}{\partial c_i}$ all be equal to zero. These lead to a set of $N$ simultaneous linear homogeneous equations. These so-called secular equations are

$$\sum_{i=1}^{N} c_i (\phi_i^* H \phi_j \, d\tau - E \phi_i^* \phi_j \, d\tau) = 0,$$

$j = 1, 2, \ldots, N$. The necessary and sufficient condition that there be a non-trivial solution to these equations is that the secular determinant be equal to zero.
The matrix elements are

\[ H_{ij} = \int \phi_i \phi_j \, d\tau, \]

called the Coulomb integral, \( \alpha \), when \( i=j \), and the resonance integral, \( \beta \), when \( i \neq j \). The third matrix element is

\[ S_{ij} = \int \phi_i \phi_j \, d\tau, \]

the overlap integral. \( S_{11} = 1 \) because the individual atomic orbitals are normalized.

The \( N \) values of \( E \) obtained as the roots of the characteristic \( N^{th} \) order polynomial equation of the secular determinant are the molecular orbital energy levels of the molecule. For example, the six molecular orbital energy levels for the \( \Pi \)-bonds of benzene are \( \alpha - 2\beta \), \( \alpha - \beta \) (doubly degenerate), \( \alpha + \beta \) (doubly degenerate), and \( \alpha + 2\beta \). The determination of these energy levels and their significance is described in detail later (pages 55-56).

In saturated organic molecules, the atomic orbitals which overlap to form single bonds are the \( 1s \) orbital of hydrogen, the \( sp^3 \) orbitals of carbon, the \( p_x \) orbital of oxygen, etc. The bonds which are formed are called \( \sigma \) bonds.
In unsaturated molecules, and in particular in the case of carbon-carbon double or triple bonds, in addition to the overlap of \(sp^2\) or \(sp\) orbitals to form sigma bonds, there is overlap of \(p_z\) orbitals or of \(p_z\) and \(p_y\) orbitals to form one or two \(\pi\) bonds. In the case of conjugated polyunsaturation, the \(p_z\) overlap extends continuously the entire length of the conjugated system. This is called orbital delocalization. From considerations of molecular symmetry it is possible to treat the \(\pi\)-bond energy levels independently of the \(\sigma\)-bond energies.\(^4\)


In the molecular orbital calculations of \(\pi\)-electron energies the resonance integral \(\beta\) is usually taken as -18 to -20 kcal. per mole. These values are derived from the measured resonance energies of a number of aromatic hydrocarbons.\(^5\) The value of \(\alpha\) is less well determined.


The best values seem to be those of Mulliken,\(^6\) who gives


\[\alpha = -7.18\] electron volts for benzene.

When heteroatoms are included in the aromatic \(\pi\)-bond system, the value of \(\alpha\) assigned to the atom relative to
for carbon is inversely proportion to its electronegativity on Pauling's scale. The usual form of a heteroatom Coulomb integral is

\[ \alpha_x = \alpha_c + d_x \beta \]

in which \( \beta \) is the carbon-carbon resonance integral, \( \alpha_c \) is the carbon Coulomb integral, and \( d_x \) is a parameter which depends on the heteroatom. The resonance integral for the carbon atom-heteroatom bond is also affected by the electronegativity of the heteroatom and is written as

\[ \beta_{c=x} = k_x \beta_{c=c} \]

where \( k_x \) is a disposable parameter which depends on the heteroatom. The effect on the \( \sigma \) bonds of the conjugated system is not usually taken into account, explicitly, although the Coulomb integral of a carbon atom adjacent to a heteroatom must show some variation because of the changes in both the \( \sigma \)- and indw-electron charge distribution induced by the heteroatom. Its form is

\[ \alpha_2 = \alpha_c + d_2 \beta \]

where the heteroatom is numbered "one" and the adjacent carbon atom is numbered "two." Wheland and Pauling

\[ (7) \text{L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1940, p. 65.} \]

\[ (8) \text{G. W. Wheland and L. Pauling, J. Am. Chem. Soc., 57, 2086 (1935).} \]
examined thirteen compounds in which oxygen, nitrogen, and sulfur were the hetero atoms to discover the values of $\alpha_x$ for these atoms and $\alpha_2$ for adjacent carbon atoms which gave charge densities for the carbon atoms in the aromatic system that were consistent with observed reaction rates at these positions. Sandorfy\(^9\) has continued this treatment

\[\text{(9) C. Sandorfy, Bull. soc. chim. France, Memoires, 5e Série, 16, 615 (1949)}\]

with inclusion of values of $k$ based, in part, on carbon atom - heteroatom bond lengths. The three terms, $d_x$, $d_2$, and $k_x$, are in effect a set of disposable parameters for which many authors have suggested sets of plausible values.\(^8,9,10\) Unfortunately it is not possible to make an


unambiguous selection of parameters for a particular heteroatom which will reproduce both the chemical reactivities and physical properties of the heteroaromatic systems to which they are applied.

As an extension of work of this nature, a study of substituted fluorenyl systems appears to be profitable.
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These systems offer potential advantages not realizable in other situations. Thus fluorenyl cations, anions, and radicals are well-known and there exists the possibility of applying the same molecular orbital substituent parameters to correlate these diverse reactions in the same system. This has never before been done or attempted and would result in a considerable generalization of substituent effects.

X-Ray crystallographic structure determinations on fluorene have shown that the molecule is planar. The planarity of the 13-orbital fluorenyl system obviates the consideration of reduction of orbital overlap arising from rotation of part of the molecule relative to the rest, as would be the case with the diphenylcarbinyl system. The substituents were placed in the 3 and 6 positions because those positions were "para" to the methylene bridge and would exhibit the maximum effect on reactions taking place at the methylene bridge. The 1 and 8 positions are "ortho" to the methylene bridge and substituents in ortho positions to reaction centers are known to interact with the reaction center in a complicated fashion. To ensure that reactions at the 9 position were not affected by a degenerative side-reaction at the same site, the remaining valence of that

carbon was blocked by a phenyl group (9-phenylfluorenyl derivatives). The phenyl group is inert to all the processes which were used to generate carbonium ions, carbanions, or radicals. It cannot be part of the fluorenyl $\pi$-bond system either in the unionized molecule, nor in the ionized (or free radical) form in which the methylene carbon atom has three $\sigma$ bonds with trigonal hybridization. In this ion or radical the 9-phenyl group is rotated out of the plane of the fluorenyl nucleus by at least $68^\circ$ along its bond.\(^{12}\) According to Dewar\(^{13}\) the

\(^{12}\) This rotation angle was calculated from the structure of the fluorene nucleus given by Brown and Bortner,\(^{11}\) carbon-carbon and carbon-hydrogen bond lengths collected by Dewar (M. J. S. Dewar and H. N. Schmeising, Tetrahedron, 11, 99 (1960), and the hydrogen atom van der Waals radius given by Pauling (Reference 7, p. 260).

\(^{13}\) M. J. S. Dewar, J. Am. Chem. Soc. 74, 3341 (1952).

effectiveness of orbital overlap decreases as the square of the cosine of the angle of rotation between two orbitals. For the 9-phenylfluorenyl system, the orbital overlap of the phenyl group with the fluorenyl nucleus is therefore less than 15% of that for a completely co-planar structure.

Mention of the brilliant orange-red fluorenyl anion occurs many times in the chemical literature. It was most often prepared by the action of phenyllithium on an ether
The sodium derivative has been made in boiling decalin by using sodamide. An interesting internal nucleophilic substitution gives 9-phenyl-9-fluorenyllithium from the action of phenyllithium on trityl methyl ether. Shaking fluorene and solid potassium hydroxide in dry ether slowly gives potassium fluorenylethyl, an intense orange compound. The authors considered the formation of hydrated potassium hydroxide to be the driving force for the reaction. Measurements of the acidities of fluorene and 9-phenylfluorene were made by Conant and Wheland as part of a study of very weak acids.
The 9-phenylfluorenyl radical was prepared by Bachman by the action of magnesium on 9-phenyl-9-bromofluorene in n-propyl or n-butyl ether, or benzene.\textsuperscript{19} The radical easily coupled with atmospheric oxygen to give a red peroxide. This oxidation reaction was used by Bowden to determine the rate of dissociation of bis-9-phenylfluorenyl into 9-phenylfluorenyl radical in bromobenzene solution at 25°C.\textsuperscript{20}

\textsuperscript{19} W. E. Bachman, J. Am. Chem. Soc., 52, 3287 (1930).


The fluorenyl carbonium ion in concentrated sulfuric acid is deep blue colored. It has been obtained from 9-fluorenol,\textsuperscript{21} 9-acetoxyfluorene,\textsuperscript{22} and four different 9-fluorenyl ethers.\textsuperscript{23} The transient existence of a 9-oxy-9-fluorenyl carbonium ion has been suggested in the reaction of 9-diazofluorene with perbenzoic acid to give

\textsuperscript{21} E. Bamberger and S. C. Hooker, Ann., 229, 157 (1885).

\textsuperscript{22} J. Schmidt and R. Mezger, Ber., 39, 3899 (1906).

fluorenone.\(^{24}\) Equilibrium constants for the conversion of


9-fluorenol and 9-methyl-9-fluorenol to the corresponding
carbonium ions in sulfuric acid have been determined by
Deno, Jaruzelski, and Schriesheim.\(^{25}\)

\[(25)\] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim,

There are three obvious general routes for the prep­aration of 3,6-disubstituted fluorene derivatives and two
more of a less general nature. One may close a methylene
bridge across the ortho positions of an appropriately sub­stituted biphenyl, for which there is considerable precedent
in the literature.\(^{26}\) Barker and Barker attempted the acid-

63, 1948 (1941); W. E. Bachman, R. Hoffman, and R. Whitehead,
J. Org. Chem., 8, 320 (1943); C. K. Bradsher and E. S.
Smith, J. Am. Chem. Soc., 65, 854 (1943); H. H. Hatt, A.
Pilgrim, and E. F. M. Stephenson, J. Chem. Soc., 478 (1941);
L. Mascarelli and B. Longo, Gazz. chim. ital., 71, 289
(1941); Gazz. chim. ital, 68, 29 (1938); Gazz. chim. ital.
67, 812 (1937); D. V. Nightingale, R. L. Sublett, and
R. H. Wise, J. Am. Chem. Soc., 74, 2557 (1952); G. Wittig
and W. Merkle, Ber., 75B, 1491 (1942); G. Wittig, G. Pieper,
and G. Fuhrmann, Ber., 73B, 1193 (1940); G. Wittig and
G. Fuhrmann, Ber., 73B, 1197 (1940).

catalyzed condensation of formaldehyde across the ortho
position of 3,3'-diaminobiphenyl to give 3,6-diaminofluorene
directly. No product was isolated. When the same

reaction was attempted on 3,3'-bis-(dimethylamino)-biphenyl
in a sealed tube, condensation took place at the 4 position. The general approach of closing a methylene bridge across
the ortho positions of a biphenyl derivative introduces
considerable ambiguity into the structure of the resulting
fluorene because of the possibility of obtaining two isomers,
the 1,6-disubstituted fluorene and the 3,6-disubstituted
fluorene, depending on which way the second phenyl ring was
oriented when the closure took place. The four remaining
synthetic routes avoid this question.

A second route to the desired fluorene compounds is
by use of 4,4'-disubstituted 2-aminodiphenyl ketones in the
Pschorr reaction. By diazotizing the amine and decompos-
ing the diazonium salt, a carbonium ion generated at the site of the amine
attacks the ortho position of the other ring to give, 3,6-disubstituted fluorenones. This reaction has been
applied several times to fluorenone syntheses.


(28a) DeLos F. DeTar, "The Pschorr Synthesis and Re-
lated Diazonium Ring Closure Reactions," Organic Reactions,
Volume IX, Roger Adams, ed., John Wiley and Sons, New York,
Soc., 76, 1680 (1954); D. F. DeTar and S. V. Sagmanli, ibid.,
72, 865 (1950). (b) F. Ullman and E. Mallett, Ber., 31,
1694 (1898); F. Ullman and J. Broido, Ber., 39, 356 (1906);
The third synthetic route, direct sulfonation, nitration, or bromination of fluorenone, is useful only when the desired products are produced in reasonable yield and can be proved to have the correct structure by transformations to known fluorenes. Barker and Barker have used direct nitration of fluorenone, followed by reduction of the nitro groups, acetylation of the amine, and renitration, to give a series of well-characterized fluorenone derivatives of great utility.29


There are two instances recorded of the pyrolysis of diphenic acids to give fluorenes. The first was described by Huntress, et al.,30 who obtained fluorenone in quantitative yield from the uncatalyzed pyrolysis of diphenic acid at 360°C. The second was described by Chardonnes and Würml, who obtained 3,6-dimethylfluorenone in low yield by the calcium oxide catalyzed pyrolysis of 5,5'-dimethyldiphenic acid.31 An improved method of pyrolysis is reported in

the experimental section of this dissertation.

The benzilic acid rearrangement of 3,6-dibromo-phenanthraquinone to give 3,6-dibromo-9-carboxy-9-fluorenol, which was then decarboxylated and oxidized to give 3,6-dibromofluorenone has been described by Courtot and Kronstein.\(^\text{32}\) The starting material was obtained by the direct bromination of phenanthraquinone.\(^\text{33}\)


The use of copper powder to produce bis-(9-phenylfluorenyl) from 9-chloro-9-phenylfluorene has been described by Schlenk, et al.\(^\text{34}\) The starting material was easily prepared from 9-phenyl-9-fluorenol and \(\text{POCl}_3\) by the method of Arcus and Coombs.\(^\text{35}\) Guyot and Kovache have described a general method for reducing aryl carbinols to


\[\text{(34) W. Schlenk, A. Herzenstein, and T. Weickel, Ber., 43, 1754 (1910).}\]

aryl methanes using sodium formate and formic acid. This can be applied to the 9-phenyl-9-fluorenol series of derivatives in most cases.

(36) A. Guyot and A. Kovache, Compt. rend., 155, 839 (1912).
RESULTS

Preparation of Compounds

The five flow sheets which follow describe the preparation of all the compounds used in this study. They are arranged in the order in which they are described in the experimental section.

The synthesis of 3,6-dimethoxy-9-phenyl-9-chlorofluorene, 3,6-dimethyl-9-phenyl-9-chlorofluorene, 9-phenyl-9-chlorofluorene, 3,6-dibromo-9-phenyl-9-chlorofluorene, and 3,6-dicyano-9-phenyl-9-chlorofluorene are described in the experimental section. These five compounds were prepared for use in copper powder catalyzed coupling reactions to produce the corresponding bis-(3,6-dimethoxy-9-phenyl-9-fluorenyl), bis-(3,6-dimethyl-9-phenyl-9-fluorenyl), etc. Two of the five coupling reactions were actually carried out to give bis-(3,6-dimethoxy-9-phenyl-9-fluorenyl) and bis-(9-phenyl-9-fluorenyl). The first of these proved very difficult to purify because of its sensitivity to atmospheric oxygen and was never properly characterized. The second compound had been reported in the literature and was somewhat easier to work with. These reactions were not pursued further.

The preparation of 5,5'-dinitrodiphenic acid from o-toluidine, which is given in the experimental section, was
Flow Sheet I

\[ \text{Flow Sheet I} \]

\[ \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{Ether} \]

\[ \text{HCOONa} \]

\[ \text{HCOOH} \]

\[ \text{Reflux} \]

\[ \text{PCl}_3 \]

\[ \text{Benzene} \]

\[ \text{Cu powder} \]

\[ \text{Benzene} \]

\[ \text{Flow Sheet I} \]
Flow Sheet 2

\[ \text{Flow Sheet 2} \]

\[ \begin{array}{cccccc}
\text{NO} & \text{NHCOCH}_3 & \text{SnCl}_2 & \text{Ac}_2\text{O} & \text{fuming} & \text{NHCOCH}_3 \\
\text{NH}_2 & \text{HNO}_3 & \text{CH}_3\text{COOH} & \text{CH}_3\text{COOH} & \text{SnCl}_2 & \text{HNO}_3 \\
\text{H}_2\text{SO}_4 & \text{H}_2\text{O} & \text{HNO}_3 & \text{H}_2\text{PO}_4 & 30\% & \text{SnCl}_2 \\
\text{NHCOCH}_3 & \text{HCl} & \text{SnCl}_2 & \text{HCl} & \text{HCl} & \text{SnCl}_2 \\
\text{H}_2\text{O} & \text{H}_2\text{SO}_4 & \text{H}_2\text{O} & \text{H}_2\text{PO}_4 & \text{H}_2\text{PO}_4 & \text{H}_2\text{O} \\
\text{CH}_3\text{O} & \text{C}_6\text{H}_5\text{MgBr} & \text{C}_6\text{H}_5\text{MgBr} & \text{C}_6\text{H}_5\text{MgBr} & \text{C}_6\text{H}_5\text{MgBr} & \text{C}_6\text{H}_5\text{MgBr} \\
\text{CH}_3\text{O} & \text{HCOONa} & \text{HClO}_4 & \text{HClO}_4 & \text{HClO}_4 & \text{HClO}_4 \\
\text{CH}_3\text{O} & \text{Cu powder} & \text{Benzene} & \text{Benzene} & \text{Benzene} & \text{Benzene} \\
\end{array} \]
Flow Sheet 4

1. n-C_{12}H_{25} + K_{2}Cr_{2}O_{7} + H_{2}SO_{4} →

2. Br_{2} + C_{6}H_{5}NO_{2} → 100°

3. NO_{2}Cr_{2}O_{7} + NaOH + H_{2}O → 90° stir 7 days

4. C_{6}H_{5}MgBr + Ether →

5. CH_{3}COOH + HCOONa Reflux

6. PCl_{5} + Benzene

7. Br_{2} + Cl_{2} →
Flow Sheet 5

1. 2-Bromo-4,6-dihydroxy-3,5-diphenyl-1,4-benzocyclohexadiene reacts with CuCN in pyridine to form 2-bromo-4,6-dicyano-3,5-diphenyl-1,4-benzocyclohexadiene.

2. 2-Bromo-4,6-dicyano-3,5-diphenyl-1,4-benzocyclohexadiene reacts with \( \text{PCl}_5 \) in benzene to form 2-mono-cyano-3,5-diphenyl-1,4-benzocyclohexadiene.

3. 2-Mono-cyano-3,5-diphenyl-1,4-benzocyclohexadiene reacts with \( \text{Zn dust} \) and \( \text{CH}_3\text{COOH} \) to form 2,4-dicyano-3,5-diphenyl-1,4-benzocyclohexadiene.
developed to give optimum yields in the expectation that it would be an inexpensive and trouble-free route to 3,6-dintrofluorenone and all of the compounds which might be obtained through reduction of the nitro groups and transformations effected on the resulting 3,6-diaminofluorenone. In contrast to the facile ring closure of 5,5'-dimethyldiphenic acid to give 3,6-dimethylfluorenone, 5,5'-dinitrodiphenic acid gave only tars and char from the same reaction.

A good route to 3,6-bis-(dimethylamino)-fluorenone appeared to be a Pschorr reaction\textsuperscript{28a} using 2-amino-4,4'-bis-(dimethylamino)-diphenyl ketone. One sequence of reactions which have been reported in the literature,\textsuperscript{37} which started with N,N-dimethylaniline, was undertaken. The results of attempting to reproduce this work were not encouraging, and the entire series of reactions was abandoned. Later it was discovered that improvements in the synthesis had been made,\textsuperscript{38} but it was thought that the best route to

\[\text{(37) G. Cohn, Chemiker-Zeitung, 24, 564 (1900); R. Ullman and A. Maric, Ber., 34, 4315 (1901); A. Kliegl, Ber., 39, 1266 (1906).}\]

3,6-bis-(dimethylamino)-fluorenone was by way of 3,6-diaminofluorenone, which was expected to have become available in quantity.

**Fluorenyl Cation Formation**

The free energies of formation of a series of 3,6-disubstituted 9-phenylfluorenyl cations are a logarithmic function of the equilibrium constants for the reaction

\[
R^\ominus + BOH \rightleftharpoons ROB + H^\ominus,
\]

where ROB signifies the fluorenol or its ester. In this study, the equilibrium constants were calculated from spectrophotometric measurements on solutions of the fluorenols in a mixture of sulfuric acid and aqueous acetic acid. The five fluorenols used gave very intensely colored carbonium ions when dissolved in concentrated sulfuric acid. The extinction coefficient and wavelength characteristic of each carbonium ion were determined. A known quantity of each fluorenol was dissolved in the sulfuric acid - aqueous acetic acid solution and the extent to which it was converted to the carbonium ion was calculated using the previously determined extinction coefficient at the proper wavelength. This information and the acidity of the sulfuric acid - aqueous acetic acid solution are sufficient for calculating the desired equilibrium constant.

The form of the equilibrium constant for the fluorenol ionization reaction in acid solution is

\[
K_R = \frac{a_{ROB} \times a_{H^\ominus}}{a_{R^\ominus} \times a_{BOH}},
\]

where "a" signifies the activity of the species shown as a subscript. The relationship between this equilibrium
constant and the acidity of the acid solution has been proposed as an acidity function of the type introduced by Hammett\(^{39}\) and given the designation \(C_O, J_O, \text{ or } H_R\)\(^{40}\). The


\[(40)\] N. C. Deno, J. J. Jaruzelski, and A. A. Schriesheim, J. Am. Chem. Soc., 77, 3044 (1955); N. C. Deno and A. A. Schriesheim, J. Am. Chem. Soc., 77, 3051 (1955). In a later paper (N. C. Deno, H. E. BerlKheimer, W. L. Evans, and H. J. Peterson, J. Am. Chem. Soc., 81, 2344 (1959), the symbol was changed from \(C_O\) to \(H_R\). The author will use the latter designation.

\(H_R\) function is defined as

\[H_R = pK_R^\Phi - \log \left(\frac{C_R^\Phi}{C_{ROH}}\right),\]

where \(C_R^\Phi\) and \(C_{ROH}\) are, respectively, the concentrations of the carbonium ion which can be measured spectrophotometri-
cally and the un-protonated alcohol which can be obtained by difference. The \(H_R\) values determined by Deno and co-
workers\(^{40}\) for aqueous sulfuric acid could not be used for
the determination of \(K_R^\Phi\) values for the fluorenols, since
all of the fluorenols were insoluble in sulfuric acid -
water mixtures. This difficulty was alleviated by the use of sulfuric acid diluted with an 80% acetic acid - 20% water
solution. This change of diluent required a complete
redetermination of \(H_R\) for the new solvent system.
The determination of an acidity function is a step-by-step process which begins at a very low sulfuric acid concentration. The equilibrium constant is

\[ pK_R^0 = \log \frac{a_{BOH} a_{R^0}}{a_{ROB} a_{H^0}} \]

\[ = \log \left( \frac{C_R^0}{C_{ROH}} \right) + \log \left( \frac{f_{R^0}}{f_{ROH}} \right) + \log \left( \frac{a_{BOH}}{a_{H^0}} \right), \]

where "f" is the activity coefficient for the species shown as a subscript. Having started with a known \( pK_R^0 \) value (see following paragraph) the concentration of sulfuric acid is increased and \( H_R \) is determined from observed \( C_R^0 \) values and the known \( pK_R^0 \). When the sulfuric acid concentration is such that about 90% of the indicator alcohol (ROH) has been converted to the carbonium ion (R\(^\circ\)), a second indicator alcohol (R\(^\prime\)OH) must be chosen which, at this sulfuric acid concentration, is about 10% converted to the carbonium ion (R\(^\prime\)\(^\circ\)). Thus, the useful indicator range for each alcohol must overlap the useful indicator range for the alcohols above and below it throughout the entire range of sulfuric acid concentrations. A further requirement is that in the region of overlap of indicator ranges, the slopes of the graphs of \( C_R^0/C_{ROH} \) vs. per cent sulfuric acid and of \( C_{R^\prime}^0/C_{R^\prime OH} \) vs. per cent sulfuric acid must be equal. This means that the difference

\[ pK_R^0 - pK_{R^\prime}^0 = \log \left( \frac{C_R^0}{C_{ROH}} \right) - \log \left( \frac{C_{R^\prime}^0}{C_{R^\prime OH}} \right) \quad (1) \]

is independent of the point within the overlap region where the two indicator \( pK_R^0 \) values are compared. If
these criteria are met, each successive indicator pKR\$ can be calculated from the pKR\$ value of its lower neighbor using equation (1).

For very dilute solutions of several strong acids in acetic acid the value of the H_R function for infinite dilution varies over several units.\(^{41}\) Because of this, an attempt to extend the H_R function in aqueous acetic acid to the region below 4% H_2SO_4 might be expected to give meaningless results. In the review of Paul and Long,\(^ {40}\) Table 1, it is shown that pKB_BH\$ values for a large number of bases do not change appreciably on going from aqueous to acetic or formic acid solutions. This demonstrates that pKB_BH\$ - pKB'_BH\$ for two indicator bases (B and B') does not depend on the solvent system is used. A similar independence of pKR\$ - pKR'_\$ has been found on going from aqueous solutions to 80% acetic acid - 20% water. Four aryl carbinols used by Deno et al.\(^ {40}\) were included in the present H_R determination in aqueous acetic acid. The pKR\$ values determined by Deno agree very closely with those found in the present determination when referred to infinitely dilute aqueous solution as a standard state. The scale of the present determination was adjusted to make the differences between the two sets of pKR\$ values a

minimum. An estimated value of \( pK_R^0 \) for di-\( p \)-tolylphenylcarbinol (\(-4.49\)) was obtained by taking the average of \( pK_R^0 \) values for tri-\( p \)-tolylcarbinol and \( p \)-tolyldiphenylcarbinol given by Deno. This method appears reasonable in view of the fact that the known \( pK_R^0 \) value for di-\( p \)-anisylphenylcarbinol, is very close to the average of the \( pK_R^0 \) values for \( p \)-anisyldiphenylcarbinol and tri-\( p \)-anisylcarbinol given by Deno.\(^{40}\)

For the determination of the \( H_R \) function the five 3,6-disubstituted 9-phenyl-9-fluorenols were supplemented by seven aryl carbinols. These twelve alcohols have an adequate overlap of their useful indicator ranges. The following table lists the twelve alcohols in order of decreasing \( pK_R^0 \), the wavelength and extinction coefficient of their carbonium ions, the values of \( pK_R^0 \) from the present work, and the values of \( pK_R^0 \) given by Deno et al.\(^{40}\)
<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\lambda_{\text{max.}}$</th>
<th>$\varepsilon_{\text{max.}}$</th>
<th>pK$_R$</th>
<th>pK$_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Anisyl diphenylcarbinol</td>
<td>476</td>
<td>5.83</td>
<td>-3.23</td>
<td>-3.40</td>
</tr>
<tr>
<td>3,6-Dimethoxy-9-phenyl-9-fluorenol</td>
<td>453</td>
<td>3.71</td>
<td>-4.01</td>
<td>-4.49</td>
</tr>
<tr>
<td>Di-p-tolylphenylcarbinol</td>
<td>456</td>
<td>5.50</td>
<td>-4.39</td>
<td>-5.41</td>
</tr>
<tr>
<td>p-Tolyl diphenylcarbinol</td>
<td>450</td>
<td>4.51</td>
<td>-5.41</td>
<td>-5.41</td>
</tr>
<tr>
<td>Triphenylcarbinol</td>
<td>433</td>
<td>3.72</td>
<td>-6.65</td>
<td>-6.63</td>
</tr>
<tr>
<td>3,6-Dimethyl-9-phenyl-9-fluorenol</td>
<td>468</td>
<td>3.42</td>
<td>-8.13</td>
<td></td>
</tr>
<tr>
<td>p-Anisyl-p-tolylcarbinol</td>
<td>482</td>
<td>8.31</td>
<td>-8.32</td>
<td></td>
</tr>
<tr>
<td>9-Phenyl-9-fluorenol</td>
<td>492</td>
<td>3.75</td>
<td>-10.27</td>
<td></td>
</tr>
<tr>
<td>3,6-Dibromo-9-phenyl-9-fluorenol</td>
<td>516</td>
<td>5.97</td>
<td>-11.11</td>
<td></td>
</tr>
<tr>
<td>p-Tolylphenylcarbinol</td>
<td>456</td>
<td>7.14</td>
<td>-12.29</td>
<td></td>
</tr>
<tr>
<td>Diphenylcarbinol</td>
<td>442</td>
<td>5.47</td>
<td>-13.56</td>
<td>-13.3</td>
</tr>
<tr>
<td>3,6-Dicyano-9-phenyl-9-fluorenol</td>
<td>474</td>
<td>3.42</td>
<td>-14.92</td>
<td></td>
</tr>
</tbody>
</table>

---

- aBecause of the difficulty in obtaining this alcohol in a pure, crystalline state, p-anisyl diphenylcarbinyl chloride was used.
- Deno et al. have shown that the chloride ion introduced in this manner has no effect on the acidity function.40
- bValues given by Deno et al.40
- cEstimated as described in text.
In the following table the determined values of $H_R$ for sulfuric acid diluted with 80% acetic acid - 20% water are listed for the range of 4 to 86% by weight sulfuric acid.

<table>
<thead>
<tr>
<th>wt. % $H_2SO_4$</th>
<th>$-H_R$</th>
<th>wt. % $H_2SO_4$</th>
<th>$-H_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.80</td>
<td>46</td>
<td>9.31</td>
</tr>
<tr>
<td>6</td>
<td>2.28</td>
<td>48</td>
<td>9.65</td>
</tr>
<tr>
<td>8</td>
<td>2.69</td>
<td>50</td>
<td>10.02</td>
</tr>
<tr>
<td>10</td>
<td>3.07</td>
<td>52</td>
<td>10.38</td>
</tr>
<tr>
<td>12</td>
<td>3.44</td>
<td>54</td>
<td>10.71</td>
</tr>
<tr>
<td>14</td>
<td>3.77</td>
<td>56</td>
<td>11.00</td>
</tr>
<tr>
<td>16</td>
<td>4.16</td>
<td>58</td>
<td>11.31</td>
</tr>
<tr>
<td>18</td>
<td>4.50</td>
<td>60</td>
<td>11.62</td>
</tr>
<tr>
<td>20</td>
<td>4.84</td>
<td>62</td>
<td>11.96</td>
</tr>
<tr>
<td>22</td>
<td>5.22</td>
<td>64</td>
<td>12.30</td>
</tr>
<tr>
<td>24</td>
<td>5.61</td>
<td>66</td>
<td>12.63</td>
</tr>
<tr>
<td>26</td>
<td>6.01</td>
<td>68</td>
<td>12.88</td>
</tr>
<tr>
<td>28</td>
<td>6.39</td>
<td>70</td>
<td>13.15</td>
</tr>
<tr>
<td>30</td>
<td>6.80</td>
<td>72</td>
<td>13.51</td>
</tr>
<tr>
<td>32</td>
<td>7.20</td>
<td>74</td>
<td>13.78</td>
</tr>
<tr>
<td>34</td>
<td>7.58</td>
<td>76</td>
<td>14.09</td>
</tr>
<tr>
<td>36</td>
<td>7.97</td>
<td>78</td>
<td>14.50</td>
</tr>
<tr>
<td>38</td>
<td>8.29</td>
<td>80</td>
<td>14.95</td>
</tr>
<tr>
<td>40</td>
<td>8.58</td>
<td>82</td>
<td>15.42</td>
</tr>
<tr>
<td>42</td>
<td>8.84</td>
<td>84</td>
<td>15.71</td>
</tr>
<tr>
<td>44</td>
<td>9.09</td>
<td>86</td>
<td>15.94</td>
</tr>
</tbody>
</table>
**Fluorenyl Anion Formation**

The most direct way of obtaining the relative free energies of formation of a series of 3,6-disubstituted 9-phenylfluorenyl carbanions is by determination of the ionization constants of the corresponding 3,6-disubstituted 9-phenylfluorenes. The experimental difficulties involved in such measurements are numerous and there is a scarcity of accurate data on the basicity of very strong bases. The most complete study has been by McEwen, who determined the pK values for thirty weak acids. The carbanions were rapidly destroyed by atmospheric oxygen and all traces of moisture or greases had to be rigorously excluded. Diethyl ether was the best solvent for the organo-metallic bases but some of them slowly attacked it giving cloudy solutions unsuitable for spectroscopic work and changing the titer of the base.

However, a consideration of the Brønsted catalysis law suggests that the relative free energies of formation of anions can be estimated from the rates of their formation.

The kinetic rate constant $k_A$ of an acid catalyzed reaction is related to the ionization constant $K_A$ of the acid used by the Brønsted Catalysis Law,

$$k_A = G_A K_A^\alpha,$$

where $G_A$ and $\alpha$ are constants determined by the temperature,
solvent, and the reaction.\textsuperscript{43} Taking the logarithm of both
sides of the expression and rearranging the terms gives
\[
\log K_A = \frac{1}{\alpha} \log k_A - \frac{1}{\alpha} \log G_A
\]
showing that $\log K_A$ is a linear function of $\log k_A$. The
free energy of formation of a 3,6-disubstituted 9-phenyl-
fluorenyl cation $\Delta F_{R^Q}$ is a logarithmic function of the
ionization constant of the particular fluorene, e.g.
\[
\Delta F_{R^Q} = -RT \ln K_A
\]
Substituting equation (1) into expression (2) and denoting
the constants in the resulting linear expression by $C$ and $D$,
one obtains an expression
\[
\Delta F_{R^Q} = C \log k_A + D
\]
which gives the energy of formation of the substituted
fluorenyl anion $R^Q$ in terms of a rate constant of a reaction
involving the substituted fluorene RH. (In the following
sections $k_A$ will be designated $k_2$.) The reaction which was
studied was the exchange into the solvent of tritium (the
radioactive isotope $^{3}\text{H}$) at the 9 position on the fluorenes.
The tritium was introduced into the substituted
fluorenes by an exchange reaction in a tritium-enriched
solvent. Each of the five fluorenes was dissolved in a few
ml. of ether containing a small quantity of tritium oxide.
Enough sodium triphenylmethyl was added to the ether solution
to generate a small concentration of the fluorenyl cation
and the exchange process was allowed to proceed for about
30 minutes. (Potassium hydroxide was a sufficiently strong base to effect exchange with 3,6-dicyano-9-phenylfluorene and was used in place of sodium triphenylmethyl.) The system was then slowly quenched with a stream of wet nitrogen and the tritiated substituted fluorene was purified.

The tritium exchange rates were determined by dissolving the tritiated compound in 95% ethanolic base. At convenient times samples were withdrawn and quenched with acid. The solvent was then distilled off and counted in a scintillation counter to ascertain the amount of tritium exchanged out of the compound.

Preliminary experiments with 3,6-dimethoxy-9-phenylfluorene-9-T showed that the tritium exchange rate of 0°C. in 0.1 M sodium hydroxide in 95% ethanol was inconveniently slow. Increasing the base concentration tenfold gave a rate which appeared to be fractional order in sodium hydroxide concentration and was still exceedingly slow. This fractional order probably arose from a non-linear relationship between the concentration of hydroxide ion and its activity coefficient. For this reason, higher temperatures (20° and 40°) were employed to increase the rate so that lower base concentrations (0.5 and 0.10 M) could be used. Maintenance of constant ionic strength was achieved by adding sodium perchlorate. This latter expedient avoided severe activity coefficient changes. The rate at 0°C. was determined from
the measured rates at 20° and 40°C. by analytical solution of the linear equation

$$\log K = C \frac{1}{T} + B$$

(1)

for C and B. These constants were then used to make an analytical extrapolation to 0°C. In equation (1), "K" is the second order rate constant at temperature "T" expressed in degrees Kelvin. (If $C = E/2.303R$ and $B = \log A$, equation (1) becomes the familiar Arrhenius equation

$$k = Ae^{E/RT}.$$ )

In Table 3 are listed pseudo first order rate constants, base concentrations, second order rate constants for 3,6-dimethoxy-9-phenylfluorene-9-T at 40° and 20°C. The second order rate constant for the exchange reaction at 0°C. was calculated from these data and is

$$k = 4.54 \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$ 

The exchange rates of 3,6-dimethyl-9-phenylfluorene-9-T, 9-phenylfluorene-9-T, and 3,6-dibromo-9-phenylfluorene-9-T were measured at 0°C. in 95% ethanol solution. The sodium hydroxide concentration was adjusted to give easily measurable rates, the ionic strength being kept constant at 0.1 M with sodium perchlorate. Table 3 lists the results for each of these compounds.
<table>
<thead>
<tr>
<th>X</th>
<th>T</th>
<th>M</th>
<th>$k_1 \times 10^5$</th>
<th>$k_2 \times 10^4$</th>
<th>ave. $k_2 \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>40°</td>
<td>0.102</td>
<td>16.6</td>
<td>16.3</td>
<td>15.1 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>40°</td>
<td>0.102</td>
<td>17.2</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40°</td>
<td>0.051</td>
<td>6.47</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40°</td>
<td>0.051</td>
<td>7.33</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°</td>
<td>0.094</td>
<td>1.02</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°</td>
<td>0.094</td>
<td>1.952</td>
<td>1.02 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°</td>
<td>0.053</td>
<td>0.503</td>
<td>0.949</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°</td>
<td>0.053</td>
<td>0.517</td>
<td>0.976</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>0°</td>
<td>0.094</td>
<td>0.0974</td>
<td>0.104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>0.094</td>
<td>0.0923</td>
<td>0.0983</td>
<td>0.0970 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>0.056</td>
<td>0.0489</td>
<td>0.0870</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>0.056</td>
<td>0.0555</td>
<td>0.0988</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0°</td>
<td>0.106</td>
<td>2.73</td>
<td>2.56</td>
<td>2.39 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>0.106</td>
<td>2.45</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>0.050</td>
<td>1.11</td>
<td>2.21</td>
<td></td>
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<tr>
<td></td>
<td>0°</td>
<td>0.050</td>
<td>1.24</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>0°</td>
<td>0.0043</td>
<td>11.4</td>
<td>268.0</td>
<td>285.0 ± 12</td>
</tr>
<tr>
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<td>0.0043</td>
<td>11.8</td>
<td>278.0</td>
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<tr>
<td></td>
<td>0°</td>
<td>0.0064</td>
<td>19.1</td>
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<td>0°</td>
<td>0.0064</td>
<td>18.6</td>
<td>292.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$In 95% ethanol. $^b$Ionic strength maintained constant at 0.10 M with NaClO$_4$. $^c$sec.$^{-1}$. $^d$Mole.$^{-1}$ sec.$^{-1}$.

All attempts to measure the rate of tritium exchange of 3,6-dicyano-9-phenylfluorene-9-T in very slightly basic 95% ethanol failed, probably because of adventitious acid. For this reason a buffer of ammonium chloride and ammonia in 95% ethanol was used to provide a system of correct and stable basicity. In order to know the base concentration in this buffer the equilibrium constants for the reactions (1)
and (2) must be known for 95% ethanol (92.4 weight per cent ethanol).

\[ \text{C}_2\text{H}_5\text{OH} + \text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{C}_2\text{H}_5\text{OH}_2^+ \]  
\( \text{(1)} \)

\[ 2 \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{O}^+ + \text{C}_2\text{H}_5\text{OH}_2^+ \]  
\( \text{(2)} \)

The first of these,

\[ K_A = [\text{NH}_3][\text{C}_2\text{H}_5\text{OH}_2^+] / [\text{NH}_4^+] \]  
\( \text{(3)} \)

(brackets indicate molar concentration) can be calculated from the differential potentiometric titration data of Gutbezahl and Grunwald.\textsuperscript{44}


These authors' equation (7) which is used for the calculation is

\[ \Delta pK_A(\text{BH}) - \Delta pK_A(\text{C}_6\text{H}_5\text{NH}_3) = (m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3})Y_0 + \beta(\text{BH}) \]

where BH designates the ammonium ion, and \( (m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3}) \), \( Y_0 \), and \( \beta(\text{BH}) \) are constants which depend on the solvent.

The value of \( \Delta pK_A(\text{C}_6\text{H}_5\text{NH}_3) \) is given by

\[ \Delta pK_A(\text{C}_6\text{H}_5\text{NH}_3) = pK_A(\text{C}_6\text{H}_5\text{NH}_3) - pK_A^W(\text{C}_6\text{H}_5\text{NH}_3) \]

where \( pK_A^W \) represents the thermodynamic ionization constant of the ion at infinite dilution in water. \( \Delta pK_A(\text{NH}_4^+) \) has an analogous form. The expression for \( \beta(\text{BH}) \) is

\[ \beta(\text{BH}) = b_{\text{BH}} - b_{\text{C}_6\text{H}_5\text{NH}_3} \]
The following values for these constants have been taken from the authors' Tables IV and V, interpolating where necessary to 92.4 weight per cent ethanol:

\[ m_{BH} - m_{C_6H_5NH_3} = -0.134 \]
\[ Y_0 = -0.822 \]
\[ pK_A(C_6H_5NH_3) = 3.968 \]
\[ pK_A^W(C_6H_5NH_3) = 4.636 \]
\[ pK_A^W(NH_4) = 9.26 \]
\[ \beta = 0.021 - 0.009 = 0.012 \]

The substitution of these values in equation (7) of Gutbezahl and Grunwald gives the value

\[ pK_A(NH_4) = 9.705 \]

The value of \( K_A \) is (dropping the notation "NH_4"")

\[ K_A = 1.97 \times 10^{-10} \]

The second constant, in the form of an autoprotolysis constant,

\[ K_S = \frac{[C_2H_5OH^\Phi] [H_3O^0]}{[C_2H_5OH^0] [OH^\Phi]} \]

(4)

was taken from a graph of \( K_S \) vs. weight per cent ethanol drawn from the data of Gutbezahl and Grunwald.45

---


The value is

\[ K_S = 2.0 \times 10^{-18} \]
From equations (3) and (4) one obtains the expression

\[
([C_2H_5O^-] + [OH^-]) = K_S[NH_3]/K_A[NH_4^+] = 1.02 \times 10^{-8}([NH_3]/[NH_4^+])
\]

which was used to calculate the base concentrations from the data shown in the following table which lists ammonium chloride and ammonia concentrations, in buffers used for determination of exchange rates of 3,6-dicyano-9-phenylfluorene-9-T at 0°C.

**TABLE 4**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>M NH₄ClO₄</th>
<th>M NH₃</th>
<th>M Base</th>
<th>kₒ x 10⁴</th>
<th>k₁ x 10⁻³</th>
<th>k₂ x 10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.05</td>
<td>0.05</td>
<td>1.02</td>
<td>1.44</td>
<td>14.1</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.05</td>
<td>0.05</td>
<td>1.02</td>
<td>1.39</td>
<td>13.6</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.02</td>
<td>0.02</td>
<td>1.02</td>
<td>1.07</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.02</td>
<td>0.02</td>
<td>1.02</td>
<td>0.961</td>
<td>9.41</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.01</td>
<td>0.01</td>
<td>1.02</td>
<td>0.548</td>
<td>5.37</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.01</td>
<td>0.01</td>
<td>1.02</td>
<td>0.592</td>
<td>5.79</td>
<td></td>
</tr>
</tbody>
</table>

**a** In 95% ethanol with the ionic strength maintained at 0.01 M with NaClO₄. **b** Calculated as described above.

It is seen that the second order rate constant decreases with decreasing ammonia concentration although the ethoxide and hydroxide ion concentration was kept constant. The reaction is therefore subject to general base catalysis. To obtain the value of the second order rate constant for the ethoxide and hydroxide ion catalyzed
reaction alone, a graph of $k_2$ vs. concentration of ammonia was extrapolated to zero ammonia concentration. The rate constant for the exchange reaction catalyzed only by ethoxide and hydroxide ions is

$$k_2 = 4.76 \times 10^3 \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

Table 5 is a summary of second order rate constants for all five compounds.

**TABLE 5**

SECOND ORDER RATE CONSTANTS FOR TRITIUM EXCHANGE AT 0°C. IN 95% ETHANOL

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k^a \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,6-Dimethoxy-9-phenylfluorene-9-T</td>
<td>0.454</td>
</tr>
<tr>
<td>3,6-Dimethyl-9-phenylfluorene-9-T</td>
<td>0.97</td>
</tr>
<tr>
<td>9-Phenylfluorene-9-T</td>
<td>23.9</td>
</tr>
<tr>
<td>3,6-Dibromo-9-phenylfluorene-9-T</td>
<td>2850.0</td>
</tr>
<tr>
<td>e,6-Dicyano-9-phenylfluorene-9-T</td>
<td>476,000,000.0</td>
</tr>
</tbody>
</table>

$a$ l. mole$^{-1}$ sec.$^{-1}$. 
DISCUSSION

pK_R^* Values

The pK_R^* values for the five substituted fluorenols vary as predicted by consideration of the resonance structures and inductive effects of the substituents. The position of the methoxy substituents in 3,6-dimethoxy-9-phenyl-9-fluorenol allows the resonance interaction of an unshared pair of electrons on the oxygen atoms with the positive charge generated at the 9 position, e.g.,

![Diagram]

which stabilizes the ionized species. The effect of this completely overshadows the inductive effect of the substituent, which acts in the reverse direction to place a partial positive charge on the fluorenyl nucleus. In the case of 3,6-dimethol-9-phenyl-9-fluorenol, both the hyperconjugative resonance and inductive effects of the methyl groups contribute to the stability of the ionized form of
the molecule. Each effect is relatively slight, however, so that in combination they have less of a stabilizing influence than the methoxy substituents.

In the 3,6-dibromo-9-phenyl-9-fluorenyl carbonium ion the inductive effect of the bromine atoms and their resonance interaction with the positive center have opposing effect on the stability of the ion. The resonance structures involve a double bond to a bromine atom,

\[
\text{Br} \quad \text{Br}
\]

and it is known that double bond formation becomes progressively more difficult the more disparate the locations of the elements in the periodic chart. For this reason it was expected and observed that the 3,6-dibromo-9-phenyl-9-fluorenyl carbonium ion was less easily formed than the 9-phenyl-9-fluorenyl carbonium ion because of the predominant electron-withdrawing inductive effect of the bromine atoms.

Inductive effects alone must account for the destabilization of the 3,6-dicyano-9-phenyl-9-fluorenyl carbonium ion. Each cyano group has a strong inductive effect which withdraws electrons from the fluorenyl nucleus. This
effect makes this ion much less stable than any of the other four. Resonance structures of the type

Contribute to the stabilization of the unionized form of the molecule but are of little importance to the carbonium ion stabilization because of the juxtaposition of positive charges.

The qualitative considerations in the preceding discussion are given quantitative expression in the graph on the following page. It shows a linear relationship between the negative logarithm of the equilibrium constant ($\text{pK}_R$) and values of $\sigma^+_{\text{para}}$. The correlation shown in Graph 1

(47) The values of $\sigma^+_{\text{para}}$ were taken from a paper by H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958). They are substituent constants (Ref. 39a, pp. 186-193) applicable to reactions in which a positive charge is generated para to the substituent during the course of the reaction.

demonstrates that the various substituents at the 3 and 6 positions of the 9-phenyl-9-fluorenyl cation affect either just the potential energy portion of the energy of the
Graph I

$pK_{a}$ of 3,6-Di-X-9-phenyl-9-fluorenol

vs.

$\sigma^+$

para

$\sigma^+$

para

$X=\text{OCH}_3$

$X=\text{CH}_3$

$X=\text{H}$

$X=\text{Br}$

$X=\text{CN}$
ionization reaction, as discussed by Hammett\textsuperscript{48} or both

\textsuperscript{(48)} Reference 39a, pp. 118-119.

enthalpy and entropy of reaction, which must then be related by the linear isokinetic relationship proposed by Leffler\textsuperscript{49}.


\textbf{Tritium Exchange Rates}

The ordering of the second order kinetic rate constants for the tritium exchange experiments is that expected for a reaction involving the generation of a negative charge at the 9 position of the fluorene nucleus. The fastest reaction was found to be that of 3,6-dicyano-9-phenylfluorene, in which is negatively charged transition state is stabilized by the electron-withdrawing inductive effect as well as by resonance structures of the type

\[
\begin{align*}
N = C &
\end{align*}
\]
The 3,6-dibromo-9-phenylfluorene exchange rate was intermediate between the dicyano rate and the rate for 9-phenylfluorene. The electronegative bromine atoms stabilize the transition state by inductive electron withdrawal from the aromatic system. Resonance interaction would be minimal.

The slowest rate of exchange was observed for 3,6-dimethoxy-9-phenylfluorene. In this case structures such as the following will contribute much less to the transition state than to the initial state because of the unfavorable charge distribution in the negatively charged transition state. Thus, the initial state is more highly stabilized by resonance than the transition state which decreases the ease of reaching the activated complex.

\[ \text{CH}_3\text{O} - \text{CH}_3\text{O} \]

This resonance effect predominates over an inductive effect arising from the electronegativity of oxygen which tends to withdraw electrons from the aromatic system and thereby stabilize the transition state. In the case of 3,6-dimethyl-9-phenylfluorene the inductive effect of the methyl groups acts to destabilize the transition state. The resonance
effect will operate in much the same way as it does in the methoxy compound—to make the energy separation between initial and transition state greater.

However, neither is a strong effect and the exchange rate is slightly faster than that for 3,6-dimethoxy-9-phenyl-fluorene.

The graph (Graph 2) on the following page of log $k_2$ vs. $\sigma^-$ para shows that the substituents on the fluorenyl nucleus satisfy the criteria given by Hammett or Leffler.

(50) The values of $\sigma^-$ para were taken from a review by H. H. Jaffé, Chem. Rev., 53, 191 (1953), and are substituent constants for reactions in which a negative charge is generated para to the substituent during the course of the reaction.

fluorenyl nucleus satisfy the criteria given by Hammett or Leffler.

Molecular Orbital Calculations

In the preceding section it was demonstrated that equilibrium constants and rate constants of reactions which form fluorenyl cations or anions can be expressed as linear functions of Hammett-type substituent constants. Thus, the
Graph II

$\log k_2$ vs. $\sigma_{\text{para}}^-$

$X = -$Br$

$X = -$H$

$X = -$CH$_3$

$X = -$OCH$_3$

$X = -$CN
free energies in each reaction series are a linear function of the potential energy changes. (This relationship was derived by Hammett for the case in which the entropy change in the reaction is negligible\textsuperscript{48} and extended by Leffler to the case in which the enthalphy of the reaction is a linear function of the entropy of the reaction.\textsuperscript{49}) In the two reaction series of the 3,6-disubstituted 9-phenyfluorenyl compounds the principle potential energy changes accompanying reaction are due to changes in the π-electron bonding energy. This it should be possible to express the values of $pK_R^\Theta$ as a linear function of the changes in π-electron bonding energy corresponding to the transformations of the 3,6-disubstituted 9-phenyl-9-fluorenols to the corresponding carbonium ions and to express the values of $\log k_2$ for the tritium exchange reactions as a linear function of the differences in π-electron bonding energies of the 3,6-disubstituted 9-phenylfluorenes and the exchange reaction transition state anions. The π-electron bonding energies for each fluorene derivative and its corresponding ion can be calculated by the method of molecular orbitals. The energies obtained from the calculations depend on the parameters used for the substituents in the 3 and 6 positions. The remainder of this section is devoted to the description of the method used to select substituent parameters which give the desired linear relationship between the theoretical
\( \pi \)-electron bonding energy changes during reaction and the experimental \( \text{pK}_R \) or \( \log k_2 \) values.

In the molecular orbital calculations the phenyl ring at the 9 position was not considered as part of the \( \pi \)-electron system. In the unionized form of the 9-phenyl-9-fluorenyl derivatives the \( \pi \)-electron system of the phenyl ring is insulated from the \( \pi \)-electron system of the fluorene nucleus by the sp\(^3\) hybridized carbon at the 9 position. In the ionic species where this carbon becomes a part of the fluorenyl \( \pi \)-orbital system, steric interaction between hydrogen atoms at the 2 and 8 positions of fluorene and the two ortho positions on the phenyl ring force the phenyl ring to be almost perpendicular to the plane of the fluorene nucleus. The overlap of the two \( \pi \)-orbital systems was calculated to be at most only 15\% of that in a completely planar molecule. The phenyl ring may be expected to exert an inductive effect on the \( \pi \)-electron system of the fluorene nucleus but this must be small since the substituent constant of the meta-phenyl group is only +0.22.\(^{51}\) The

\( \)Reference 39a, p. 188.

resonance effect of the ring tends to reduce the inductive effect. This is indicated by the fact that the substituent constant for the para phenyl group is +0.009.\(^{51}\)
A disubstituted planar biphenyl molecule

![Diagram of a disubstituted planar biphenyl molecule]

was used as a model for the molecular orbital calculations of the \( \pi \)-electron bonding energy of 3,6-dimethoxy-9-phenylfluorene, 3,6-dimethoxy-9-phenyl-9-fluorenol, 3,6-dimethyl-9-phenylfluorene, 3,6-dimethyl-9-phenyl-9-fluorenol, 9-phenylfluorene, 9-phenyl-9-fluorenol, 3,6-dibromo-9-phenylfluorene, 3,6-dibromo-9-phenyl-9-fluorenol, 3,6-dicyano-9-phenylfluorene, and 3,6-dicyano-9-phenyl-9-fluorenol. In the first approximation the four substituents \((Y = ^{2}\text{OCH}_3, ^{1}\text{CH}_3, ^{1}\text{H}, ^{1}\text{Br}, \text{and} ^{1}\text{CN})\) were assumed to have a purely inductive effect on the \( \pi \)-electrons of the aromatic system. This is achieved simply by variation of the Coulomb integrals of the carbon atoms 5 and 11 to which they are attached and exclusion of the \( \pi \)-system of the substituent \( Y \) from consideration. The secular determinant for this model is a twelfth-order determinant of the usual form, with a disposable parameter included for the Coulomb integrals of carbon atoms 5 and 11. The determinant is
and is set equal to zero. In order to put this in a more tractable form, the following substitutions were made:

\[
\begin{align*}
H_{ii} &= \alpha \text{ for all } i \\
H_{ij} &= \beta \text{ for all } i \text{ bonded to } j \\
H_{ij} &= 0 \text{ for all } i \text{ non bonded to } j \\
S_{ii} &= 1 \\
S_{ij} &= 0 \text{ for all } i \notin j
\end{align*}
\]

(52) For a discussion of the errors introduced by this approximation, see G. W. Wheland, J. Am. Chem. Soc., 63, 2025 (1941).

Further, \( \Delta \) was set equal to \( d\beta \) where \( d \) becomes the disposable parameter and will be called the substituent parameter. The \( \tau \)-electron bonding energy is a function of \( d \) and the chief aim of this work was to find a unique value
of d for each substituent which would provide linear relationships for the two diverse types of reactions studied. For the substituent - H, d is of course 0. After the substitutions were made, the elements of the secular determinant were $\alpha - E$, $\alpha + d\beta - E$, $\beta$, and 0. All the elements of the secular determinant were divided by and the term $\frac{\alpha - E}{\beta}$ was designated "x." The final form of the determinant was

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & x+d & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & x & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & x & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x+d & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{vmatrix} = 0$$

The determinant is symmetric about the diagonal, all terms on the diagonal are x or x+d, and off-diagonal terms are 1 when the two atoms referred to are bonded to each other and 0 when they are not. These observations allow one to write a secular determinant for any aromatic system simply by inspection. The parameter d was given a definite value, the roots to the characteristic equation of the secular determinant were obtained and from these the molecular orbital

(53) These calculations were performed by an International Business Machines 1620 digital computer using the Jacobi-Schmidt orthogonalization diagonalization method described by E. Bodewig, Matrix Calculus, Interscience Publishers, Inc., New York, 1956. The largest off-diagonal element at the completion of each computation was less than $1.0 \times 10^{-6}$. 
energy levels were calculated using the expression
\[ E = \alpha - x\beta. \]
Because \( \beta \) is negative the bonding orbitals correspond to negative values of \( x \). The \( \pi' \)-electron bonding energy is the sum of the energy of the \( \pi' \)-electrons each of which has the energy of the molecular orbital it occupies,
\[ E_{\pi'} = \sum n_i (\alpha - x_i \beta). \]
Each orbital contains at most two electrons, with paired spin. For the 12 atomic orbital - 12 electron model the \( \pi' \)-electron bonding energies were designated by \( E_{\pi'}(12,12) \). Values of this function are shown in Table 6 for \( d \) values of -4.0, -2.0, -1.0, 0.0, 1.0, 2.0, and 4.0.

The substituted 9-phenylfluorenyl cations were represented by the 13 atomic orbital structure
### Table 6

**$\pi'$-electroN bond energy**\(^2\) of 9-phenylfluorenyl systems as a function of the substituent parameter \(d\)

<table>
<thead>
<tr>
<th>(d)</th>
<th>-4.0</th>
<th>-2.0</th>
<th>-1.0</th>
<th>0.0</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\pi}^{(12,12)}\times\pi)</td>
<td>12.786(^b)</td>
<td>13.778</td>
<td>14.766</td>
<td>16.382</td>
<td>18.766</td>
<td>21.778</td>
<td>28.788</td>
</tr>
<tr>
<td>(E_{\pi}^{(13,12)}\times\pi)</td>
<td>14.580</td>
<td>15.350</td>
<td>16.150</td>
<td>17.544</td>
<td>19.748</td>
<td>22.656</td>
<td>29.588</td>
</tr>
<tr>
<td>(E_{\pi}^{(13,14)}\times\pi)</td>
<td>13.990</td>
<td>15.068</td>
<td>16.150</td>
<td>17.906</td>
<td>20.438</td>
<td>23.564</td>
<td>30.712</td>
</tr>
<tr>
<td>(\Delta E_{\pi}^{(13,12)}\times\pi)</td>
<td>1.794</td>
<td>1.572</td>
<td>1.384</td>
<td>1.162</td>
<td>0.982</td>
<td>0.878</td>
<td>0.800</td>
</tr>
<tr>
<td>(\Delta E_{\pi}^{(13,14)}\times\pi)</td>
<td>1.204</td>
<td>1.290</td>
<td>1.384</td>
<td>1.524</td>
<td>1.672</td>
<td>1.786</td>
<td>1.924</td>
</tr>
</tbody>
</table>

\(^a\)In units of \(\alpha\) and \(\beta\). \(^b\)Coefficient of \(\beta\).
The secular determinant derived for this structure was

\[
\begin{bmatrix}
    x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
    1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 1 & x+d & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 1 & x+d & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix} = 0
\]

in which the values of \( d \) were to be uniquely determined.

The \( \Pi \)-electron bonding energies of the five cations included in the 13 atomic orbital - 12 electron model are designated by \( E^{\Phi}_{\Pi}(13,12) \). Values of this function are listed in Table 6 for \( d \) values of -5.0, -2.0, -1.0, 0.0, 1.0, 2.0, and 4.0.

The anions derived from the 9-phenylfluorene derivatives were treated in terms of the same model structure as the cations. Their molecular orbital energy levels were therefore the same and the difference in \( \Pi \)-electron bonding energy between the corresponding cation and anion arises because there are two more electrons in the anion than in the cation and these must occupy a new molecular orbital. The \( \Pi \)-electron bonding energies of the five anions included in this 13 atomic orbital - 14 electron system are designated by \( E^{\Phi}_{\Pi}(13,14) \). Values of this function for \( d = -4.0, -2.0, -1.0, 0.0, 1.0, 2.0, \) and 4.0 are listed in Table 6.
The change in \( \pi \)-electron bonding energy corresponding to the conversion of a 3,6-disubstituted 9-phenyl-9-fluorenol to the 3,6-disubstituted 9-phenylfluorenyl cation is equal to the \( \pi \)-electron bonding energy of the product less that of the starting material and is given by the expression

\[
\Delta E^\pi = E^\pi_{c(13,12)} - E^\pi_{c(12,12)}.
\]

The similar change in \( \pi \)-electron bonding energy for the transformation of a 3,6-disubstituted 9-phenylfluorene to its anion is given by the expression

\[
\Delta E^\pi = E^\pi_{c(13,14)} - E^\pi_{c(12,12)}.
\]

Values for these expressions are given in Table 6.

The method of trial and error was used to select the best set of five substituent parameters, using as criteria the linearity of the graph of \( \Delta E^\pi \) vs. \( pK_R^\pi \) and the graph of \( \Delta E^\pi - 2\alpha \) vs. \( \log k_2 \). The graphs on the following two pages show the closest approach to linearity which could be obtained using these data. (The data of Table 6 were plotted as large scale graphs to allow interpolation for fractional values of \( d \).) The substituent parameters (d) for this model are: methoxy, -0.40; methyl, -0.92; hydrogen 0.0; bromo, 0.43; cyano, \( \sim 6.0 \). Clearly the simple all-inductive model is unsatisfactory for the representation of the energy changes of these reactions.
Graph IV

$\Delta E^0_{\text{eff}} - 2e^{-} \text{ vs. } \log k_2$

$\Delta E^0_{\text{eff}} - 2e^{-}$, in units of $\beta$

- $\text{H}$
- $\text{Br}$
- $\text{CH}_3$
- $\text{OCH}_3$
- $\text{CN}$

log $k_2$
An considerable improvement in the correlation of the data could be effected by replacing the simple inductive model by a model which included the contributions of the substituents to the \( \pi \)-orbital system of the fluorene nucleus. Each substituent was treated as a heteroatom with its \( p_z \) orbital available for overlap with the \( p_z \) orbital of the ring carbon to which it was attached. (None of this discussion applies to 9-phenyl-9-fluorenol and 9-phenyl-fluorene; the substituent hydrogen is defined as a reference point for the other four substituents.) The model for the unionized substituted 9-phenylfluorene derivatives and the substituted 9-phenyl-9-fluorenol derivatives was a heteroatom-substituted planar biphenyl,

\[
\begin{align*}
\text{Y} & = \text{OCH}_3, \text{CH}_3, \text{Br}, \text{and CN}, \\
\text{as before in the case of the inductive model. The secular determinant, including the p}_z \text{ orbitals of the substituents, was}
\end{align*}
\]
The Coulomb integral of \( Y \) in this model (\( \alpha_Y \)) was varied as before in the case of the substituent-bearing carbon atom. In this case

\[
\alpha_Y = \alpha + dB
\]

\( (d = -4.0, -3.0, -2.0, -1.5, -1.0, -0.5, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, \text{ and } 4.0.) \) For each value of \( d \) two \( \pi \)-electron bonding energies were obtained, \( E_\pi(14,16) \) and \( E_\pi(14,12) \), depending on the number of electrons in the \( \pi \)-orbitals. The methoxy, methyl, and bromo substituents contribute two electrons per group to the \( \pi \)-electron total whereas the cyano group (considered to be \(-\text{C} = \text{N}\)) contributes none. These calculated energies are shown in Table 7.

The corresponding model for this treatment of substituted 9-phenylfluorenyl cations and anions was
in which fifteen atomic orbitals were considered in calculation of the \( \pi \)-orbital energy levels. The secular determinant was of order 15 and was written by inspection according to the method described on page 55. Provision was made for variation of the Coulomb integral of \( \gamma \) as above. The same values of \( d \) were used. For each value of \( d \), four \( \pi \)-electron bonding energies were obtained, \( E_{\pi}^\Theta(15,16), E_{\pi}^\Theta(15,12), E_{\pi}^\Theta(15,18), \) and \( E_{\pi}^\Theta(15,14), \) corresponding respectively to a carbonium ion with 16 \( \pi \)-electrons, a carbonium ion with 12 \( \pi \)-electrons, a carbanion with 18 \( \pi \)-electrons, and a carbanion with 14 \( \pi \)-electrons. These values are given in Table 7 for each value of \( d \).

For the carbonium ion forming reaction the change in \( \pi \)-electron bonding energy during the reaction is

\[
\Delta E_{\pi}^\Theta(16) = E_{\pi}^\Theta(15,16) - E_{\pi}(14,16)
\]

for the methoxy, methyl, and bromo substituents and

\[
\Delta E_{\pi}^\Theta(12) = E_{\pi}^\Theta(15,12) - E_{\pi}(14,12)
\]

for the cyano substituent. For the series of reactions which involve a carbanion intermediate the change in \( \pi \)-electron bonding energy on going to the transition state is

\[
\Delta E_{\pi}^\Theta(18) = E_{\pi}^\Theta(15,18) - E_{\pi}(15,16)
\]

for the methoxy, methyl, and bromo substituents, and

\[
\Delta E_{\pi}^\Theta(14) = E_{\pi}^\Theta(15,14) - E_{\pi}(14,12)
\]

for the cyano substituent. Values of these four quantities as functions of the substituent constant \( d \) are listed in Table 7. As in the case of the inductive model, the
<table>
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<tr>
<th>$d$</th>
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<th>-2.0</th>
<th>-1.5</th>
<th>-1.0</th>
<th>-0.5</th>
<th>0.0</th>
<th>0.5</th>
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<td>$E_{\pi}^{\phi}(14,12)-12\alpha$</td>
<td>16.766</td>
<td>17.000</td>
<td>17.110</td>
<td>17.258</td>
<td>17.480</td>
<td>17.824</td>
<td>18.376</td>
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<td>17.058</td>
<td>17.388</td>
<td>17.904</td>
<td>18.672</td>
<td>19.726</td>
<td>21.084</td>
</tr>
<tr>
<td>$E_{\pi}^{\phi}(15,12)-12\alpha$</td>
<td>17.884</td>
<td>18.086</td>
<td>18.180</td>
<td>18.308</td>
<td>18.498</td>
<td>18.794</td>
<td>19.276</td>
</tr>
<tr>
<td>$\Delta E_{\pi}^{\phi}(16)$</td>
<td>3.152</td>
<td>2.908</td>
<td>2.832</td>
<td>2.640</td>
<td>2.296</td>
<td>1.902</td>
<td>1.604</td>
</tr>
<tr>
<td>$\Delta E_{\pi}^{\phi}(12)$</td>
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<td>1.086</td>
<td>1.070</td>
<td>1.050</td>
<td>1.018</td>
<td>0.970</td>
<td>0.900</td>
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<td>1.306</td>
<td>1.252</td>
<td>1.192</td>
<td>1.272</td>
<td>1.352</td>
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<tr>
<td>$\Delta E_{\pi}^{\phi}(14)-2\alpha$</td>
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<td>1.672</td>
<td>1.750</td>
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<td>-------</td>
<td></td>
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<tr>
<td>$E_\pi(14,16)-16\alpha$</td>
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<td>23.108</td>
<td>25.002</td>
<td>32.766</td>
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<tr>
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<td>19.266</td>
<td>20.554</td>
<td>22.152</td>
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<tr>
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<td>22.690</td>
<td>24.454</td>
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<td>33.988</td>
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<tr>
<td>$E_\omega(14,18)-18\alpha$</td>
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<td>24.560</td>
<td>26.464</td>
<td>34.254</td>
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<td>$E_\omega(15,14)-14\alpha$</td>
<td>21.722</td>
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<td>24.994</td>
<td>32.610</td>
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<td>$\Delta E_\omega(16)$</td>
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<td>1.294</td>
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<tr>
<td>$\Delta E_\omega(18)-2\alpha$</td>
<td>1.430</td>
<td>1.452</td>
<td>1.462</td>
<td>1.488</td>
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<td>$\Delta E_\omega(14)-2\alpha$</td>
<td>2.456</td>
<td>2.698</td>
<td>2.842</td>
<td>3.046</td>
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</table>

*a* In units of $\alpha$ and $\beta$.  
*b* Coefficient of $\beta$. 
criterion by which the usefulness of the heteroatom model was measured is the linearity of the graphs of $\Delta E^\phi$ vs. $pK_R^\phi$ and $\Delta E^\phi$ vs. log $k_2$. (The values of $\Delta E^\phi$ and $\Delta E^\phi$ for hydrogen are given in Table 6.) The graphs on the following two pages show that this second model allows a closer approach to this goal than was provided by the inductive model. Only in the case of the bromo substituent does the linear relationship break down completely. This is not unexpected since the value of the resonance integral for the carbon-bromine bond is very much smaller than that for the carbon-carbon bond. This will be considered explicitly in the third refinement discussed below. The values of $d$ arising from this heteroatom model treatment are: methoxy, +0.32; methyl, +1.21; hydrogen, 0.0 (by definition); bromo, +4.0; and cyano, +0.65.

As a third refinement of the molecular orbital calculations, the reality of the heteroatom model was enhanced by including a value for the heteroatom-carbon atom resonance integral ($\beta_{Y-C}$) which takes account of the difference in orbital overlap arising from the variation in heteroatom-carbon bond distances and differences in the $p_z$ orbitals of the heteroatom and carbon. In the simple inductive model and the first heteroatom model treatments above all resonance integrals were considered to be equal to $\beta$, the "aromatic" carbon-carbon resonance integral.
Graph V

$\Delta E^\bullet_{\Pi}$ vs. $pK_R^\Phi$

$\Delta E^\bullet_{\Pi}$, in units of $\beta$

$pK_R^\Phi$

- $\text{OCH}_3$
- $\text{CH}_3$
- $\text{CN}^-$
- $\text{H}$
- $\text{Br}$
Graph VI

$\Delta E_{\Pi}^\theta - 2\alpha$ vs. $\log k_2$

$\Delta E_{\Pi}^\theta - 2\alpha$, in units of $\beta$

$\log k_2$

- $\text{H-}$
- $\text{CH}_3$-
- $\text{CH}_2\text{O}$
- $\text{CN-}$
- $\text{Br}$
Mulliken\textsuperscript{54} has proposed that $\beta$ is proportional to the overlap integral $S$. From this assumption Streitwieser\textsuperscript{55}

\textsuperscript{(55) Reference 1, p. 105.}

has calculated $\beta$ as a function of interatomic distance. The values of $\beta_{Y-C}$ which were used in the refined heteroatom model calculation were taken from the graph of this function and are $\beta_{\text{CH}_3O-C} = 1.1\beta$ ; $\beta_{\text{CH}_3-C} = 0.8\beta$ ; $\beta_{\text{Br}-C} = 0.5\beta$ ; $\beta_{\text{CN}-C} = 0.9\beta$.\textsuperscript{56,57}

\textsuperscript{(56) The interatomic distances (in Ångstroms) for the substituent attached to an $sp^2$ hybridized carbon were: methoxy oxygen, 1.36 (T. H. Goodwin, M. Przybylska, and J. M. Robertson, Acta Cryst., 3, 279 (1950)); methyl, 1.515; bromo, 1.891; and cyano, 1.439. The values for methyl, bromo, and cyano were taken from reference 12, pp. 98, 105.}

\textsuperscript{(57) The values given by Streitwieser (Reference 1, p. 135) for the resonance integrals are $\beta_{0-C} = 0.8\beta$ ; $\beta_{\text{CH}_3-C} = 0.7\beta$ ; $\beta_{\text{Br}-C} = 0.3\beta$.}

The model for the substituted 9-phenylfluorene derivatives and the substituted 9-phenyl-9-fluorenol derivatives was a heteroatom-substituted planar biphenyl
for which the secular determinant is

\[
\begin{vmatrix}
1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
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0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{vmatrix} = 0
\]

The symbol \( k \) represents \( \beta_{\text{Y-O}}/\beta \). For each substituent the calculated total \( \Pi \)-electron bonding energy was dependent on the value of \( k \) for the substituent and the number of electrons in the \( \Pi \)-bond system, and is a function of the Coulomb integral assigned to the substituent considered as a heteroatom. For the methoxy substituent, \( k = 1.1 \); there are 16 \( \pi \)-electrons and the \( \pi \)-bonding energy is designated \( E_\pi(\text{OCH}_3) \). For the methyl substituent, \( k = 0.8 \); there are 16 \( \pi \)-electrons and the \( \pi \)-bonding energy is designated \( E_\pi(\text{CH}_3) \). For the bromo substituent, \( k = 0.5 \); there are 16 \( \pi \)-electrons and the \( \pi \)-bonding energy is designated \( E_\pi(\text{Br}) \). For the cyano substituent, \( k = 0.9 \); there are 12 \( \pi \)-electrons and the \( \pi \)-bonding energy is designated \( E_\pi(\text{CN}) \). These four functions are listed in Table 8 for the values of the substituent parameter \( d \).
<table>
<thead>
<tr>
<th>$d$</th>
<th>$0.0$</th>
<th>$1.0$</th>
<th>$1.5$</th>
<th>$2.0$</th>
<th>$3.0$</th>
<th>$4.0$</th>
</tr>
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<tbody>
<tr>
<td>$E_{\pi}(OCH_2)-16\alpha$</td>
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<td>$21.438$</td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
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<td>$\Delta E_{\pi}(OCH_3)$</td>
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<td>$1.474$</td>
<td>$1.322$</td>
<td>$1.264$</td>
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<td></td>
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<td>$1.416$</td>
<td>$1.452$</td>
<td>$1.470$</td>
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<tr>
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<td>$17.346$</td>
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<td>$24.776$</td>
<td>$28.686$</td>
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<td>3.0</td>
<td>4.0</td>
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<tr>
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<td>2.748</td>
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\(^{a}\)In units of $\alpha$ and $\beta$. \(^{b}\)Coefficient of $\beta$. 
The corresponding model for this treatment of the substituted 9-phenylfluorenyl cation and anion was a fifteen atomic orbital system. The secular determinant for this structure may be written by inspection as before for the heteroatom model, but with the inclusion of "k" in place of "l" for the four matrix elements which are the heteroatom-carbon resonance integrals. The total $\pi$-electron bonding energy for each substituted 9-phenylfluorenyl cation and anion ($E_\pi^\phi(OCH_3)$, $E_\pi^\phi(CH_3)$, $E_\pi^\phi(CH_3)$, $E_\pi^\phi(Br)$, $E_\pi^\phi(Br)$, $E_\pi^\phi(CN)$, $E_\pi^\phi(CN)$) were calculated using the appropriate value of k and the proper number of $\pi$-électrons. These, as before, are functions of the substituent parameter d and are listed in Table 8 for various values of d.

For the carbonium ion forming reaction the change in $\pi$-electron bonding energy is

$$\Delta E_\pi^\phi(Y) = E_\pi^\phi(Y) - E_\pi(Y)$$

where $Y = OCH_3, CH_3, Br, and CN$. The corresponding expression for the energy change in forming the carbanion is

$$\Delta E_\pi^\phi(Y) = E_\pi^\phi(Y) - E_\pi(Y)$$
in which \( Y = \text{OCH}_3, \text{CH}_3, \text{Br}, \text{and CN} \). Values for these two expressions are given in Table 8 for various values of the substituent parameter \( d \).

The success of the refined heteroatom model for molecular orbital calculations of the energy changes in the two reaction series is shown by the plots of \( \Delta E_\sigma^\Theta \) vs. \( pK_R^\Theta \) and \( \Delta E_\pi^\Theta \) vs. long \( k_2 \) on the following two pages. A set of substituent parameters has been determined which correlate the behavior of a family of reactions. These are: methoxyl, \( d = +0.60 \); methyl, \( d = +1.00 \); hydrogen, \( d = 0.0 \) (by definition); bromo, \( d = +1.5 \); cyano, \( d = +0.55 \). It is seen that the principal accomplishment of the inclusion of specific resonance integrals for the heteroatom-carbon atom bonds is to give a less extreme value to the bromo substituent constant. The over-all correlation of experimental data is not much improved over that provided by the simple heteroatom model. Further improvements in the calculations may be effected by including an Auxiliary Inductive Parameter\(^{58}\)

\(^{58}\) Reference 1, pp. 128-131.

which takes account of the polarization of the \( \sigma \)-bond system by the electronegativity of the heteroatom substituent and the resulting change in the Coulomb integral of the carbon atom to which the heteroatom is attached. In the present treatment, the poor correlation of the bromo substituent...
Graph VIII

$\Delta E^{\ominus}_{H} - 2\alpha$ vs. $\log k_2$

$\Delta E^{\ominus}_{H} - 2\alpha$, in units of $\beta$

$\log k_2$
data may thus be ascribed to the neglect of the effect of the electronegativity of the bromine atom. A further refinement in the treatment of the fluorenyl ions is the use of the \( \omega \)-Technique\(^{59}\) which allows for the differences in the Coulomb integrals for each carbon atom in the aromatic system which arise from redistribution of the \( \pi^* \)-electrons when the charged species is generated.

It would be profitable to extend this study to include the free-radical generating reactions and to employ several other substituents at positions 3 and 6 on the fluorene nucleus. The effects of placing the same set of substituents at positions 2 and 7 on the fluorene nucleus ("meta" to the reaction site) would allow one to test the possibility that a completely self-consistent unique set of substituent parameters independent of the three different reaction types (carbanion, carbonium ion, and free radical) and the position of the substituent could be obtained. A systematic relationship between this set of substituent parameters and Hammett-type substituent constants, \( \sigma_{\text{meta}}, \sigma_{\text{para}}, \sigma_{\text{para}}^+ \), etc. might be attainable. Since a large number of these are known, this would permit direct calculation of other substituents parameters for molecular orbital calculations from existing data. Such a set of substituent parameters could be tested and used in several

\(^{59}\) Reference 1, pp. 115-116.
ways. Calculation of dipole moments and ultra-violet absorption spectra of substituted aromatic molecules would allow a comparison with the large body of data of this type in the literature. Comparison could also be made between position of aromatic substitution and calculated localization energies of substituted benzenes, and between monomer reactivity ratios and calculated free valence indices. In general, one would compare the calculated values of a given property of a series of aromatic molecules with available experimental data for any reaction or measurement which would be expected to reflect changes in the particular property under consideration.
EXPERIMENTAL

Syntheses

"Naturkupfer."—The method of W. Schlenk, A. Herzenstein, and T. Weickel was used for preparing copper powder. To a solution of 249 g. (one mole) of copper sulfate pentahydrate and 20 ml. of concentrated hydrochloric acid in one-half liter of warm water was slowly added one mole (65 g.) of zinc dust with stirring. The reaction mixture was warmed on a steam bath for 45 minutes. The copper powder was then collected on a Büchner funnel and washed with hot dilute hydrochloric acid, distilled water, and grain alcohol. After most of the alcohol had been removed by pulling air through the filter cake, the powder was dried at 95° for four hours.

9-Phenyl-9-fluorenone.—A solution of phenylmagnesium bromide in 10 ml. of ether was prepared from 0.3 g. (0.12 mole) of magnesium turnings and 1.97 g. (0.125 mole) of bromobenzene (Matheson, Coleman, and Bell reagent, used without further purification). To the Grignard reagent was added a solution of 2 g. (0.011 mole) of fluorenone (Eastman Kodak reagent) in 4 ml. of sodium-dried benzene. A vigorous reaction took place and a solid formed at once. The mixture was boiled under reflux for one hour, cooled,
and poured onto a mixture of 10 g. of ice and 2 g. of ammonium chloride. The organic layer was separated, dried over sodium sulfate, and evaporated to a volume of about 5 ml. Addition of 5 ml. of petroleum ether (b. p. 65-69°) gave a crystalline product. Three recrystallizations from benzene and petroleum ether (b. p. 65-69°) gave 1.84 g. (64%) of slightly yellow cubes melting at 83.5-84° (lit. 35 m. p. 85°).

9-Phenylfluorene.—A solution of 0.5 g. (0.003 mole) of 9-phenyl-9-fluorenol and 4.68 g. of sodium formate in 14.4 g. of anhydrous formic acid was boiled under reflux for 3.25 hours. At the end of the first hour a solid had begun to form in the solution. After cooling to room temperature, the solution was extracted four times with 10 ml. of benzene which removed all suspended solid material. The extracts were dried over sodium sulfate and evaporated almost to dryness. Cooling caused the formation of white needles, which were collected and recrystallized twice from benzene and petroleum ether (b. p. 65-69°) to give 0.33 g. (74%) of white needles, m. p. 145.4-147.4° (lit. 60 m. p. 145.5°).

(60) W. Hemilian, Ber., 11, 838 (1878).

9-Chloro-9-phenylfluorene.—In a 20-ml. flask fitted with a reflux condenser and a calcium chloride drying tube were mixed 0.845 g. (0.004 mole) of phosphorous pentachloride, 1.0 g. (0.0039 mole) of 9-phenyl-9-fluorenol, and
20 ml. of dry benzene. When the solution became homogeneous, the flask was warmed on the steam bath for 20 minutes and then cooled to room temperature. The contents of the flask, a yellow solution, were poured over 20 g. of ice and stirred vigorously. When the system had returned to room temperature, the organic layer was separated and dried over sodium sulfate. A current of air evaporated the solution to a yellow oil which gave colorless pellets. These were crystallized twice from petroleum ether (b. p. 65-69°) to give 0.695 g. (67%) of product, melting at 77-78° (lit.61 m. p. 78-79°).

(61) A. Kliegl, Ber., 38, 292 (1905).

Bis-9-phenyl-9-fluorenyl.—A mixture of 1.0 g. of 9-chloro-9-phenylfluorene, 3 g. of "Naturkupfer" and 16 ml. of sodium-dried benzene through which carbon dioxide had been bubbled to remove dissolved oxygen was refluxed under a carbon dioxide atmosphere for 28 hours. After cooling the benzene solution was filtered to remove the copper powder and was then chilled to the freezing point of benzene. The solid which formed was collected and dried to give 0.475 g. (55%) of white powder, m. p. 246-248° under carbon dioxide (lit.34 m. p. 254°). Despite the use of a carbon dioxide atmosphere for all these operations, small amounts of atmospheric oxygen made
further work with the mother liquors unprofitable. All that could be obtained was a viscous, deep-red oil.

Synthetic Route to 3,6-Dimethoxyfluorennone

2,7-Dinitrofluorennone.— Twenty g. (0.111 mole) of fluorennone (Matheson, Coleman, and Bell reagent) was added over a period of two minutes to 600 ml. of rapidly stirred ice-cold fuming nitric acid\(^{62}\) causing the temperature to rise from -2\(^{\circ}\) to 13\(^{\circ}\). The clear orange solution was kept at room temperature for eleven hours before being poured over 1.5 kg of cracked ice and water. The resulting thick yellow slurry was collected on a Büchner funnel and pressed down to a hard cake which was washed with about one liter of distilled water and dried, to give 24.6 g. (81.9\%) of yellow powder, m. p. 286-291\(^{\circ}\) (lit.\(^{29}\) m. p. 290\(^{\circ}\)).

2,7-Diaminofluorennone.— This procedure and those for the five syntheses to follow were adapted from the methods of Barker and Barker.\(^{29}\) In a one-liter three-necked flask with a condenser and a paddle stirrer were placed 167 g. of stannous chloride dihydrate, 137 ml. of concentrated hydrochloric acid, and 243 ml. of acetic acid. The stirrer

\(^{62}\) J. Schmidt, P. Retzhoff, and A. Haid, Ann., 390, 210 (1912), state that boiling, red fuming nitric acid must be used to obtain 2,7-dinitrofluorennone and that trinitrofluorenones were obtained by the use of ordinary fuming nitric acid. The author found just the reverse to be true.
was started and after all of the stannous chloride had dissolved, 24.6 g. of powdered 2,7-dinitrofluorenone prepared in the preceding step was added. Gentle heat was applied to the resulting yellow slurry and it was kept just at the boil for two hours. During this time it became much thicker and the color changed from light yellow to orange.

After cooling to room temperature the solid was collected on a fritted glass filter, washed with 20 ml. of concentrated hydrochloric acid, and pressed dry. The filter cake was then broken up, put into 1.5 liters of water and while being stirred was heated to a boil. There resulted a deep blood-red solution which stayed homogeneous on cooling to about 70°. Concentrated sodium hydroxide solution (20 ml.) was added with vigorous stirring, causing the 2,7-diaminofluorenone to form as a thick, almost black, slurry. The solid was collected and thoroughly washed with water on a Büchner funnel, pressed partly dry, and air dried, giving 19.1 g. (100%) of very dark brown product. A gram of this material, recrystallized from 20 ml. of nitrobenzene and washed with 10 ml. of petroleum ether (b. p. 65-69°) melted at 278-281° (lit.29 m. p. 284-286°).

2,7-Diacetamidofluorenone.29--The entire product (19.1 g.) of the foregoing reaction was suspended in about 350 ml. of acetic acid. A solution of 37 g. of acetic anhydride in 150 ml. of acetic acid was added all at once
to the rapidly stirred slurry. In about 30 seconds the slurry gelled to a thick sludge and over a period of two to three minutes its color changed from brownish-black to a brilliant orange-red. The beaker containing the thick mixture was covered and allowed to digest for an hour on the steam bath. After cooling, the solid was collected on a Büchner funnel, pressed to a hard cake, and partly dried before being used for the following step. The yield of bright orange solid was 27.4 g. (102%). A small sample, vacuum dried, melted at 344-345.2°C (lit. 29 m. p. 348-349°C).

2,7-Diacetamido-3,6-dinitrofluorenone. 29—A mixture of 332 ml. of fuming nitric acid and 75 ml. of acetic acid was cooled to 0°C. The product of the foregoing reaction (27.4 g.) was broken up into small chunks and added to the rapidly stirred acid mixture to give a deep red solution. One ml. samples were removed at one minute intervals, beginning five minutes after the addition of the starting material, and dropped into a 50-ml. beaker containing 25 ml. of cold water. The color of the solid which formed when the sample was diluted with water was an indication of the progress of the reaction. Examined under incandescent light (fluorescent lighting is too blue), an incomplete reaction gives a red solid whereas a complete or nearly complete reaction gives an orange solid. The reaction was allowed to continue for four minutes after an orange-
colored test was obtained, and then poured into ice water. The heavy orange slurry was collected on a Büchner funnel, washed with about one liter of distilled water and air dried under a lamp to give 33.6 g. (96%) of orange powder, melting with decomposition at 229-230° (lit.29 m. p. 335-336°). A small portion recrystallized from nitrobenzene melted at 332°, with decomposition.

3,6-Dinitrofluorenone.29—The product (33.6 g.) of the foregoing reaction was dissolved in a mixture of 118 ml. of concentrated sulfuric acid and 63 ml. of water to give a black, viscous solution which was stirred for 50 minutes on the steam bath. The material was then cooled to 0° and a cool solution of 18.6 g. of sodium nitrite in 104 ml. of concentrated sulfuric acid was added rapidly with stirring. The system was allowed to warm to room temperature during 40 minutes with occasional thorough mixing and then poured slowly into 740 ml. of vigorously stirred 30% hypophosphorous acid chilled to 0°. The system was kept at 0° overnight. The tan-colored solid was collected and washed on a Büchner funnel with 50 ml. of water and then air dried.

Purification of the crude product was accomplished by sublimation at 1 mm. Hg pressure and 245°. The product collected as orange-red nodules which were recrystallized twice from nitrobenzene to give brown metallic flakes, m. p. 342-344.5° (lit.29 m. p. 344-346°). The yield was 13.34 g. (56.5%).
3,6-Diaminofluorenone.\textsuperscript{29}—In the manner described for the reduction of 2,7-dinitrofluorenone, 13.3 g. (0.049 mole) of 3,6-dinitrofluorenone was treated with 90.6 g. of stannous chloride dihydrate dissolved in 74 ml. of concentrated hydrochloric acid and 132 ml. of acetic acid. The brown slurry was stirred and boiled under reflux for four hours. After cooling, the solid was collected on a fritted glass filter and washed with 10 ml. of concentrated hydrochloric acid. It was pressed partly dry and then dissolved in 400 ml. of warm water giving a blood red solution. Sufficient concentrated sodium hydroxide was added to make the system strongly basic which precipitated an orange solid. This was collected on a Büchner funnel and washed with a liter of water. After partial drying on the filter, the product was dissolved in 300 ml. of hot pyridine and the deep red solution filtered through a bed of Celite to remove a finely divided solid. The pyridine solution was passed through a 3.5 x 30 cm. dry-packed column of Fisher Activated Alumina. A wide green band of impurity developed and moved down the column slowly as the desired product was eluted with liberal quantities of pyridine. This impurity was discarded with the alumina. Elution was discontinued when the eluate was only moderately colored by the intensely colored fluorenone. The pyridine solution of 3,6-diaminofluorenone was boiled to reduce its volume to about 100 ml., and hot water was added to the
point of turbidity. After standing overnight, blade-like red crystals were present in quantity. Two additional crops were obtained from the mother liquors. The total yield was 9.72 g. (94%), m. p. 250.5-251.5° (lit. 29 m. p. 252-253).

3,6-Dihydroxyfluorenone. 29—The product (9.72 g.) from the preceding reaction was dissolved in 61 ml. of concentrated sulfuric acid and the solution was cooled to 0°. A solution (at 15°) of 6.38 g. of sodium nitrite in 61 ml. of concentrated sulfuric acid was added during a 30-minute period to the stirred amine sulfate solution. The mixture was kept cold and stirred for an additional 30 minutes before being poured over 600 g. of cracked ice. Five hours later, 5 g. of sulfamic acid was added to destroy the excess nitrous acid and the solution was slowly brought to a boil. During the heating, considerable nitrogen was evolved and a dark solid scum developed. After brief boiling, the mixture was allowed to cool. The dark solid was collected and dissolved in 150 ml. of 10% sodium hydroxide, giving a deep red solution. The base-insoluble material was removed by filtration and the phenol was regenerated by the addition of 40 ml. of concentrated hydrochloric acid to the filtrate. The product was recrystallized from ethanol and water to give 4.36 g. (45%) of orange needles of 3,6-dihydroxyfluorenone, m. p. 344-347° (dec.) (lit. 29 m. p. 345-348°).
3,6-Dimethoxyfluorenone.—All of the product of the preceding reaction (4.36 g.) was suspended in 200 ml. of water in a 500-ml. round bottom flask fitted with a short reflux condenser, a dropping funnel, and a paddle stirrer. The boiling slurry was stirred rapidly while 30 ml. of dimethyl sulfate was added dropwise. Simultaneously 50% aqueous sodium hydroxide was added at such a rate that the 3,6-dihydroxyfluorenone was partly converted to its sodium salt. This process could be followed visually because the hydroxyfluorenone anion is intensely red colored. Base was added to keep this color always just in evidence. The addition of the dimethyl sulfate required 80 minutes. After cooling, the yellow granular solid was collected and washed with water. Recrystallization from ethanol gave 4.09 g. (83%) of long yellow needles melting at 143.4-144.0°.

Anal. Calcd. for C_{15}H_{12}O_3: C, 74.99; H, 5.03. Found: C, 74.90; H, 5.09.

Anomalous reaction of 3,6-dimethoxyfluorenone with phenylmagnesium bromide.—A benzene solution of 3.68 g. (0.015 mole) of 3,6-dimethoxyfluorenone was added to an ethereal phenylmagnesium bromide solution prepared from 24.1 g. (0.15 mole) of bromobenzene and 3.68 g. (0.15 mole) of magnesium. The system was stirred for three hours and warmed slowly to boiling twice during this time. Dilute hydrochloric acid (50 ml.) was added and the organic phase
was separated. The aqueous phase was extracted three times with 20 ml. of ether. After drying the combined organic solutions over sodium sulfate, the solvent was removed under a stream of air and the resulting oil taken up in 30 ml. of ethanol and decolorized with activated charcoal. Crystals obtained from ethanol melted at 167-184°, so the solvent was changed to benzene-petroleum ether (b. p. 65-69°). After three recrystallizations from benzene-petroleum ether, 1.4 g. of white plates melting at 271.8-273° was obtained. This material gave a greenish-yellow solution in sulfuric acid only upon standing several minutes. Its spectrum taken in a potassium bromide pellet showed a strong peak between 2.8 and 3.0 microns, indicating the presence of a hydroxyl function.

**Anal. Calcd. for C_{21}H_{18}O_{3}:** C, 79.22; H, 5.70.

**Found: C, 82.45; H, 5.71.**

Repeated crystallizations from ethanol of the residue from the mother liquors gave 0.61 g. of long white needles melting at 140.0-140.4°. In acetic acid-sulfuric acid mixtures these instantaneously gave the intense greenish-yellow color which took minutes to develop in pure sulfuric acid using the first product.

**Anal. Calcd. for C_{21}H_{18}O_{3}:** C, 79.22; H, 5.70.

**Found: C, 79.46; H, 5.90.**

Its spectrum, however, showed no absorption whatsoever in the region of 3.0 microns.
3,6-Dimethoxy-9-phenyl-9-fluorenol.—To a solution of 5.0 g. (0.021 mole) of 3,6-dimethoxyfluorenone in 175 ml. of warm dry benzene was added 60 ml. of 0.41 M phenylmagnesium bromide in ether. A solid formed and vanished during the addition of the Grignard reagent, leaving a dark red solution. After four hours at room temperature, the reaction was quenched with water and sufficient concentrated hydrochloric acid was added to dissolve the magnesium hydroxide. The light greenish-yellow organic phase was separated and the aqueous phase was extracted three times with 50-ml. portions of ether. After drying the combined organic layers over magnesium sulfate, the solvent was removed under a current of air and the resulting yellow crystalline crust taken up in 20 ml. of warm benzene. Addition of 30 ml. of petroleum ether (b. p. 65-69°) gave 5.6 g. of grey needles which gave a purple-colored solution in benzene. Several recrystallizations from benzene-petroleum ether (b. p. 65-69°) gave 2.6 g. (44%) of 3,6-dimethoxy-9-phenyl-9-fluorenol as white needles melting at 178.9-180.2°. The spectrum of this material in a potassium bromide pellet showed a strong peak at 2.9 microns.

**Anal.** Calcd. for C_{21}H_{18}O_{3} : C, 79.22; H, 5.70. Found: C, 79.48; H, 5.85.

The combined mother liquors were reduced to 100 ml. and passed through a 2.5 X 5.0 cm. dry-packed column of
Woelm Alumina, activity grade III. The column was eluted with 200 ml. of benzene. The eluate gave a yellow, waxy solid when evaporated to dryness. This was recrystallized twice from benzene-petroleum ether (6. p. 65-69°) twice from carbon tetrachloride, and twice again from benzene-petroleum ether to give 2.0 g. of white needles melting at 177.4-178.8°. A mixed melting point with the analyzed sample above gave no depression. The total yield of 4.6 g. represents a 69% yield.

It was found in subsequent preparations that if the reaction mixture was allowed to stand 8 hours between addition of the Grignard reagent and quenching with water, the yield dropped to 13%. If this time was reduced to 45 seconds, a 64% yield was obtained.

3,6-Dimethoxy-9-phenylfluorene.--A solution of 0.50 g. (0.0016 mole) of 3,6-dimethoxy-9-phenyl-9-fluorenol and 10 g. of sodium formate in 40 g. of 98% formic acid was boiled for 10 minutes with intermittent vigorous shaking. After cooling somewhat the reaction mixture was poured into 75 ml. of water and allowed to stand overnight. The solid was filtered off and dissolved in 10 ml. of hot chloroform. The hot solution was filtered to remove salts, reduced to a volume of 4 ml. and then diluted with 10 ml. of petroleum
ether (b.p. 65-69°). The crystals which formed were recrystallized twice more from chloroform-petroleum ether, (b.p. 65-69°) and twice from chloroform to give 250 mg. (53%) of long, silky, white needles melting at 150.0-151.1°.

**Anal.** Calcd. for C_{21}H_{18}O_{2}: C, 83.42; H, 6.00.
Found: C, 83.39; H, 6.03.

3,6-Dimethoxy-9-phenyl-9-chlorofluorene.—Preliminary experiments showed that the use of phosphorous pentachloride on 3,6-dimethoxy-9-phenyl-9-fluorenol either destroyed the molecule or under milder conditions gave back starting material. Thionyl chloride even under very mild conditions also destroyed the fluorenol.

A solution of 200 mg. of 3,6-dimethoxy-9-phenyl-9-fluorenol in 10 ml. of pure benzene was treated with a stream of dry hydrogen chloride at room temperature for 7 minutes. The colorless solution turned slightly yellow and opalescent during this treatment. The small flask containing the yellowish solution was then loosely stoppered and frozen in a Dry Ice-acetone bath. The solution turned black as it solidified. After the solution was frozen, the flask was removed from the bath and evacuated to 2 mm. Hg pressure. The solvent slowly sublimed away from the black, frozen solid, leaving a feathery crust of white solid. This solid was dissolved in reagent grade cyclohexane and the slightly yellow solution slowly forced through a 5 x 10 mm. column of activated charcoal. The compound was destroyed
by even the least active grade of chromatographic absorption alumina and even by Celite. Most of the solvent was removed under a stream of filtered air. Filtered petroleum ether (b. p. 65-69°) was then added to the colorless oily solution, giving 170 mg. (80%) of a slightly yellow crystalline mass, melting at 117.1-119° (dec.).

**Anal.** Calcd. for C_{21}H_{17}ClO_2 : C, 74.88; H, 5.09. Found: C, 75.08; H, 5.29.

**Bis-(3,6-dimethoxy-9-phenyl-9-fluorenyl).**—A solution of 500 mg. of 3,6-dimethoxy-9-phenyl-9-fluorenol in 25 ml. of benzene was treated with hydrogen chloride gas and then subjected to freeze-drying as described above. The white, fluffy product was redissolved in 25 ml. of benzene and 1.6 g. of Naturkupfer was added. The mixture was boiled with stirring under a carbon dioxide atmosphere for 75 minutes. After cooling, the liquid was filtered through a glass wool plug to remove suspended copper and once again freeze-dried to yield a grey, fluffy solid, which sintered at 190°, darkened at 200°, and slowly melted to a black oil at 216-229° (the melting point was taken in a carbon dioxide-flushed, evacuated capillary). Further attempts at purification failed because of the intrusion of small quantities of atmospheric oxygen to give a very insoluble fine white powder. Activated alumina appeared to destroy the compound.
Attempted preparation of 3,6-dinitro-9-phenyl-9-fluorenol.—The 3,6-dinitrofluorenone was treated with phenylmagnesium bromide in anisole, tetrahydrofuran, ethylene glycol dimethyl ether, and in diethylene glycol dimethyl ether, and with phenyllithium in dioxane, benzene, and ether. Only starting material was recovered in each case.

 Attempted preparation of 3,6-diamino-9-phenyl-9-fluorenol.—Treatment of a suspension of 3,6-diamino-fluorenone in ether with phenyllithium in ether resulted only in the recovery of starting material. The use of a tetrahydrofuran solution of 3,6-diaminofluorenone, and phenylmagnesium bromide prepared in tetrahydrofuran gave only intractable red oils which could not be purified.

 Attempted preparation of 3,6-bis-(dimethylamino)-fluorenone.—In a three-liter three-neck round-bottomed flask was placed a solution of 13.67 g. (0.065 mole) of 3,6-diaminofluorenone in one liter of grain alcohol. The flask was fitted with a dropping funnel, a reflux condenser, and a Hershberg stirrer. The ethanol solution was brought to boiling and 277 g. (1.95 mole) of methyl iodide was dropped slowly into the boiling, stirred ethanol solution which caused it to turn from yellow to deep red. Then 207 g. (1.95 mole) of sodium carbonate in one liter of water was added over a 16-hour period. Air was then drawn briskly over the surface of the stirred, heated solution
for 6 hours, 1.5 liters of water being added during this time. When the solution was allowed to cool, copious quantities of short, fine, crimson needles formed. These were collected and washed with 20 ml. of cold water and dried over calcium chloride.

The fine needles were packed into a 250-ml. round-bottomed flask and pyrolyzed at 170-180° under 1 mm. Hg pressure for 2.5 hours (the time required for the visible surface of the crystalline mass to turn from red to dark yellow). The pyrolyzed material was repeatedly extracted with hot acetone, giving 1.5 liters of solution and a small amount of colorless inorganic residue. The acetone solution was passed rapidly through a 3.5 x 60 cm. dry-packed column of Fisher Activated alumina. The eluate was evaporated to a dark red crust with a stream of air. This crust was washed twice with petroleum ether (b. p. 65-69°) and vacuum dried to obtain 15.2 g. (88%) of product. This was purified by four crystallizations from benzene-petroleum ether (b. p. 65-69°) to give a product in the form of brilliant orange needles, sintering at 235.2°, and melting at 238.2-238.9°.

Anal. Calcd. for C_{17}H_{18}N_{2}O: C, 76.66; H, 6.81. Found: C, 76.50; H, 6.63.

Barker and Barker\textsuperscript{38} prepared the desired material by two different routes and obtained authentic 3,6-bis-(dimethylamino)-fluorenone which melted at 250-252° and readily
gave 3,6-bis-(dimethylamino)-9-phenyl-9-fluorenol when reacted with phenylmagnesium bromide.

**Attempted preparation of 3,6-bis-(dimethylamino)-9-phenyl-9-fluorenol.**—Two attempts at synthesis of this material from supposed 3,6-bis-(dimethylamino)-fluorenone and phenylmagnesium bromide in tetrahydrofuran gave only intractable dark red oils. In the first case the reaction system was kept at boiling temperature for eight hours. In the second attempt it was allowed to stand at room temperature for 24 hours.

**3,6-Diacetamidofluorenone.**—Two g. (0.0074 mole) of 3,6-dinitrofluorenone was reduced with stannous chloride as described in the preparation of 2,7-diaminofluorenone. The crude product of the reduction was dissolved in hot glacial acetic acid giving a deep red solution. A solution of 5 ml. of acetic anhydride in 20 ml. of acetic acid was added all at once and within seconds the red color vanished and solid 3,6-diacetamidofluorenone precipitated. The compound was collected and slurried in 400 ml. of boiling acetic acid, in which it was slightly soluble. Upon cooling, the product was collected, recrystallized from nitrobenzene and dried to obtain 1.8 g. (83%) of a bright yellow powder, m. p. 373-376° (dec.).

**Anal.** Calcd. for C_{17}H_{14}N_{2}O_{3}: C, 69.38; H, 4.80.

**Found:** C, 67.53; H, 5.03.
Attempted preparation of 3,6-diacetamido-9-phenyl-9-fluorenol.—3,6-Diacetamidofluorenone appeared to be insoluble in both ether and tetrahydrofuran. Attempts to react phenylmagnesium bromide with a suspension of the material gave only recovered starting material. The use of phenyllithium produced an intractable red oil.

**Synthetic Route to 3,6-Dimethylfluorenone**

3-Nitro-5-cyanotoluene.—The procedure of Morgan and Coulson\(^{(64)}\) was used. A solution of 60 g. (0.395 mole) of


3-nitro-4-aminotoluene (Matheson, Coleman, and Bell reagent) in a mixture of acetic and hydrochloric acids was treated with 30 g. of sodium nitrite dissolved in 80 ml. of water. The resulting diazonium salt solution was poured into a rapidly stirred hot suspension of cuprous cyanide (prepared by the addition of 120 g. of potassium cyanide to a solution of 167 g. of copper sulfate pentahydrate in one liter of water). After the addition of the diazonium salt solution the mixture was stirred and boiled for 4.5 hours. The brown oil which formed during this time solidified when the system cooled to room temperature. The solid was broken up and extracted in a Soxhlet apparatus for 24 hours with a mixture of 250 ml. of acetone and 500 ml. of ether. This
solvent mixture was removed and replaced by benzene, and
the product recrystallized 4 times from benzene and petrol­
eum ether (b. p. 65-69°) to give 48.4 g. (57%) of almost
colorless needles, m. p. 98.0-98.8° (lit.65 m. p. 101°).

(65) S. Niementowski, Ber., 21, 1535 (1888).

p-Methylanthranilic acid.—A solution of 20.9 g.
(0.129 mole) of 3-nitro-4-cyanotoluene in 20 ml. of acetic
acid was heated to 60° and stirred rapidly as 31 ml. of
concentrated hydrochloric acid was added. The solution was
again heated to 60° and 63 cc. concentrated hydrochloric
acid was added slowly accompanied by 40 g. of granular tin
added in small quantities. At no time was the temperature
of the reaction allowed to rise above 60°. Stirring at
60° was continued for 30 minutes following the addition of
the last of the tin. After cooling the mixture, the unre­
acted tin was filtered off and the dark liquid diluted with
water, cooled in ice, and filtered to remove a small amount
of insoluble black tar.

The filtrate was made basic with 50% sodium hydroxide.
Celite was added to the thick slurry and it was cooled in
ice several hours before being collected on a Büchner
funnel. The filter cake was broken up and thoroughly dried
and then put into a Soxhlet extraction thimble and extracted
with ether for 76 hours. The ether was evaporated and the
brown crust which was left was dissolved in 90 ml. of ethylene glycol containing 16.8 g. of potassium hydroxide and 10 ml. of water. The solution was boiled under reflux for 32 hours during which time ammonia was evolved at a slow rate. Concentrated hydrochloric acid was added until a small amount of solid material formed. This was filtered off and discarded. Hydrochloric acid (6 molar) was added to the filtrate until it was neutral to acid-base indicator paper. The tan solid which precipitated was filtered off and washed with 100 ml. of distilled water. The p-methylanthranilic acid (7.62 g., 39%) was obtained as a light tan powder melting at 174.5-176° (lit. m.p. 177-178°).

(66) S. Niementowski, Ber., 21, 1539 (1888).

5,5'-Dimethyldiphenic acid.—A solution of 32.98 g. (0.218 mole) of p-methylanthranilic acid in 436 ml. of 1 M hydrochloric acid at 0° was slowly diazotized with a solution of 13.7 g. (0.218 mole) of sodium nitrite in 50 ml. of water. The solution of diazonium salt was kept at 0° while the cuprous hydroxide was prepared.

A ground mixture of 86.3 g. (0.873 mole) of commercial cuprous chloride and 10 g. of sodium bisulfite was washed into a beaker with a liberal quantity of water. The slurry was brought briefly to boiling and while hot, 50% aqueous sodium hydroxide was added until no more precipitate formed. The brick-red cuprous hydroxide so prepared was
washed thrice by decantation with water and then stirred into one liter of water. The diazonium salt solution was added during 30 minutes to the stirred cuprous hydroxide suspension at room temperature. Five 16-ml. portions of concentrated ammonium hydroxide were added during the course of the addition of the diazonium salt solution. Following the addition of the diazonium salt, the solution was slowly heated to about 80° and then left on a steam bath overnight.

The mixture was treated with 25 ml. of 50% sodium hydroxide solution and a quantity of Celite. It was filtered and the filtrate acidified with concentrated hydrochloric acid. A pink solid separated and was collected, dried, and recrystallized from ethanol and water to give 22 g. (75%) of pure crystals. Clarification with charcoal and two additional recrystallizations from ethanol-water gave off-white flakes melting at 264.7-267° (lit. m.p. 269°).

3,6-Dimethylfluorenone.--The observation that the 5,5'-dimethyldiphenic acid sublimes readily suggested a modification of the procedure of Chardonnes and Würml. One g. (0.0034 mole) of 5,5'-dimethyldiphenic acid was packed lightly into the bottom of the 18-mm. Pyrex test tube and covered with a loose plug of glass wool. The test tube was cut off just above the glass wool plug and sealed onto a 38 cm. length of 16 mm. Pyrex tubing. The sides of the tube were indented just above the junction point with the test tube and pea-sized calcium oxide pellets were
dropped in and packed down to give a column 31 cm. long. The tube was also indented just above the column of calcium oxide in order to hold it in place. This left about 7 cm. of empty tube open at the end. This end was attached with 8 mm. tubing to a vacuum system. The apparatus was clamped at a slight angle with the horizontal, the end containing the diphenic acid being higher than the end to which the vacuum connection was made. An open-end electrical furnace 31 cm. long was slipped down to cover only the calcium oxide filled portion of the tube and another smaller furnace was placed over the end of the apparatus which contained the diphenic acid. The apparatus was slowly evacuated to 1 mm. Hg pressure and allowed to degas for about one hour. The calcium oxide furnace was then brought to 450-460° and heat was slowly applied to the diphenic acid by means of the smaller furnace. The temperature was adjusted to about 170° so that 4 to 8 hours was required to sublime the 5,5'-dimethyldiphenic acid through the pyrolysis section of the apparatus.

After the apparatus had cooled, the end of the tube containing the reddish yellow, partially crystallized product was cut off and washed out with hot benzene and petroleum ether (b. p. 65-69°). These washings were concentrated and introduced onto the top of an 18 x 150 mm. column of Woelm Alumina, activity grade II, made up in
petroleum ether (b.p. 65-69°). Elution with 40% benzene-60% petroleum ether (b.p. 65-69°) resulted in the separation of the material into a green band which was eluted and collected and a pink band which was discarded with the alumina. Crystallization of the eluted material from petroleum ether (b.p. 65-69°) gave 399 mg. (56%) of 3,6-dimethylfluorenone as yellowish-green needles. It was found that some samples of this material crystallized as yellowish plates melting at 114.5-115.9° (lit. 3° m.p. 118°) whereas other samples formed yellowish-green fibrous needles, melting at 113.5-114.5°. The crystalline modification could be changed at will by seeding with the appropriate type of seed.

3,6-Dimethyl-9-phenyl-9-fluorenone.—Preliminary small scale preparations showed that it was not necessary to purify the 3,6-dimethylfluorenone produced by pyrolysis before using it for this preparation. The impurity constituting the pink band found on chromatography of the pyrolysate was easily separated from the desired product by simple recrystallization. The crude 3,6-dimethylfluorenone (3 g., 0.014 moles) from a single pyrolysis was dissolved in 40 ml. of dry benzene and treated with 50 ml. of 0.6 M phenylmagnesium bromide in ether. After two hours at room temperature, the reaction was quenched with 70 ml. of 1 M hydrochloric acid. The organic phase was separated and the
aqueous layer was washed with three 15-ml. portions of ether. The combined organic layers were dried over magnesium sulfate and evaporated. The residue was taken up in hot ethanol and decolorized with charcoal. After evaporation of the ethanol, the residue was crystallized from petroleum ether (b.p. 65-69°) to give rosettes of light tan short stout needles. Several recrystallizations from petroleum ether (b.p. 65-69°) gave 2.8 g. (69%) of almost colorless crystals, m. p. 141.0-142.2°.

Anal. Calcd. for C_{21}H_{18}O: C, 88.08; H, 6.34.
Found: C, 87.90; H, 6.12.

3,6-Dimethyl-9-phenyl-9-chlorofluorene.—A solution of 1.0 g. (0.0035 mole) of 3,6-dimethyl-9-phenyl-9-fluorenol in 15 ml. of dry benzene was treated with 0.8 g. of phosphorous pentachloride. The solution was swirled and then kept at about 50° for 78 hours under a calcium chloride drying tube. The light yellow solution was washed several times with 5 ml. of cold water, treated simultaneously with magnesium sulfate and charcoal, filtered and evaporated to dryness. The yellow crust which resulted was recrystallized twice from petroleum ether (b.p. 65-69°). It was then redissolved in petroleum ether (b.p. 65-69°) and filtered through Celite to remove all traces of charcoal. The celite also retained the greater part of the yellow color. A final crystallization gave 0.63 g. (60%) of shiny colorless nodules, melting at 130.8-132.3°.
3,6-Dimethyl-9-phenylfluorene.—A mixture of 0.50 g. of 3,6-dimethyl-9-phenyl-9-fluorenol, 5 ml. of water, 45 ml. of 98% formic acid, and 5 g. of sodium formate was refluxed for 71 hours. Water (50 ml.) was then added to the solution and the precipitated product collected and dried. The white granular product was dissolved in 10 ml. of hot benzene and the small quantities of insoluble material removed by filtration. The benzene was evaporated and replaced by petroleum ether (b.p. 65-69°) from which grew white crystals melting at 127-160°. Two additional recrystallizations from petroleum ether (b.p. 65-69°) gave a white powder melting at 127-131°. It was discovered that washing this material with petroleum ether (b.p. 65-69°) at 25° would selectively dissolve the major portion of the crystalline material. The small residue could be recrystallized from carbon tetrachloride to give a solid melting at 132.4-145°. This was not further investigated.

The petroleum ether (b.p. 65-69°) washings were concentrated and yielded 236 mg. (50%) waxy crystals. After three recrystallizations from petroleum ether, they melted at 132.0-133.4°.

Anal. Calcd. for C₂₁H₁₇Cl: C, 82.75; H, 5.62.
Found: C, 82.74; H, 5.88.

Found: C, 93.25; H, 6.85.
This reduction may be accomplished in 15 minutes instead of 71 hours by using a solution of 10 g. of sodium formate in 37 g. of formic acid to reduce one gram of 3,6-dimethyl-9-phenyl-9-fluorenol.

**Synthetic Route to 3,6-Dim bromofluorenone**

*Phenanthraquinone.*—This material was prepared from technical grade phenanthrene (Matheson, Coleman, and Bell product) by the method of Anschutz and Schultz.\(^{67}\)


solution of 150 g. of potassium dichromate, 750 ml. of water, and 450 g. of sulfuric acid was heated to boiling in a large porcelain evaporating dish. Slowly 50 g. (0.29 mole) of phenanthrene was added as the solution was stirred. When the initial reaction had subsided an additional 150 g. of potassium dichromate was added in small portions. After 15 minutes of heating and stirring the dish was set aside to cool. When cool the contents were washed into 2 liters of water and the solid collected and washed on the filter with one liter of water. It was allowed to air dry and then added to 100 ml. of concentrated sulfuric acid. The resulting solution was stirred for 24 hours. The dark green solution was poured into 1.5 liters of water and the solid which formed filtered off and washed on the filter with 500 ml. of water, 200 ml. of cold
1% sodium hydroxide, and again with 500 ml. of water. The filter cake was slurried in 2 liters of water and stirred as 75 g. of sodium bisulfite was added during a five minute period. The bisulfite addition compound formed at once, giving a tan solution containing a small amount of suspended solid material which was filtered off. The filtrate was treated with 75 ml. of concentrated hydrochloric acid and 40 g. of sodium dichromate. This immediately regenerated the phenanthraquinone which was filtered off, and washed with one liter of water, giving 32 g. (53%) of product, m. p. 205-206°C (lit. m. p. 205°C). (68) C. Graebe, Ann., 167, 142 (1873).

3,6-Dibromophenthraquinone.--The method of Schmidt and Eitel was used. A solution of 10.2 g. (0.05 mole) of phenanthraquinone in 60 g. of nitrobenzene was kept at 110°C as 16 g. of bromine was added during a 30 minute period. The temperature of the solution was kept between 100°C and 120°C for 5 hours. After cooling the partially solidified mixture was mixed with 500 ml. of ether and the dark brown needles collected and air dried. These were dissolved in two liters of boiling glacial acetic acid and allowed to recrystallize slowly. After drying the product in air there was 8.23 g. (49%) of orange needles, m. p. 286.5-287.5°C (lit. m. p. 286-287°C). A second crop of 1.61 g. m. p. 274-276°C, was also obtained.
3,6-Dibromofluorenone.—The benzilic acid rearrangement of 3,6-dibromophenanthraquinone to 3,6-dibromo-9-carboxy-9-fluorenol was found to proceed much less readily than the literature implied. 32

A mixture of 10.0 g. (0.027 mole) of 3,6-dibromophenanthraquinone, 16 g. of sodium dichromate dihydrate, 20 g. of potassium hydroxide, and 180 ml. of water were placed in a 250-ml. Erlenmeyer flask and stirred rapidly for seven days. During this time the flask was heated on a steam bath. At the end of this period the yellow solid product was collected, washed with water, and air dried. It was combined with the product from a duplicate reaction and slurried in 400 ml. of boiling toluene. The boiling toluene solution was filtered through a coarse fritted glass filter stick and allowed to cool. The solid was collected. A total of 13.3 g. (72%) of flaky metallic yellow 3,6-dibromofluorenone, m. p. 313-317° (lit.32 m. p. 321°) was obtained.

3,6-Dibromo-9-phenyl-9-fluorenol.—To a slurry of 2.0 g. (0.0059 mole) of 3,6-dibromofluorenone in 20 ml. of dry ether was added 20 ml. of 0.633 M phenylmagnesium bromide in ether. After shaking vigorously for five minutes all of the starting material had vanished. The reaction mixture was quenched with 10 ml. of 1 M hydrochloric acid and the organic phase separated. The aqueous
layer was extracted with three 10-ml. portions of ether. After drying the combined organic solutions over sodium sulfate, the solvent was evaporated under an air stream. The residual yellow oil was dissolved in hot petroleum ether (b.p. 65-69°) and the solution set aside for two days to give 1.76 g. (72%) of large cubes, m.p. 307-316.1° with sublimation. A small portion of this material was sublimed at 160° and 1 mm. pressure to give white cubes melting at 189.5-190.3°.

**Anal. Calcd. for C₁₉H₁₂Br₂O: C, 54.85; H, 2.88. Found: C, 54.79; H, 2.78.**

The main part of the product (m. p. 307-316.1°) was pulverized and boiled gently in 300 ml. of petroleum ether (b. p. 65-69°) for 45 minutes. Only a small amount of material failed to dissolve and was discarded. The petroleum ether was boiled down to a volume of 50 ml. and allowed to stand for several days. Large colorless cubes formed very slowly. These melted at 189.8-190.8°. The yield was 1.6 g. (65%).

**Anomalous reaction of 3,6-dibromofluorenone with phenylmagnesium bromide.**—In a 500-ml. Erlenmeyer flask were placed 47.5 g. (0.141 mole) of 3,6-dibromofluorenone and 200 ml. of dry ether. To this was added over a 15 minute period 200 ml. of 0.94 M phenylmagnesium bromide in ether. A vigorous reaction took place during the addition but at no time did a clear solution result. Stirring was
continued for an additional 15 minutes. The thin yellow slurry was then slowly poured into one-half liter of water to yield a thick green paste. Concentrated hydrochloric acid (330 ml.) was added to dissolve the magnesium hydroxide and the organic layer was separated. The aqueous layer was extracted with six 100-ml. portions of ether. The combined organic solutions were dried over sodium sulfate and the solvent was evaporated to yield a thick green gum. This was dissolved in 400 ml. of benzene and the dark green solution diluted with three volumes of petroleum ether (b.p. 65-69°). A green fluocculent solid separated at once and was collected and dried. It weighed 5.9 g., was slightly soluble in hot ethanol, and turned light yellow in either acid or base.

The greenish mother liquor slowly deposited green cubes of 3,6-dibromo-9-phenyl-9-fluorenol. These could not be freed of the color by repeated recrystallization from petroleum ether (b.p. 65-69°) so the material was dissolved in benzene and passed through a short column of Woelm Alumina, activity grade III. The green coloration stayed strongly adsorbed on the alumina as the column was flushed with benzene. The eluate was evaporated to dryness and the oil which was obtained was taken up in petroleum ether (b. p. 65-69°). Large colorless cubic crystals were obtained. They were collected and recrystallized from
petroleum ether (b. p. 65-69°) to give 12.2 g. (21%) of 3,6-dibromo-9-phenyl-9-fluorenol, m. p. 189.2-190.9°.

The combined mother liquors from the fluorenol crystallizations were treated with decolorizing charcoal and evaporated to dryness, giving a hard yellow crust. This residue was dissolved in benzene and caused to crystallize by the addition of petroleum ether (b. p. 65-69°). Two additional recrystallizations from benzene-petroleum ether gave 11.3 g. of long colorless needles, m. p. 91.0-92.8°, with gas evolution.

3,6-Dibromo-9-phenylfluorene.—A solution of 3.3 g. of 3,6-dibromo-9-phenyl-9-fluorenol, 60 ml. of acetic acid, 60 ml. of formic acid, and 20 g. of sodium formate was refluxed for 65 hours. The progress of the reaction was indicated by the slow appearance of a white solid. The reaction mixture was cooled, diluted with 50 ml. of water, and the product was collected and dried in vacuum. It was recrystallized three times from petroleum ether (b. p. 65-69°) to give 2.8 g. (90%) of white shiny nodules, m. p. 142.5-146.8°. Passing a benzene solution of 200 mg. of this material through a 5 X 10 mm. column of Fisher alumina, followed by three recrystallizations from petroleum ether (b. p. 35-55°), raised the melting point to 144.6-146°.

Anal. Calcd. for C₁₉H₁₂Br₂: C, 57.17; H, 2.78.
Found: C, 57.31; H, 2.95.
3,6-Dibromo-9-phenyl-9-chlorofluorene.—To a solution of 2.0 g. (0.005 mole) of 3,6-dibromo-9-phenyl-9-fluorenol in 25 ml. of dry benzene was added 1.1 g. of phosphorous pentachloride. The yellow solution was boiled for 35 hours under reflux while protecting it from atmospheric moisture by a calcium chloride drying tube. After cooling, the solution was washed three times with 10 ml. portions of water and dried over magnesium sulfate. The solvent was evaporated under a stream of air. The product was recrystallized five times from petroleum ether (b. p. 65-69°) and four times from carbon tetrachloride-petroleum ether to give 1.98 g. (95%) of colorless plates which melted at 150.1°, followed by resolidification and remelting at 160.9-161.7°.

Anal. Calcd. for C_{19}H_{11}Br_{2}Cl: C, 52.51; H, 2.55.
Found: C, 52.47; H, 2.37.

3,6-Dicyano-9-phenyl-9-fluorenol.—A mixture of 30 ml. of N-methyl-2-pyrrolidone, 5 ml. of pyridine, 1.0 g. (0.0024 mole) of 3,6-dibromo-9-phenyl-9-fluorenol, and 0.775 g. (0.0086 mole) of cuprous cyanide was refluxed (160°) for 15 hours and then poured while still warm into 114 ml. of water containing 1.4 g. (0.0086 mole) of ferric chloride and 24 ml. of concentrated hydrochloric acid. A grey solid precipitated at once. The system was saturated with sodium chloride and extracted five times with 20 ml. portions of benzene. The benzene extracts were, in turn, washed three times with 10 ml. portions of water and dried.
over magnesium sulfate. The solution was treated with activated charcoal and then most of the benzene was evaporated. Petroleum ether (b. p. 65-69°) was added to the residue. The crystals which formed were recrystallized six times from chloroform-petroleum ether to give 370 mg. (50%) of white platelets melting at 276.1-276.5°.

Found: C, 81.70; H, 4.13.

3,6-Dicyano-9-phenyl-9-chlorofluorene.—A solution of 0.5 g. (0.0016 mole) of 3,6-dicyano-9-phenyl-9-fluorenol and 0.37 g. (0.0017 mole) of phosphorous pentachloride in 30 ml. of dry benzene was refluxed for 24 hours under a calcium chloride drying tube. After cooling, the solution was diluted with an equal volume of ether and the ether solution was washed three times with 10-ml. portions of water. After drying over magnesium sulfate, the solvent was evaporated under a stream of air. The almost colorless solid residue was recrystallized twice from benzene-petroleum ether (b. p. 65-69°) to give a solid melting at 189-192° (uncorrected). This was taken up in benzene and passed through a 1.5 x 2.5 cm. dry-packed column of Woelm Adlumina, activity grade I, using benzene as eluant. The residue from evaporation of the eluate was subjected to four more recrystallizations from benzene-petroleum ether (b. p. 65-69°) to obtain 0.3 g. (60%) of colorless product which melted at 203.7-204.3° with sublimation.
Anal. Calcd. for C_{21}H_{11}ClN_{2}: C, 77.18; H, 3.39.
Found: C, 77.06; H, 3.30.

3,6-Dicyano-9-phenylfluorene.—It was found that the rate of hydrolysis of the cyano groups was equal to or greater than the rate of reduction of 3,6-dicyano-9-phenyl-9-fluorenol in formic acid-sodium formate. All attempts to convert 3,6-dibromo-9-phenylfluorene to the desired 3,6-dicyano-9-phenylfluorene with cuprous cyanide gave only gums and tars. The compound was therefore obtained by reducing 3,6-dicyano-9-phenyl-9-chlorofluorene.

A solution of 1.0 g. of 3,6-dicyano-9-phenyl-9-chlorofluorene in 25 ml. of acetic acid was treated with 2.0 g. of zinc dust. The mixture was boiled and stirred vigorously for 8 minutes. The unreacted zinc was filtered from the warm solution and the filtrate poured into cold water. The voluminous white solid which resulted was collected and dried. After five recrystallizations from benzene-petroleum ether (b. p. 65-69°) there was obtained a mixture of two crystal forms, one melting at 219-220° and the other at 230-233°. Four further recrystallizations from chloroform-petroleum ether (b. p. 65-69°) did not effect a separation. Another recrystallization from chloroform-petroleum ether (b.p. 65-69°) was conducted in such a manner that only one crystal modification, fans of centimeter-long white needles appeared to form. However, these melted at 218.7-232.7°, with darkening.
The mother liquor, which contained the greater part of the reaction product, was concentrated and allowed to crystallize. The solid was collected and once again crystallized from chloroform-petroleum ether (b. p. 65-69°) to give 670 mg. (75%) of white plates sintering at 218.3°, and melting at 223.5-233.5°, with darkening. Infrared spectra of both fractions were identical. The fraction melting at 223.5-233.5° was dissolved in chloroform and passed through a Celite filter pad. Addition of petroleum ether (b. p. 35-55°) gave fine, white plates, melting at 218-225°.

**Anal.** Calcd. for C_{21}H_{12}N_2: C, 86.28; H, 4.14.
Found: C, 86.13; H, 4.34.

**General Synthetic Technique for the Aryl Carbinols**

Four carbinols, p-anisyl diphenylcarbinol, di-p-tolyl diphenylcarbinol, p-tolyl diphenylcarbinol, and p-tolyl-p-anisylcarbinol, were made via the Grignard reaction using readily available starting materials. In each case the carbonyl compound was dissolved in about ten ml. of dry benzene. To this solution was added quite rapidly a 10 to 30% excess of an ether solution of the Grignard reagent. A deep red color developed and usually vanished within 30 seconds. Water (10 ml.) was added to the reaction mixture about two minutes after the addition of the Grignard reagent. This was followed by enough concentrated hydrochloric acid to make the solution acid to litmus. The organic phase was
separated and the aqueous phase was washed three times with 10 ml. portions of ether. The combined ethereal solutions were dried over magnesium sulfate and evaporated to a viscous oil under a stream of air. Details regarding the individual carbinols prepared are given below.

**p-Anisyl diphenylcarbinyl chloride.**—From 200 mg. of p-anisyl phenyl ketone and 2 ml. of 0.7 M phenylmagnesium bromide in ether was obtained a light yellow oil which resited all attempts at crystallization. It was dissolved in 5 ml. of benzene and a slow stream of dry hydrogen chloride was passed through the solution at room temperature for 5 minutes. The resulting light yellow solution was frozen in a Dry Ice-acetone bath which caused it to turn dark red. The flask containing the frozen solution was allowed to warm slowly to room temperature under vacuum (5 mm.) to remove the benzene. The solid yellow residue was recrystallized twice from petroleum ether (b. p. 35-55°) giving 130 mg. (45%) of light yellow granules which melted at 119.0-122.0° (lit. 70 m. p. 122-123°).

(70) A. Baeyer and V. Villiger, Ber., 36, 2789 (1903).

**Di-p-tolylphenylcarbinol.**—From 1.6 g. of p-tolyl phenyl ketone and 25 ml. of 0.4 M p-tolylmagnesium bromide in ether was obtained a light yellow oil which slowly solidified upon cooling in ice. This material was
recrystallized twice from petroleum ether (b.p. 35-55°)
giving 590 mg. (42%) of colorless granules melting at
75.5-76.4° (lit. 71 m. p. 76.5-77.5°)

(71) A. Kliegl, Ber., 38, 86 (1905).

p-Tolylidiphenylcarbinol.— From 1.1 g. of p-tolyl
phenyl ketone and 10 ml. of 0.7 M phenylmagnesium bromide
in ether was obtained a slightly yellow-green oil which
crystallized at room temperature. Two recrystallizations
from petroleum ether (b. p. 35-55°) gave 920 mg. (60%) of
colorless granules melting at 70.8-72.8° (lit. 72 m.p. 73-74°).

(72) A. Bistrzycki and J. Gyr, Ber., 37, 663 (1904).

p-Tolyl-p-anisylcarbinol.— From one ml. of
p-anisaldehyde and 25 ml. of 0.4 M p-tolylmagnesium bromide
in ether was obtained a light tan oil which yielded by
crystallization from benzene-petroleum ether (b.p. 65-69°)
610 mg. (32%) of small white needles melting at 59.5-60.5°
(lit. 73 m. p. 61-62°).

(73) M. P. Balfe, E. A. W. Downes, A. A. Evans, J.
Kenyon, R. Popett, C. G. Searle, and A. L. Tarnoky, J.

p-Tolylphenylcarbinol.— This compound was prepared
by reducing 1.96 g. of p-tolyl phenyl ketone in 25 ml. of
95% ethanol with 1.89 g. of sodium borohydride, added slowly
over a 10 minute period. The reaction solution was acidified
with 20 ml. of 1 M hydrochloric acid and the majority of the ethanol removed by directing a stream of air over the liquid surface. The residue was then extracted four times with 20 ml.-portions of ether. The ether extracts were dried over magnesium sulfate and evaporated to obtain a light yellow oil. This was taken up in 10 ml. of petroleum ether (b. p. 35-55°). Upon cooling, a white gel formed which persisted at room temperature. The solvent was allowed to evaporate slowly and long white needles formed. This material was dissolved in petroleum ether (b. p. 65-69°) and cooled in ice. The gel which slowly formed was seeded with the crystalline product and allowed to stand at room temperature for four hours. During this time long, silky, white needles grew down from the surface of the gel and eventually there resulted a clear, fluid mother liquor and 1 gm. (50%) of a beautifully crystalline product, melting at 52.8-54.8° (lit. 74 m. p. 52-53°).

(74) E. Fischer and O. Fischer, Ann., 194, 265 (1878).

Triphenylcarbinol.—A commercial sample melting at 159.8-161.0° (lit. 75 m. p. 159°) was used.

Diphenylcarbinol.—Eastman Kodak diphenylcarbinol, m. p. 66.2-67.2° (lit.76 m. p. 67.5-68°) was employed.

(76) E. Linnemann, Ann., 133, 9 (1865).

pK_R© Determinations

A Beckman Model DU Spectrophotometer, equipped with thermospacers supplied with water at 24°C., was used. The solutions of sulfuric acid, acetic acid, and water were made up, by weight, in glass-stoppered flasks from 99.9% sulfuric acid (concentration determined by titration), made by adding duPont Reagent Grade 30% fuming sulfuric acid to duPont Reagent Grade concentrated sulfuric acid in order to give the desired concentration. The diluent, 80% aqueous acetic acid, was distilled water (80.0 g. acetic acid and 20.0 g. water). Each sulfuric acid solution, at 25°C., was used to dilute 2.00 ml. of an acetic acid solution77 of the

(77) Eighty per cent aqueous acetic acid was used for solutions for those indicators requiring sulfuric acid concentrations greater than 67%, since the use of glacial acetic acid would have made a significant change in the water - acetic acid ratio in the final solution.

appropriate indicator to volume in a 50-ml. volumetric flask. Because some of the indicator solutions showed a slow decrease in optical density with time, the optical density of each solution was measured within five minutes of its being made up, whenever this precaution was required.
Tritium Exchange

Sodium triphenylmethyl.—The procedure of W. B. Renfrow and C. R. Hauser was used to prepare a solution of sodium triphenylmethyl in ether. The starting materials were 240 ml. of ether, 1.8 g. of sodium metal, 183 g. of distilled mercury, and 10 g. of triphenylmethyl chloride which had been freshly recrystallized from a mixture of 2.3 g. of acetyl chloride and 16.7 g. of petroleum ether (b. p. 65-69°). The sodium triphenylmethyl solution was found to be 0.1 M by titration with standardized hydrochloric acid. After standardization, the solution was kept under an atmosphere of dry methane, and samples were withdrawn through a serum bottle cap seal by means of a hypodermic syringe and needle. A small stainless steel petcock between the syringe and the needle greatly facilitated transfer of the ether solution with minimum loss.

General tritiation procedure.—Two hundred mg. of the 3,6-disubstituted 9-phenylfluorene was dissolved in five ml. of dry ether in a 25-ml. Erlenmeyer flask closed by a serum bottle cap. Two ml. of ether containing tritium oxide was added to the solution followed by four ml. of 0.1 M ethereal sodium triphenylmethyl solution. The flask was swirled to thoroughly mix the solutions and allowed to
stand at least 30 minutes before being opened. Water-
saturated nitrogen was then blown slowly across the surface
of the ether solution until the solvent was entirely
removed. The remaining crust was thoroughly triturated with
1 M hydrochloric acid, collected by filtration, washed with
water, and vacuum dried. Final purification procedures for
each compound are outlined below.

3,6-Dimethoxy-9-phenylfluorene-9-T.—The general
tritiation procedure described above produces a yellow
crude product which was dissolved in five ml. of benzene
and passed through a Celite filter pad to remove a small
amount of insoluble material. The benzene was removed and
the product recrystallized two times from 10 ml. of
petroleum ether (b. p. 65-69°) to give 100 mg. of white
needles, melting at 147.7-148.8°. The measured radio-
activity was 16400 counts/minute/mg.

3,6-Dimethyl-9-phenylfluorene-9-T.—The general
tritiation procedure starting with 247 mg. of pure
3,6-dimethyl-9-phenylfluorene produced a yellow crust of
crude product which was decolorized in benzene solution by
passing it slowly through a 5 x 10 mm. column of a 5:1
Celite-activated charcoal mixture. One recrystallization
from 5 ml. of petroleum ether (b. p. 65-69°) produced
150 mg. of white needles, m. p. 132.0-133.4°, having a
measured radioactivity of 16000 counts/minute/mg.
9-Phenylfluorene-9-T.— The almost colorless crust of crude product from the general tritiation procedure was recrystallized once from 5 ml. of petroleum ether (b. p. 65-69°) to give 100 mg. of long white needles, m. p. 145.6-147.1°, having a measured radioactivity of 455000 counts/minute/mg.

3,6-Dibromo-9-phenylfluorene-9-T.— The yellow crust of crude product given by the general tritiation procedure was dissolved in five ml. of benzene and decolorized by passing it through a 1 x 2.5 cm. column of a 5:1 Celite - activated charcoal mixture, and then through a 1 x 5 cm. dry-packed column of Fisher activated alumina. After removing the benzene and recrystallizing the residual solid three times from five ml. of petroleum ether (b. p. 35-55°) there was obtained 98 mg. of white needles, m. p. 144.6-146.0°, having a measured radioactivity of 67500 counts/minute/mg.

3,6-Dicyano-9-Phenylfluorene-9-T.— Because of the relatively acid proton in this molecule sodium triphenylmethyl was not required to effect the exchange reaction. A solution of 100 mg. of 3,6-dicyano-9-phenylfluorene in two ml. of benzene and two ml. of tritium oxide-enriched ether was treated with one drop of a 10% solution of potassium hydroxide in ethanol. A deep orange color developed at once and an orange solid settled to the bottom.
Nitrogen which had been bubbled through 6 M hydrochloric acid was blown gently across the surface of the solution to remove the solvent. The orange residue was ground under this nitrogen, water vapor, and hydrochloric acid atmosphere until the color was completely discharged. It was dissolved in two ml. of hot chloroform and filtered through a Celite pad to remove the finely divided insoluble solid salts. The chloroform solution was evaporated to one ml. and rapidly diluted with 15 ml. of hot petroleum ether (b. p. 35-55°). The fine tan crystals formed were collected, washed two times with one ml. of petroleum ether (b. p. 35-55°) and vacuum dried. This procedure gave 50 mg. of a product which melted at 217-219° and had a measured radioactivity of 17000 counts/minute/mg.

Ethanolic sodium hydroxide solution.—This was made up to a constant ionic strength of 0.1 M by dissolving solid sodium hydroxide in ethanolic sodium perchlorate solutions of the appropriate concentration. The basic solution was allowed to stand in a closed Erlenmeyer flask for 24 hours during which time a small quantity of white powder collected on the bottom, and the solution became crystal clear. The supernatant liquid was standardized against standard hydrochloric acid using phenolphthalein as indicator. From three determinations a precision of one part per thousand was commonly obtained. The standardized solutions were
stored in the refrigerator when not in use. For volumetric dilutions they were slowly brought to 25°C. so as not to disturb the sediment on the bottom of the flask.

**Ammonia buffer.**—For the determination of the rate of exchange of 3,6-dicyano-9-phenylfluorene-9-T a buffer solution of ammonium perchlorate and ammonia in 95% ethanol was required, since the reaction proceeded at a very rapid rate even in almost neutral solutions. (Ionic strength of the buffer was maintained at 0.10 M by the use of sodium perchlorate.) The buffer solution was made by dissolving weighed amounts of ammonium perchlorate and sodium perchlorate in 95% ethanol in a volumetric flask and adding the required volume of a standardized solution of ammonia in 95% ethanol. The ammonium perchlorate-ammonia solution was diluted to volume with 95% ethanol. The ammonia in 95% ethanol was prepared by adding enough concentrated aqueous ammonia to absolute ethanol to bring the water concentration to 5%. The ammonia concentration was determined by the Winkler method.79

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**Kinetic method.**—Reactions at 20° and 40°C. were conducted in 3 x 20 cm. test tubes almost completely immersed in a stirred water bath. The temperature of the
bath was controlled by an electric immersion heater that was regulated by a Sargent Mercurial Thermoregulator and a Sargent Laboratory Relay. To obtain the lower temperature a copper cooling coil was used. The temperature was controlled to $\pm 0.02^\circ C$. and read directly from a 0-100$^\circ$C. Central Scientific Company precision thermometer that was graduated in tenths of a degree.

In conducting the reactions at 0$^\circ$C. the test tubes, containing the reacting solutions, were almost completely immersed in a firmly packed mixture of cracked ice and water contained in a large Dewar flask. In each run, before the first point was taken, the reaction solution and the air space above it were thoroughly flushed with methane which had been passed through 20% sodium hydroxide in water, concentrated sulfuric acid, a Dry-Ice and acetone cooled trap, and finally through grain alcohol. During the course of the run the test tubes were kept tightly stoppered and under a slight positive pressure of methane. Whenever opened for sampling they were continuously flushed with methane.

All kinetic runs were made in duplicate. The rate constants are the averages of at least two determinations. For a typical run between 10 and 15 mg. of the radioactive substrate was carefully placed in the bottom of a large test tube. This was completely dissolved in 1.0 ml. of
dioxane. The dioxane used was purified by being passed slowly through one-third its weight of Fisher activated alumina. Then, the tube was clamped in place in the constant temperature bath, and 50.0 ml. of standardized ethanolic (95%) sodium hydroxide solution was added. When the exchange reaction was rapid this standard solution was chilled in an ice bath before adding. After thoroughly mixing the reactants, the solution was allowed to equilibrate with the temperature bath for 10 to 25 minutes before the first sample was taken. The time depended on the temperature of the ethanol solution before it was added.

For each point in a kinetic run a 5.0 ml. aliquot was removed from the reaction solution and delivered by blowing out the pipette into a 25 ml. Erlenmeyer flask which contained 1.0 ml. of 1 M sulfuric acid solution. The sampling and quenching required an average of 35 seconds. The contents of the flask were swirled thoroughly and allowed to stand for several hours in order that the tritium in the ethanol be allowed to reach a constant partition between the ethanol and the water in the sulfuric acid. Then, each flask was packed three-quarters full of glass wool and attached to a vacuum distilling apparatus. A 15 x 125 mm. "Pyrex" test tube, chilled in Dry-Ice and acetone, was used as a receiver. The apparatus was evacuated to 5 mm. Hg pressure, or less, and a cup of warm water was used to warm the Erlenmeyer flask. After about two
minutes when the receiver contained about three ml. of distillate, the distillation was halted by admitting dry methane to the system. Each receiver was closed with aluminum foil and set aside to return to room temperature. Then each was swirled and a 2.0-ml. aliquot was added to 15 ml. of aqueous scintillator solution in a clear glass cylindrical bottle (25 x 85 mm.) with a polyethylene stopper. The sample bottles were placed in the refrigerated dark box of the scintillation counter for at least one hour before being counted.

To determine the count rate at infinite reaction time a 2.0-ml. aliquot of the reaction solution was delivered directly into a cylindrical sample bottle and diluted with 15 ml. of scintillator solution and counted. For each kinetic point a 5.0 ml. aliquot of reaction solution was combined with 1.0 ml. of acid quench solution, and 2.0 ml. of this was actually counted. Therefore, to determine the infinite time count rate corresponding to the kinetic point

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(80) Aqueous scintillator solution:
- 770 ml. of toluene, Baker Reagent Grade
- 230 ml. of absolute ethanol
- 4 g. of 2,5-diphenyloxazole (Aldrich Chemical Company)
- 5 mg. of 1,4-bis-(2-(5-phenoxazolyl))-benzene (Aldrich Chemical Company)

(81) Tracerlab, Inc., Liquid Scintillation Counter, Model CE-1B, modified to use E. M. I. photomultiplier tubes.
count rates, the observed count rate for the infinite time sample was multiplied by 5/6. The accuracy of this method for determining count rate at infinite reaction time was checked by delivering a 5.0 ml. aliquot of reaction solution into a 25 ml. Erlenmeyer flask containing 1.0 ml. of 2 M sodium hydroxide in ethanol and allowing the system to stand at room temperature for several hours. This insured better than 99% approach to complete exchange into the solvent. The mixture was then distilled as described above for an ordinary kinetic point and the count rate was compared with that determined as just outlined. The two count rates differed by 0.9%.

A typical run gave the following data.
TABLE 9
DETERMINATION OF TRITIUM EXCHANGE RATE

Run No. 43
9-Phenylfluorene
(0.050 M NaOH and 0.05 M NaClO₄ in 95% ethanol)
T=0°C.

<table>
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<tr>
<th>Point</th>
<th>Time (min.)</th>
<th>C₁ᵃ</th>
<th>Cᵇ = C¹-B</th>
<th>C₀ - C</th>
<th>log (C₀ - C)</th>
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<tr>
<td>1</td>
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<td>152</td>
<td>15231</td>
<td>74385</td>
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<td>43799</td>
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<td>60265</td>
<td>17351</td>
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<td>corrected</td>
<td>93291</td>
<td>93139</td>
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<td></td>
</tr>
</tbody>
</table>

ᵃUncorrected count in counts per minute. ᵇ Count rate corrected for background. ᶜ Background count rate.

From the graph on the following page the pseudo first order rate constant is calculated to be

\[ k = \frac{(4.874 - 4.100) \times 2.303}{60 \times 2400} = 1.24 \times 10^{-5} \text{ sec}^{-1}. \]
Graph IX

Run Number 43

log (Ce - C) vs. Time, minutes
AUTOBIOGRAPHY

I, Charles Allison Stout, was born in Beaumont, Texas, on September 20, 1930. I went to grade school in the public schools of Beaumont and received my undergraduate training at The Rice Institute, which granted me the Bachelor of Arts degree in chemistry in 1952. In 1953 I received the Master of Arts degree in chemistry from The Rice Institute. I entered the graduate school of The Ohio State University in 1956. While in residence there I was an assistant in chemistry for two years and also received the Sinclair Oil Company Fellowship in chemistry and the Monsanto Fellowship in chemistry.