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May 12 1949

I hereby recommend that the thesis prepared under my supervision by John H. Weisburger

entitled The Stereochemistry of Fluorene

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Francis E Ray

Ralph E Oesper

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THE STEREOCHEMISTRY OF FLUORENE

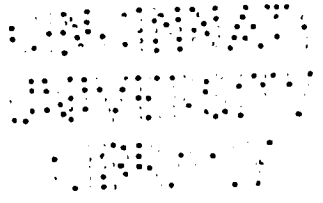
A dissertation submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1949

by

John H. Weisburger
A.B. University of Cincinnati 1947
M.S. University of Cincinnati 1948



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ACKNOWLEDGMENTS

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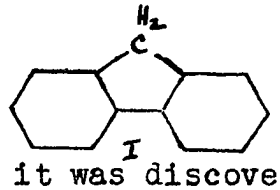
Part I

INTRODUCTION

A. Discovery of Fluorene

Fluorene, I, is a polynuclear hydrocarbon, m.p.113°C,

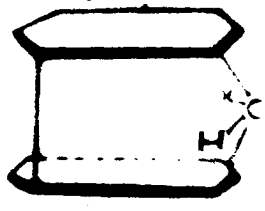


I

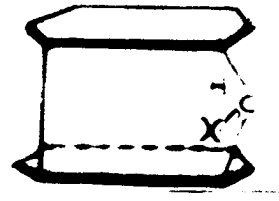
known since 1867 when it was discovered in coal tar by Berthelot (1). Its structure was shown to be that indicated in formula I by syntheses from diphenylene ketone (2), and from diphenylmethane (3).

B. Stereoisomerism of Fluorene

According to classical theory the rings in polynuclear hydrocarbons are coplanar. However in the case of fluorene repeated claims were made that it had a folded structure with the six-membered rings inclined to the plane of the five-membered ring. A 9-substituted molecule could thus exist in two forms, depending on whether the substituent is cis (II), or trans (III) to the inclined six-membered rings.



II



III

In the past a number of such 9-substituted isomers have been reported (4). However none of these claims has

withstood the test of a thorough investigation. In each case it was shown that the purported isomers really were not isomers but different substances. A detailed discussion of these claims has been given by Weisburger (5).

C. Stereochemistry of Fluorene

The failure to isolate isomers of 9-substituted fluorenes does not alone prove that fluorene possesses a planar structure. Indeed even such classical stereoisomers as the 9,2-substituted fluorenes, possessing an asymmetric carbon atom at the 9-position had not been resolved until recently (6). This fact aroused the suspicion of many previous workers that the spatial configuration of fluorene had to be a special one, endowed with unusual properties. Ray and Kreiser's work therefore placed fluorene within the scope of normal, expected behavior. The problem of whether the structure of fluorene is planar or folded can now be re-examined.

1. Physical evidence -

a. X-Ray studies: The data obtained from such work have been interpreted differently by various investigators.

Crystal lattice studies by Hengstenberg and Mark (7) led these authors to propose a structure in which the six-membered rings were puckered (as in the accepted models for cyclohexane "boat" and "chair" forms). Bergmann and Mark (8) explained the Schlenk and Bergmann isomers on the basis of this puckered structure.

However, the six-membered rings are aromatic rings,

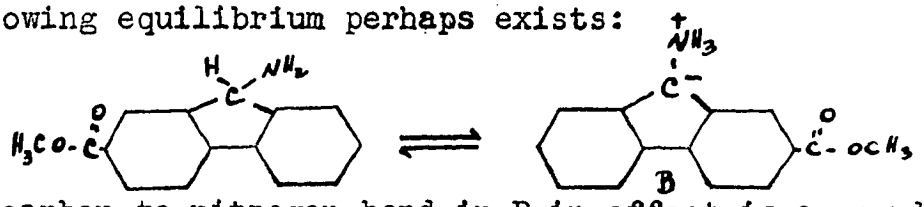
hence they must lie in one plane. The puckered structure is therefore not acceptable. Stuart (9) reinterpreted Hengstenberg and Mark's data as evidence for the planar configuration.

Sundarajan (10) deduced a planar structure for fluorene from his optical studies. Data on magnetic anisotropy led Krishnan and Banerjee (11) to an identical conclusion.

Cook and Iball (12) interpreted the data reported above, together with Iball's (13) X-ray data on solid fluorene as evidence for a non-planar structure, in which the planes of the six-membered rings were inclined at 20° to the plane of the five-membered ring and at 40° to each other. They suggested that the molecule may possess sufficient elasticity to undergo oscillation between two non-planar forms, thus preventing the isolation of isomers. In view of the resolution of 9,2-substituted fluorenes by Ray and Kreiser-Weisburger (6), Cook and Iball's structures appear to be more doubtful. Indeed, if the folded model be substituted at the 9 and 2 positions, cis and trans forms of each optical isomer should exist. Ray and Kreiser-Weisburger did not detect any such isomers, although they kept the possibility of their existence in mind. If, as Cook and Iball suggested,there be an oscillation between the two folded forms, the optically active compounds should racemize easily. This seems to be verified by the fact that 2,9-diaminofluorene could not be resolved by Bennett and Noyes (14). Also, Ray and Kreiser-Weisburger (6) reported the rapid racemization of 9-amino-2-carbomethoxyfluorene which occured during attempted

crystallizations. However, a recent check on the activity of a sample of d-9-hydroxyfluorene-2-carboxylic acid, resolved in 1945, shows undiminished activity after three years (15). Hence it is apparent that in this case no oscillation between two folded models, with the ensuing racemization, could have taken place.

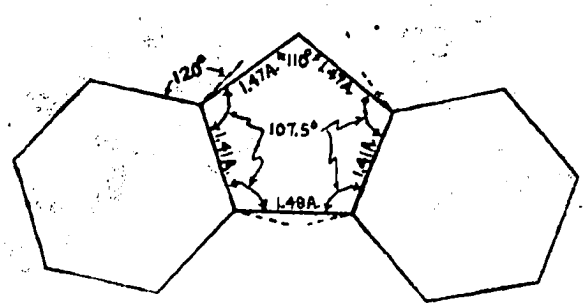
It is suggested that the ease of racemization of certain 9-substituted fluorenes is not caused by oscillation between two spatial structures. The following explanation is proposed: The acidity of fluorene due to the ease of removal of a proton from the 9-position is well known. If one of the valences of the 9 carbon atom is linked to an amino group, the tendency for a proton to be removed is still greater and the following equilibrium perhaps exists:



B

The carbon to nitrogen bond in B in effect is a coordinate covalent bond which even if it does not quite remove the asymmetry at the 9 position of a substituted fluorene, renders the molecule quite unstable. Hence racemization occurs. The tendency for a hydroxy group to accept a proton is very much smaller than for the amino group. Therefore the 9-hydroxy derivatives do not racemize. It is to be pointed out also that alkali will facilitate the removal of a proton from the 9 position, whereas acid would have just the opposite effect. The tartrate salt of the aminofluorene derivative was decom-

posed with sodium hydroxide, which might conceivably contaminate in catalytic amounts the free resolved base, thus accelerating the racemization. On the other hand, the strychnine salt of the hydroxyfluorene derivative was decomposed by acid, which would stabilize the resolved compound by decreasing the ionization of fluorene.



Pinck and Hilbert (16) favor the planar model IV on the basis of X-ray and electron diffraction data obtained by Robertson and Hendricks (17). Pinck and Hilbert suggested that considerable strain should exist in such a structure due to a distorsion of valence angles in the five-membered ring. This will be discussed in detail in the section on bond angles.

b. Measurements of dipole moments: Bergmann, Engel and Hoffmann (18) favored a planar structure on the basis of measurements of dipole moments of fluorene derivatives in inert solvents.

In their first paper, Hughes, Le Fevre and Le Fevre (19) were led to suggest a planar model on the basis of dipole moments of fluorene compounds. The authors noted, however,

that their results did not necessarily contradict those of Cook and Iball, since their own measurements were carried out in solution, while Cook and Iball's results were based on solid forms. This would imply that in the solid state the fluorene molecule is held in a non-planar configuration due to the rigidity of the crystal lattice. This idea does not seem very likely, since in general the crystal lattice forming slowly in a saturated solution will adapt itself to the contours of the molecule, without forcing the molecule into another configuration. If the molecule is planar in solution, it should be so in the solid state. In a subsequent investigation, these authors were (20) unable to obtain evidence for one specific configuration. Probably Hughes and his collaborators neglected to take into consideration the polar character of fluorene itself. This would appear in the calculated value of the dipole moment. Hence their experimental value could not check the theoretical since the latter was based on the wrong picture of the molecule.

Recently the dipole moment of the fluorene was measured in dioxane and in benzene solution (21). It was found that fluorene possessed a definite dipole moment, which the authors attribute to the considerable contribution made to the normal state of the molecule by charged, ionic structures (see: Discussion, Resonance). The moment in dioxane was higher than in benzene due to hydrogen bonding in the former solvent. The authors seem to imply that fluorene is planar, an opinion which is apparently shared by Bergmann (22).

It is evident, however, that even if the molecule is assumed to be planar, such a condition represents the average position of the elementary particles composing the molecule. Due to the vibrational, rotational or electronic energy, there might be deviations from the planar equilibrium position. Such deviations are normally small. Perhaps it would be best to state that only at the absolute zero of temperature is the fluorene molecule strictly planar.

2. Chemical evidence -

If the planar strained model proposed by Pinck and Hilbert (16) is assumed to represent the structure of fluorene, the strain should be evident in the chemical properties of fluorene compounds. The folded model of Cook and Iball (12) should be perfectly strainless.

There seems to be evidence for both structures in the chemical reactions of fluorene derivatives. 9-Methyl-9-chloroaminofluorene expands when treated with sodium methylate to 9-methylphenanthridone. Phenanthrenequinone, when treated with alkali contracts to 9-hydroxyfluorene-9-carboxylic acid. Other examples are given by Weisburger (5).

In summary, the resolution of some 9,2-substituted fluorenes shows that classical stereochemical methods can be employed in the investigation of fluorene. There exists negative stereochemical evidence for the planar configuration since no isomers of 9-substituted fluorenes were obtained. Physical methods give no clue as to the structure of fluorene, although

the planar configuration appears to be favored by recent measurements of dipole moments. The chemical evidence points both ways and so far is of no avail.

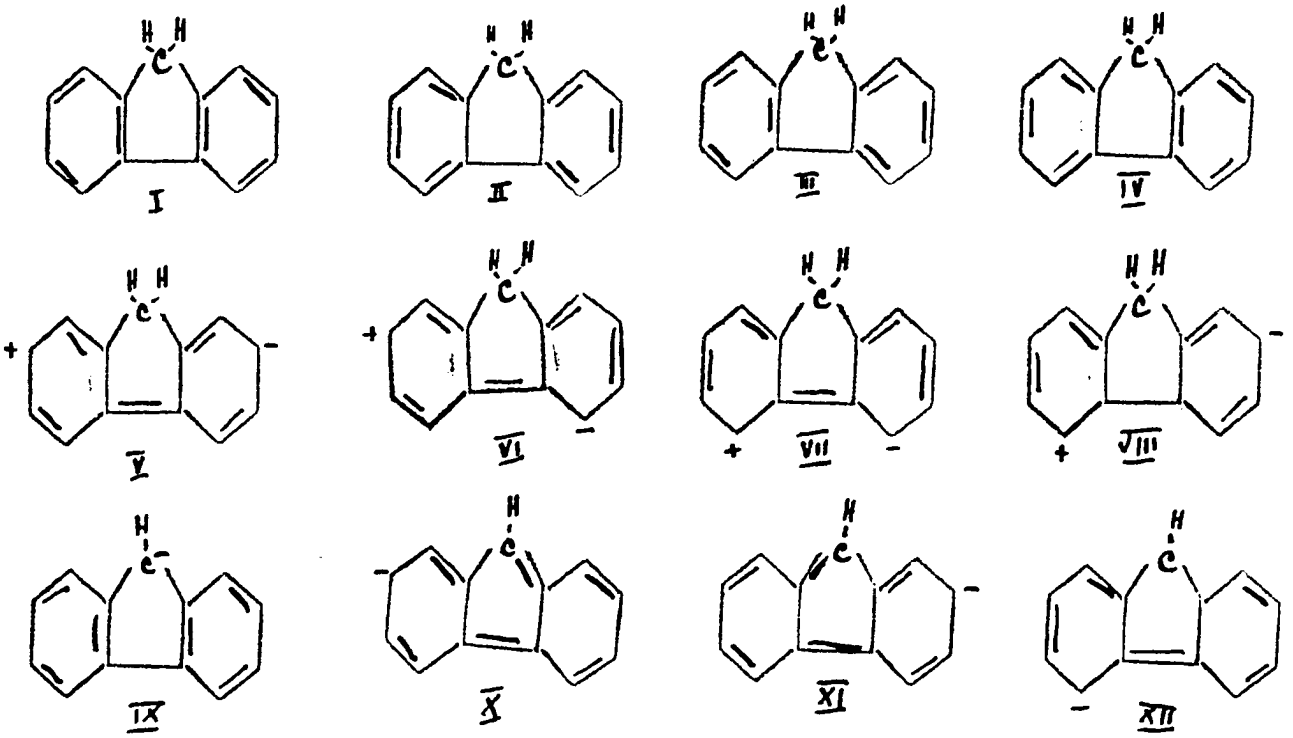
Part II

PROCEDURE AND DISCUSSION

A. Theoretical Approach

An evaluation of the available data dealing with fluorene in the light of modern theoretical chemistry might conceivably shed some new light on the spatial configuration of this hydrocarbon.

Considering resonance as applied to fluorene the following structures, among others, may be postulated if fluorene possesses a planar configuration. In a folded molecule only the Kekule' resonance in the two benzene rings is possible. (I to IV)



Evidence for such structures may be sought in substitution reactions, bond lengths, bond angles, dipole moments (see introduction), resonance energy and the absorption spectra of fluorene and its derivatives.

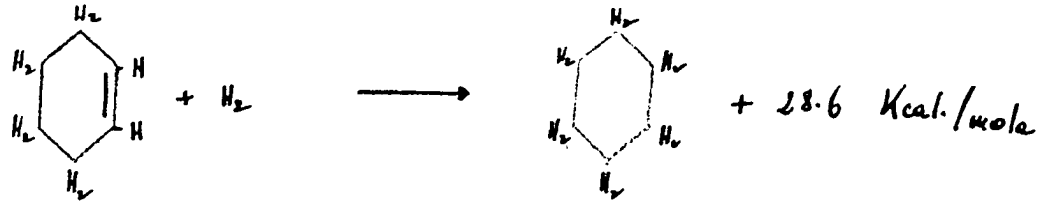
1. Substitution reactions -

a. It is well known that fluorene monosubstitutes in the 2 position. Structures V and VIII would confirm this behavior. At the same time structures VI or VII would indicate that a small amount of 5-monosubstituted fluorene could be formed. While this has not yet been observed experimentally, fluorene dinitrates in the 2,5 as well as in the 2,7 positions.

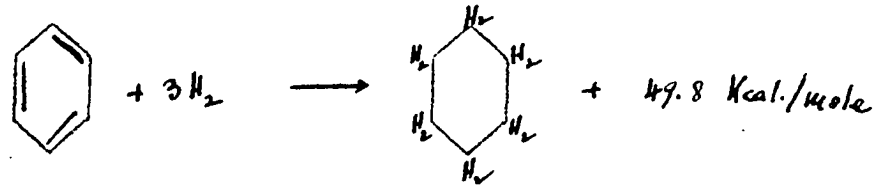
b. Fluorene possesses an acid character, forming a 9-potassium salt. This would be indicated by the stability of the ions (IX-XII) and their various resonance forms (23).

2. Resonance energy -

Resonance results in an increased stability, or a decreased energy for any molecule in which it occurs. Resonance can occur only in a planar system (24). The resonance energy is a measure of the amount of resonance in a molecule. It is defined as the quantity obtained by subtracting the actual energy of a molecule from that of the most stable contributing structure. Experimentally the resonance energy is calculated from the heats of hydrogenation or combustion. For example, the heat of hydrogenation of cyclohexene is 28.6 Kcal/mole:



Benzene, having three double bonds, should have a heat of hydrogenation three times as large as that of cyclohexene, i.e. 3 X 28.6 or 85.8 Kcal/mole. The experimentally determined heat of hydrogenation is 49.8 Kcal/mole. This value is sensibly

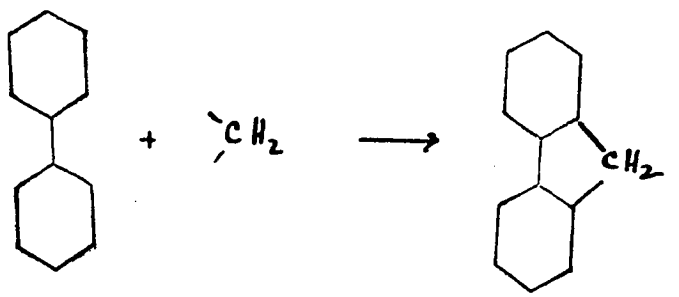


lower than that calculated. This difference, 38 Kcal/mole is considered to be the resonance energy. Similarly, the experimental heat of combustion of benzene is 788 Kcal/mole; the calculated value is 829 Kcal/mole. Again the difference or 41 Kcal/mole represents the resonance energy. Naturally, all values so obtained are approximate, since they are the differences of large numbers, which are not always known with great precision.

Fluorene has a resonance energy of 101 Kcal/mole, biphenyl one of 91 Kcal/mole, diphenylmethane 93 Kcal/mole and benzene 41 Kcal/mole (24). The rather high resonance energy of fluorene is quite striking. Indeed, if the hydrocarbon were folded, the only possible resonance would be in the two benzene rings. Under those conditions the resonance energy could only amount to twice the value (82 Kcal/mole) in a single benzene ring. The excess of 19 Kcal/mole must be attributed to interaction of the benzene rings and the methylene group. For this interaction to be at all possible the entire system must be planar.

This conclusion is supported by a breakdown of the

resonance energies of diphenylmethane and biphenyl as follows: The resonance energy of diphenylmethane can be assumed to be due primarily to the Kekule structures in the two benzene rings (82 Kcal/mole). The balance (93-82 Kcal/mole or 11 Kcal/mole) must be attributed to interaction of the benzene rings with the $-CH_2-$ grouping. Identically the resonance energy of biphenyl (91 Kcal) can be divided into two component parts: 82 Kcal for the two benzene Kekule structures and the remaining 9 Kcal must be contributed by the interaction of the two benzene rings. With these data on hand the resonance energy of fluorene appears closely related to that of biphenyl and diphenylmethane. Indeed if the resonance energy of biphenyl is added to that of the $-CH_2-$ component of diphenylmethane, the sum is strikingly close to that of fluorene.



Resonance energies: 91 + 11 ⟶ 102 (found: 101) Kcal./mole

Biphenyl has been shown to be planar (25)(26). The addition of a $-CH_2-$ to biphenyl has increased the resonance energy, therefore the resulting compound, fluorene, ought to be planar also. The increased resonance energy may be attributed to the stabilization of the molecule by formation of a new ring in which resonance can take place. If fluorene were folded a considerable decrease in resonance energy would be expected.

3. Bond Length -

Further information can be obtained from a consideration of bond lengths. The bond lengths between atoms give an indication of the per cent double bond character of these bonds (27). A carbon-carbon single bond (100%) as in ethane is 1.54 Å long, while a carbon to carbon double bond (100 %) as in ethene was shown to be 1.33 Å. A partial double bond will have an intermediate length.

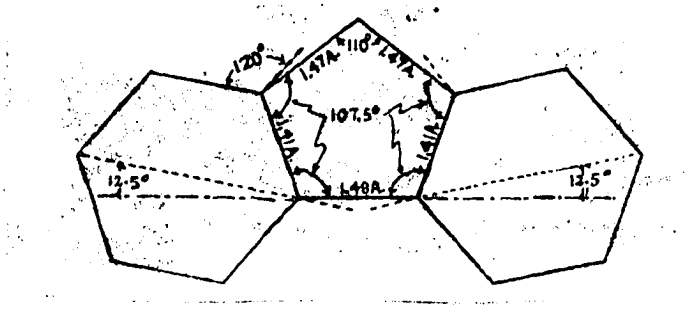
The fluorene model (IV), page 5, may be accepted as embodying the best structural data available presently. From the bond length the average double bond character of the bonds can be calculated. Thus in fluorene the average double bond character of the bonds in the benzene rings is 38 % (1.41 Å), that of the bond joining the benzene nuclei, 12.5 % (1.48 Å) (as in biphenyl), and that of the bonds between the 9 carbon atom and the benzene rings, 15 % (1.47 Å). Further evidence for the partial double bond character of the last cited bond arises from dipole measurements of 9-chlorofluorene by Bergmann, Engel and Hoffmann (18). The dipole moment indicated that the C-Cl bond was more aromatic than aliphatic.

Hence these bond lengths provide considerable evidence for some of the resonance structures of fluorene, postulated previously, in which double bonds are located in the five-membered ring. These necessarily require planarity.

4. Bond Angles -

Pinck and Hilbert stated that their planar model for

fluorene was endowed with considerable strain since the normal benzenoid valence angles were distorted 12-13°.



However, the following line of reasoning from Gilman's "Organic Chemistry" (28) seems to modify Pinck and Hilbert's strain theory for fluorene somewhat.

"According to the van 't Hoff model, the free bonds in the system $>C = C<$ of an aliphatic compound lie in a plane and the angle α between each pair of single bonds is the same as that between the carbon valences of methane (109.5°). The angle β which the single bonds make with the plane of the double bond is then $\frac{1}{2}(360-109.5^{\circ}) = 125.25^{\circ}$ (see fig.2a).

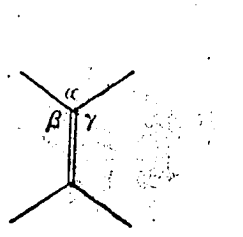


Fig. 2a

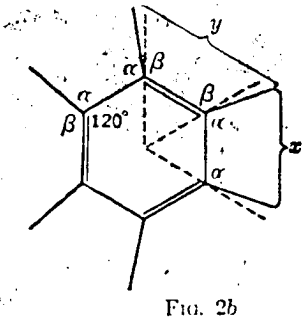


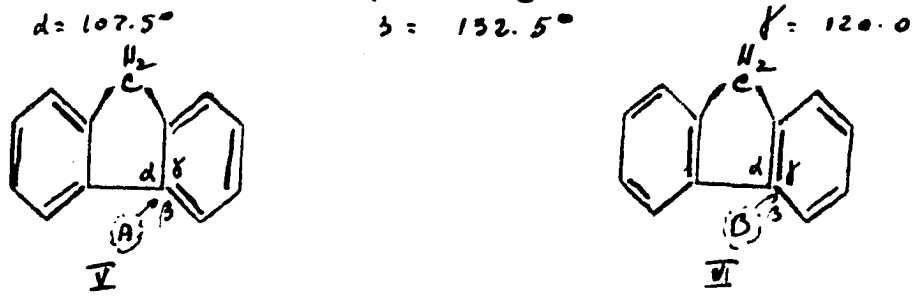
Fig. 2b

The angles β and γ are in this case identical and they are considerably greater than the angle α. When the double bond becomes incorporated into a Kekule' ring (fig.2b) the situation

is altered slightly, for the internal angle γ is reduced from 125.25° to 120° to accomodate ring formation and $\alpha + \beta$ consequently is increased by 5.25°. Whether this increment is considered to increase one or the other external angles, or to be distributed proportionally between them, β will remain appreciably larger than α. The conclusion is reached that the external valences in the Kekule ring are not directed toward the center of the hexagon but are inclined at a greater angle from the double bonds of the ring than from the single bonds."

A five-membered ring can be fused to the Kekule structure with little distorsion of the normal tetrahedral angles if it is attached to <u>ortho</u> carbon atoms joined by a single bond (position x, fig. 2b), for two of the smaller α angles are then incorporated in the new ring. If, however, the attachments were made to doubly bound carbon atoms (y), the new ring including the β angles would be under considerable strain.

According to the best modern data (Pinck and Hilbert's model) for fluorene, the angles are:



If the angles around carbons A and B in structures V and VI are considered in the light of Gilman's development, it is found that β_A equals 125.25° + 5.25° = 130.5° and α_A = 109.5°,

β_B equals 125.25° and α_B = 109.5° + 5.25° = 114.75°. These two structures differ in the location of the double bonds. By comparing the actual angles β = 132.5° and α = 107.5°. with these values, it is seen that V is nearly strainless ($\Delta\alpha = \alpha - \alpha_A = -2°$; $\Delta\beta = \beta - \beta_A = +2°$) whereas VI is highly strained ($\Delta\alpha = \alpha - \alpha_B = -7.25°$; $\Delta\beta = \beta - \beta_B = +12.5°$). When Pinck and Hilbert stated that fluorene was strained, they evidently based their calculations on a model such as VI.

Model V looks quite attractive to the chemist: It is planar and it is very nearly strainless. If the molecule existed in this form, it would imply a fixation of the double bonds as shown in the figure and it would be another example of the Mills-Nixon effect (29). Lothrop (30), Bergmann and Berlin (31) have investigated the possible fixation of bonds by rearrangements of properly substituted 2-and 3-alkyloxy-fluorenes and fluorenones and by coupling of the hydroxy-fluorenes with diazotized anilines. They arrived at the conclusion that the bonds in fluorene were not fixed. This naturally implies that the highly strained model VI in which the bonds are also fixed, does not correspond to the true state of the fluorene molecule. An answer may be found in an intermediate structure, where the actual state of the fluorene molecule lies between these extremes (see Discussion : Resonance). In such a model the bonds would not be fixed, i. e. all bonds would contain some amount of partial double bond character. The angles α and β would be intermediate also.

The resulting fluorene molecule would not be as highly strained as indicated by Pinck and Hilbert, yet it would still retain some strain. The latter is evident in the absorption spectra which will be considered next.

5. Absorption spectra - (32)

When light energy is absorbed by a molecule, one or more of three changes may occur: The electronic structure of the molecule may be altered, the amplitude of vibration of the atoms may be increased, or the frequency of rotation of the molecule may undergo a change.

When the light absorbed by a molecule results in a change in its electronic structure, the molecule is said to be electronically excited; when the light causes a change in the amplitude of vibration of the atoms, the molecule is vibrationally excited; when the absorbed light changes the rate of rotation of the molecule, the molecule is rotationally excited. Generally the absorption of light by a molecule results in simultaneous changes in its electronic, vibrational and rotational states. In an analysis of the spectral absorption data it is necessary to separate the absorbed light into the three components which contribute to the three types of excitation.

Changes in the electronic structures of molecules require relatively large amounts of energy as compared with those necessary to produce vibrational and rotational excitations. The energy necessary for electronic excitation corresponds to light in the ultra-violet or visible region of the

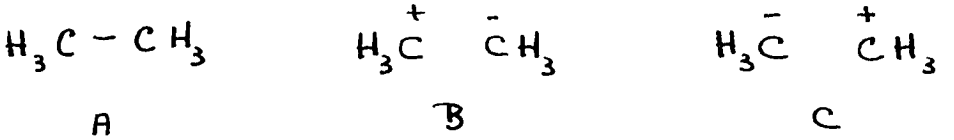
spectrum; that for vibrational excitation, to near infra-red light, and that for rotational excitation, to far infra-red light. Consequently, absorption of visible or ultra-violet light usually results in electronic excitation, which is accompanied by rotational and vibrational changes. With the absorption of infra-red light, simultaneous vibrational and rotational excitations usually take place.

It frequently happens that there are two groups in the molecule which absorb light. If these groups are isolated from each other in the sense that there is little or no electronic interaction between them, the absorption spectrum usually exhibits two separate absorption bands, each characteristic of one absorbing group. If the two groups interact electronically, usually through conjugation, the resultant absorption shows a strongly modified band or bands. Absorption of light by organic compounds in any region but the far ultra-violet is definitely associated with the phenomenon of resonance in systems containing multiple bonds. (33)

It has been possible to classify and interpret the spectra of organic compounds on the basis of the assumption that the electrons in the molecule are acting as oscillators subject to the rules of quantization. Their types of oscillation are given by certain of the resonance forms contributing to the state of the molecule.

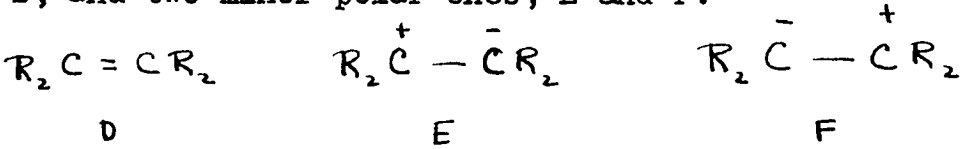
For example, consider the single bond as represented in a molecule such as ethane. The following three structures

may be written for that molecule, where A is the major form, while B and C represent two very minor polar forms.



A B C

It is to the excitation of electronic oscillations whose extremes are represented by B and C that the absorption of light is attributed. If it is assumed that these oscillations are those of a linear harmonic oscillator, the energy states associated with it are given by $E_m = (n+1/2)h\nu_0$; the fundamental frequency $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ where k is the restoring force constant for the oscillator and m is its reduced mass. Similar considerations apply to the isolated double bond, which may be written in terms of three resonance forms: A major homopolar one, D, and two minor polar ones, E and F:



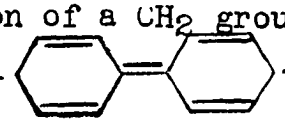
D E F

The polarization of the second bond of the double bond is neglected since such a polarization would have an extremely high energy. In other terms, the restoring force constant k would be very high, and hence its absorption would appear only in the far ultra-violet. The essential difference between the single and the double bond is the considerably higher restoring force constant of the former, giving the single bond an absorption in the far ultra-violet, while the double bond has its characteristic absorption at lower frequencies. Further, the varying chromophoric power of the different double bond struc-

tures can be represented by a different value of k for each type of double bond. The order of decreasing k, or increasing chromophoric activity, has been shown to be:

$$R_2C=CR_2\ ,\quad R_2C=NR\ ,\quad R_2C=O\ ,\quad RN=NR,\quad R_2C=S$$

In order that the absorption extend into the visible region, a molecule must contain more than one oscillator of any of the first three types. Moreover, those oscillators must be connected by a system capable of conducting electric charges, i.e. a conjugated or resonating system. A break in the conjugation is called "insulation effect", since the conjugated system acts as a conductor. It is to be expected that a completely conjugated system will have an absorption characteristic of the molecule as a whole. If the conjugation is broken, by the insertion of a CH_2 group, for example, the absorption will be more nearly characteristic of the two independent parts, although some interaction still is perceivable. If two CH_2 groups are inserted, the insulation is practically complete and the absorption spectrum is that of the two isolated parts (34).

There are other ways in which insulation between parts of a molecule may be effected, though in general not so completely as by the insertion of a CH_2 group. In order that the resonance of biphenyl  occur, the two rings must be coplanar. If, however, a number of large ortho groups be inserted, this coplanarity cannot occur

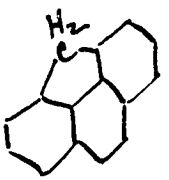
without a large expenditure of energy. Hence this type of resonance, which is so important for the absorption of light, will be considerably inhibited. This effect is well illustrated by the work of O'Shaughnessy and Rodebush (35).

In certain molecules the steric requirements may be such as to reduce the conjugation without completely inhibiting it. In this case the conjugation resonance absorption will appear, but with diminished intensity, or at a higher frequency, or both. For example, the molecule of trans-stilbene is entirely planar and the optically important resonance can readily occur. For cis-stilbene, on the other hand, a model to scale will show that the ortho hydrogen atoms will interfere to such an extent as to prevent the complete planarity of the molecule. This will inhibit the optically important resonance to a certain extent. The absorption of the cis compound is both reduced in intensity and shifted to a higher frequency with respect to the trans (36).

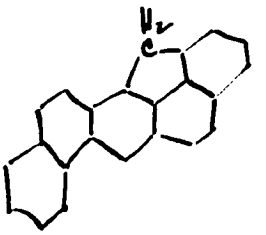
If the molecule of fluorene were not planar (model postulated by Cook and Iball), resonance between the two benzene rings could not occur. In view of the preceeding discussion the absorption spectra of the folded fluorene should very nearly be that of benzene but with the intensity twice as large, since the optically important resonance would be limited to the two benzene rings.

If the molecule of fluorene were planar, the absorption of light would be due to the composite action of all

the resonance forms postulated previously. The absorption spectrum should present a curve similar to that of biphenyl, due to resonance structures V-VIII, suitably modified owing to the interaction with structures of the type IX-XII. It is found indeed (37), (38), (39) that the spectrum of fluorene is displaced toward longer wave-lengths when compared to that of biphenyl, while maintaining approximately the same intensity of absorption. Moreover, there are two additional peaks at longer wave lengths, probably due to the effect of the methylene bridge across the biphenyl rings. This bridging displaces the spectrum toward longer wave lengths; it presents a B-effect as defined by Jones (39) and causes a sharpening of the resolution (Fs-effect of Jones). The latter fact might indicate that the fluorene molecule is somewhat strained. Actually, the strainless and planar 9, 10-dihydrophenanthrene has nearly the same absorption spectrum as fluorene except for the fine structure effect (39). Jones gives several examples of similar compounds presenting an identical effect due to bridging with one or two methylene groups. Sometimes, however, the fine structure effect is absent and only a bathochromic effect is noted, as for example in 4,5-methylenephenanthrene (VII) or 1',9-methylene-1,2,5,6-dibenzanthracene (VIII).



VII

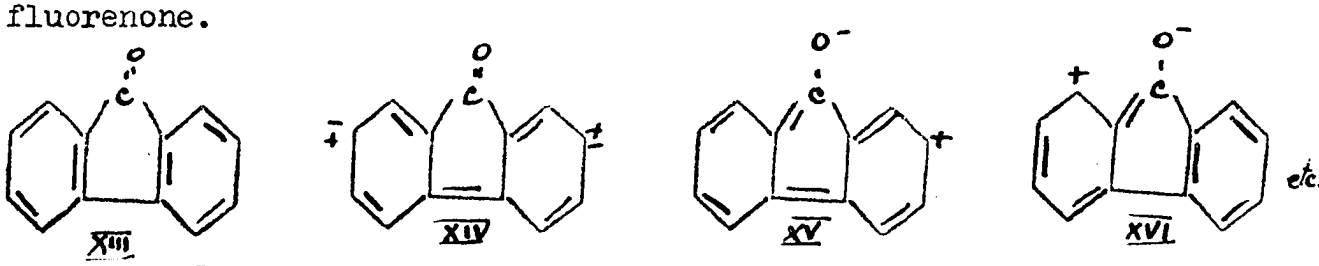


VIII

According to Lewis and Calvin (40) the loss of fine structure resolution, frequently observed when chromophoric groups are loaded with saturated substituents, results from the facilitation of rapid dissipation of the energy of electronically activated systems among the several vibrationally activated states. On the contrary it would seem reasonable to suppose that a somewhat strained bridge linkage, such as occurs in fluorene may increase the rigidity of the structure and hinder the dissipation of the energy of the electronically activated molecules. It is very important to note the pronounced B- (bathochromic) effect of the methylene bridge. The B-effect commonly occurs when a hydrogen attached to any chromophore is replaced by an alkyl group.

Shifting the spectrum to longer wave lengths implies a decrease in the energy level differences between the ground and activated states. Since the introduction of the alkyl substituent cannot give rise to any new resonance structures of the normal type, Mulliken and co-workers (41) have suggested that a small increase in the resonance stabilization energy of the molecule of the alkyl derivatives may result from hyperconjugation (see also Watson (42)). These authors have calculated that the increase in resonance stabilization energy from this source is of the correct order of magnitude to account for the observed spectral shifts. In fluorene, resonance structures X-XII represent this effect of hyperconjugation. The following types of structures can be used to describe the properties of

fluorenone.



Due to the unshared electrons on the oxygen atom the latter can easily take a negative charge (43). Hence the structures XV and XVI contribute rather heavily to the resonance of fluorenone. Since there is resonance along two axes, the absorption of fluorenone may be expected to be displaced toward the visible, which is the case (44). Fluorenone is a yellow compound, whereas benzophenone and anthrone are colorless.

The carbon atom exhibits but little tendency to assume either a positive or a negative charge. Therefore the dipolar structures V to VIII contribute relatively little to the resonance of fluorene. However, if those charges can be transferred to a nitrogen atom as in the nitro-,amino-,nitroamino-fluorenes, the contribution to the resonance of these structures is increased considerably. This is borne out in the absorption spectra (and consequently colors, if the absorption takes place in the visible) of these compounds (45).

It may be concluded then from a consideration of the absorption spectra of fluorene that the planar model for fluorene is favored over the folded structure.

6. Crystal dimensions -

The dimensions of the unit cell of crystals of fluorene, phenanthrene and biphenyl are very similar (11).

All three crystallize in the monoclinic system.

	a	b	c	
Fluorene	8.48	5.73	9.62×2	Å
Phenanthrene	8.60	6.11	9.62×2	Å
Biphenyl	8.22	5.69	9.50	Å

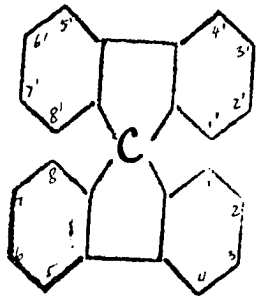
Thus the close relationship between those three compounds is maintained in the solid state. Since the latter two molecules have been shown to be planar, the inference is that the first ought to be so. Evidently, if the fluorene molecule were folded, it should be shorter, and thicker than biphenyl or phenanthrene.

7. Summary and conclusions -

The following physical-chemical and chemical properties of fluorene were examined in the light of modern chemical theories: Substitution reactions, resonance energy, bond lengths, bond angles, absorption spectra and crystal structure. In every case no evidence was found for the folded structure, and none was found against the planar structure. The theoretical consideration appeared to favor the planar configuration.

B . Experimental approach

The theoretical evidence relating to the spatial configuration of fluorene was substantiated experimentally by means of a stereochemical investigation of 9,9'-Spirobifluorene (IX) derivatives. The following discussion will show that

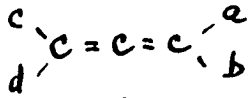


IX

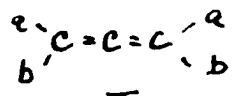
unambiguous results concerning the problem can be obtained by such a study.

1. Stereochemistry of the spiranes -

Van 't Hoff (46) in 1875 pointed out that an allene of the formula (X) should be resolvable since such a compound could exist in two forms. A model would show that there is no plane of symmetry, although the molecule does not contain an asymmetric carbon atom. The groups ab and cd do not lie in the



X

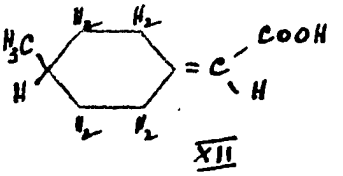


XI

same plane; the two forms are non-superposable mirror images. Somewhat later it was predicted that compound (XI) also should be resolvable. It was not until sixty years later that such allenes were resolved (47).

Molecules not far different from allenes, in which one double bond is replaced by a ring, for example 4-methylcyclo-

hexylideneacetic acid (XII) were resolved in 1909 (48).



XII

If both double bonds of an allene are replaced by rings, spiranes result. Space models will show that the planes of the rings are perpendicular to each other. In 1902 Aschan (49) pointed out that properly substituted spiranes of the general type shown in Fig.XIII are asymmetric and therefore should be capable of resolution. In fact, such compounds have been resolved (50). Spiranes exemplified by figure XIV are not

XIII

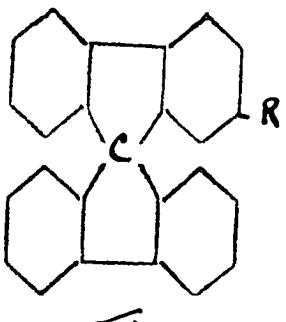
XIV

resolvable since they have a plane of symmetry. Space models of such a compound would be superposable.

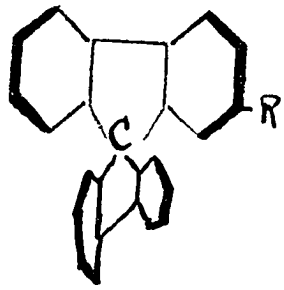
2. Stereochemistry of 9,9′-Spirobifluorene -

a. Scope - In 1930 Clarkson and Gomberg synthesized 9,9′-spirobifluorene by a series of steps to be discussed later. If this compound is substituted by a single group in the 2 position, for example, the derivative XV results. This falls into the general class illustrated by the spirane XIV. If fluorene is planar, this compound exists as a single non-resolvable form. However, if fluorene is folded according to Cook and Iball, the model XVI has no plane of symmetry, and

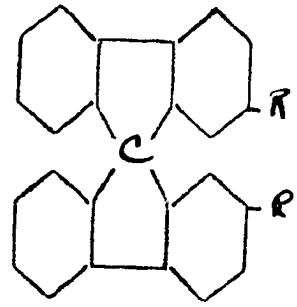
four different non-superposable isomers forming two racemates can be constructed. Such a molecule should then be resolvable. The resolution of a monosubstituted 9,9'-spirobifluorene would without doubt point to a folded structure for fluorene, whereas the non-resolution would be excellent evidence for the planar configuration.



XV



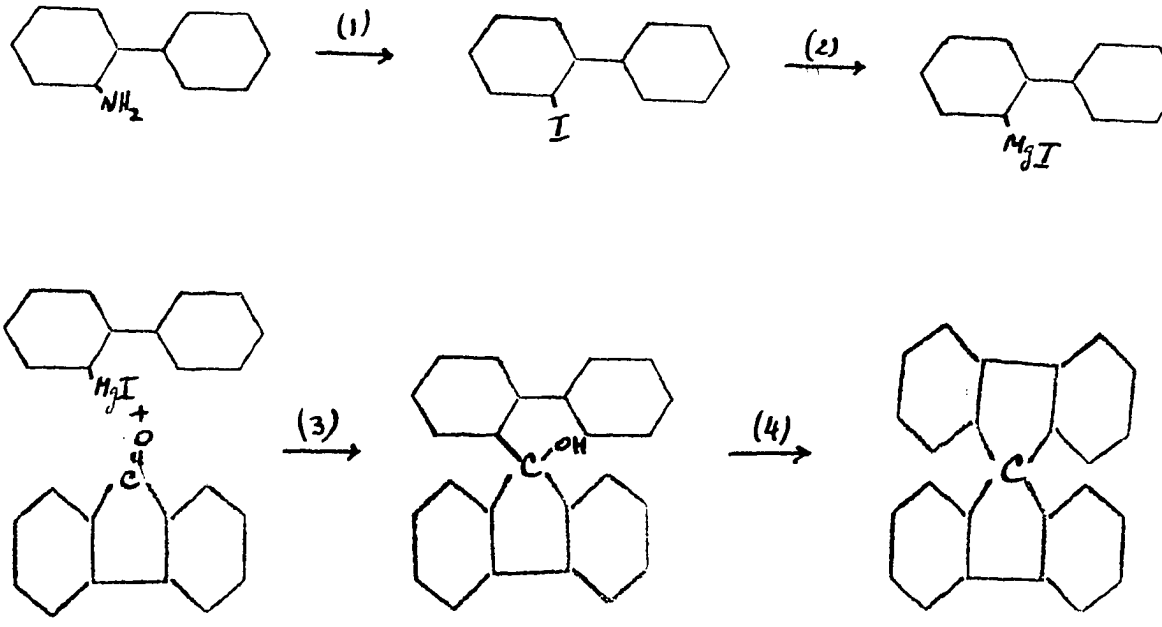
XVI



XVII

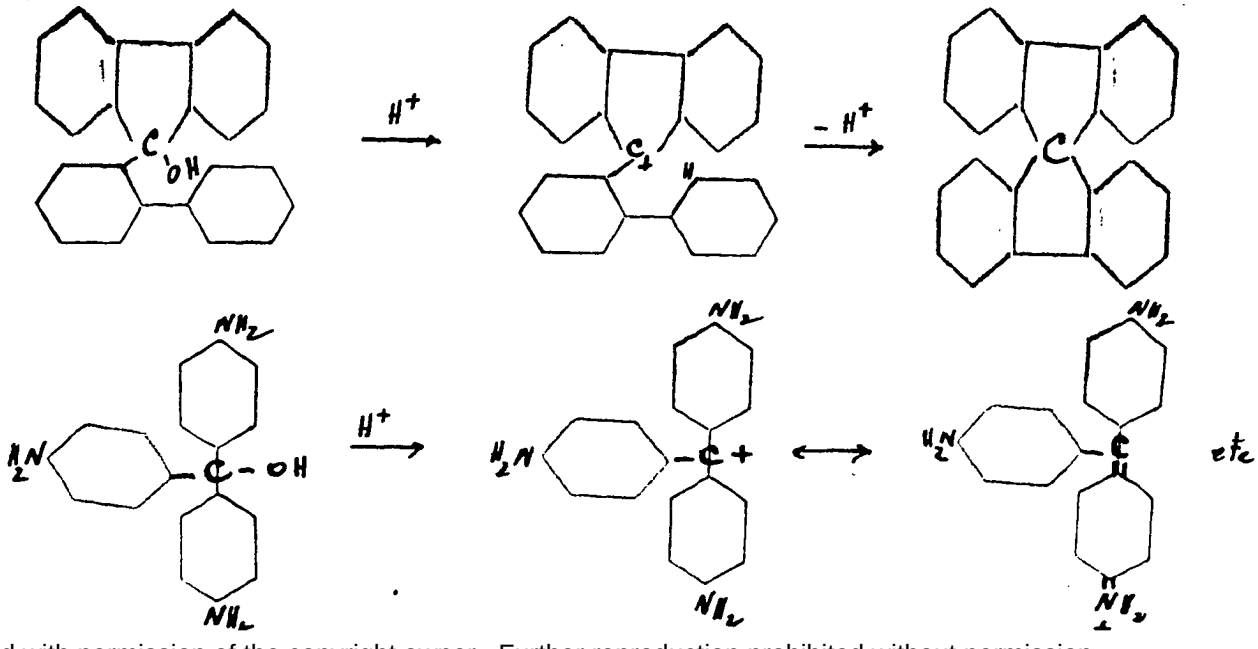
A disubstituted 9,9'-spirobifluorene such as XVII in which the two substituents are on opposite sides of the spiro carbon atom should be resolvable irrespective of a possible planar or folded structure. If fluorene is planar one resolvable racemate should exist; there should be three racemates if the molecule is folded. In order to show that compounds of the spirobifluorene type are resolvable with the proper substituents, several such compounds were resolved.

b. Discussion of experimental work - The method used by Clarkson and Gomberg (57) to prepare the hydrocarbon 9,9'-spirobifluorene consisted of the following four steps:



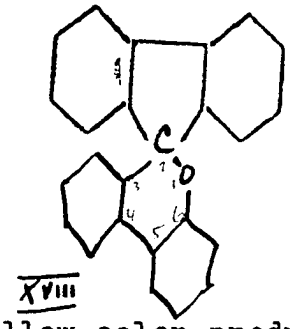
The directions given in the literature were followed for steps (1) and (2). In order to effect the reaction between the 2-biphenyl magnesium iodide and fluorenone, Clarkson and Gomberg refluxed the mixture overnight, then filtered off the insoluble addition complex. During this investigation it was noted that a precipitate appeared nearly as soon as the fluorenone was added (dropwise) to the Grignard, indicating that the addition complex formed rather rapidly. The reaction time was therefore decreased to four hours which slightly increased the yield and aspect of the product. However, the optimum time was not determined; possibly a shorter time would result in a still better material.

The ring closure in step four was carried out by dissolving the purified 9-(2-biphenyl)-9-fluorenol in acetic acid. At the boiling point a few drops of concentrated hydrochloric acid were added through the condenser. After a few seconds a rapid and violent reaction ensued during which the pure hydrocarbon precipitated in brilliant white leaflets, m.p. 200-202°. The probable mechanism of this transformation may be pictured as follows: The tertiary alcohol loses the hydroxyl by interaction with a proton with formation of a carbonium ion. The latter then stabilizes itself by the formation of a five-membered ring and ejection of a proton, producing the 9,9'-spirobifluorene. The first part of this proposed mechanism has its parallel in the triphenylmethane series. For example, the pararosaniline color base upon treatment with acid produces the corresponding dye, which is a carbonium ion stabilized by resonance in the three phenyl rings. The stability here is increased still further by the electron releasing properties of the three amino groups.



In this instance no opportunity for ring closure exists.

During one rather large scale preparation of the 9,9'-spirobifluorene it was felt advisable to moderate the violence of the reaction somewhat. Therefore as soon as the first few platelets appeared in the acetic acid solution to which a few drops of concentrated hydrochloric acid had been added, the flask containing the mixture was cooled externally. This stopped the reaction apparently for no further hydrocarbon seemed to be formed. Reheating and addition of a further amount of acid finally completed the transformation. However the resulting product was not quite pure. From the mother liquors of the recrystallization a compound m.p. 261-264° was isolated. Its analysis and molecular weight determination would indicate it to be the 2,2-(2,2'-biphenylene)-3,4,5,6-dibenzopyrane.(XVIII) Further evidence for this structure is



XVIII

obtained from the yellow color produced when crystals or chloroform solutions of the compound are treated with a strong acid such as sulfuric acid. The color probably is due to an oxonium type of compound. 9,9'-Spirobifluorene itself does not give a color reaction with concentrated sulfuric acid. The pyrane derivative may have been formed by a spontaneous dehydrogenation, or possibly an air oxidation, of the 9-(2-biphenyl)-

9-fluorenol while the acid solution was heated for an excessive length of time.

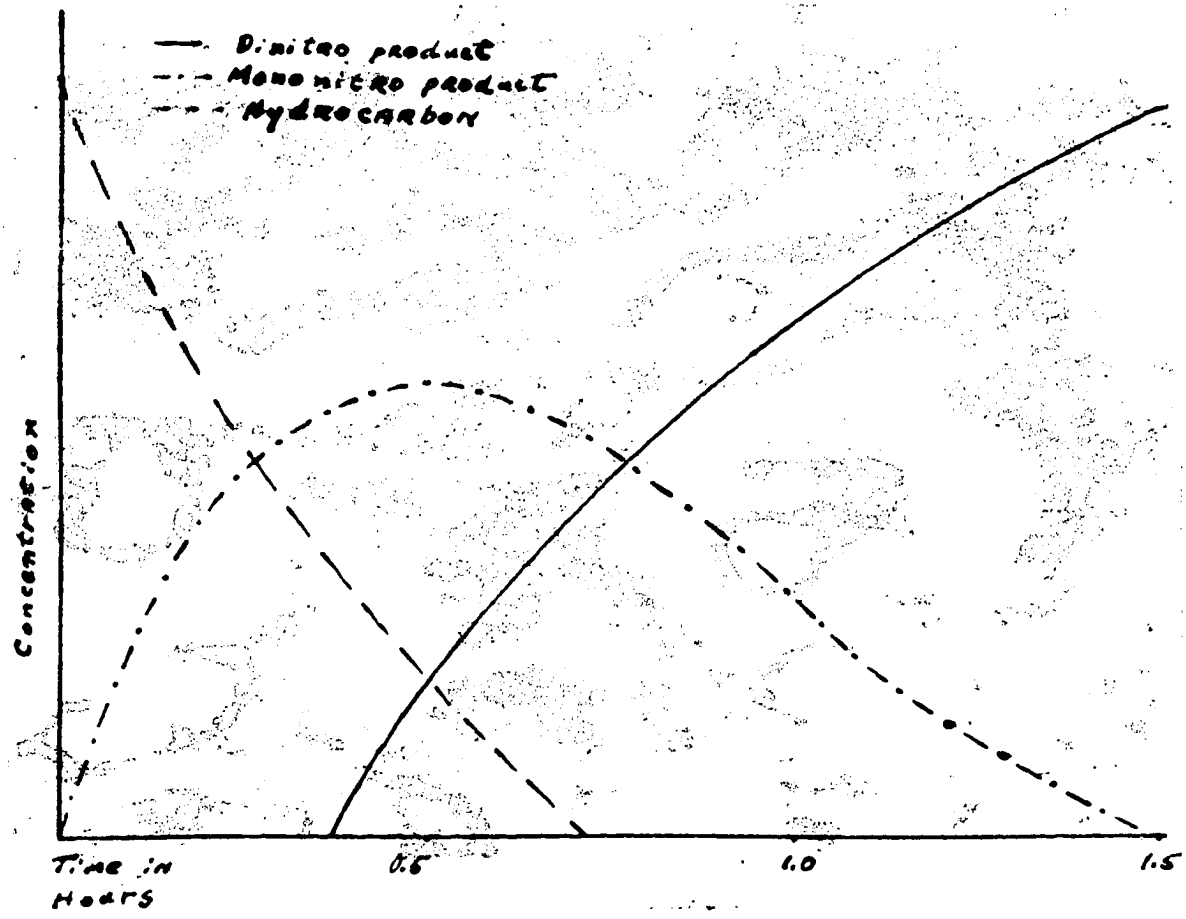
Since an amino group generally is a convenient means to effect the resolution of a compound into its optical antipodes, the nitration of 9,9'-spirobifluorene was undertaken. It was found that the spirane dinitrated very readily in a refluxing glacial acetic- nitric acid mixture to yield the 2,2'-dinitro-9,9'-spirobifluorene. Although the positions taken by the nitro groups were not proved a comparison with fluorene would make the 2 position the point of attack by an electrophilic reagent such as nitric acid.

The mononitration of the spirane proved to be much more difficult. During this work the pure 2-nitro-9,9'-spirobifluorene was obtained in low yield, in as much as the mononitro derivative was always mixed with unnitrated material and the dinitro derivative. Since the solubility of these compounds in the various solvents tried was very similar, a separation by fractional crystallization proved impractical except for the small sample required for analysis. In order to obtain a mixture rich in mononitrated material the conditions of the nitration had to be controlled rather carefully. Best results were obtained by dropping the nitrating mixture into a refluxing acetic acid solution of the spirane and refluxing for exactly one half hour. A separation of the constituents of the mixture was effected after reduction and acylation to give the acetylamino derivative. Crystallization from dioxane

yielded the latter compound pure and in satisfactory yields.

The reason for this difficulty in the mononitration may be sought in the insulating properties of the spiro or 9 carbon atom. The molecule may be visualized as two insulated fluorene systems. Fluorene nitrates rather readily in the 2 position. When the spirobifluorene is submitted to nitrating conditions such as those used for the mononitration of fluorene, each fluorene moiety reacts independently, without consideration for the possible presence of a nitro group in the other half of the molecule, because the 9 carbon atom bars the transmission of the electrical effects due to the nitro group. Under these conditions it might be expected that the control of the reaction time would be the most important factor to obtain a large relative amount of the mononitrated product. At zero time only the hydrocarbon is present. As the reaction proceeds, many molecules are mononitrated, some are dinitrated and some have not yet reacted. From that point onward the chances for unnitrated material yielding a mononitrated product or some of the latter reacting to give a dinitrated compound are very similar. Therefore a lengthening of the reaction will produce more of the dinitrated product and decrease materially the content of mononitrated product in the mixture. Since at that moment there are many more mononitrated molecules than hydrocarbon molecules it is obvious that the concentration of the dinitrated product will increase much faster than that of the mononitrospirane. The kinetics

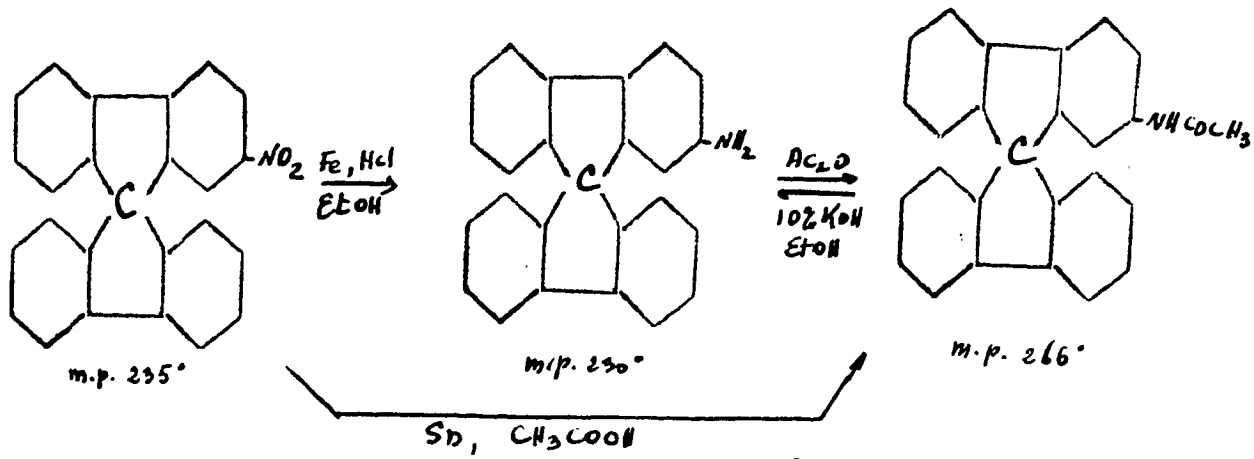
of this process have not been determined, but the following arbitrary graph will best convey the mechanism of this nitration.



Considerations of theoretical organic chemistry as well as comparison to fluorene show that the dinitrated product contains one nitro group each per fluorene moiety, i.e. spirobifluorene dinitrates at the 2 and 2' positions. Stronger reagents than the glacial acetic- concentrated nitric acids mixture would have to be employed in order to achieve dinitration in each fluorene part, i.e. tetranitration for a spirane molecule.

The 2-amino-9,9'-spirobifluorene was best prepared from the acetylamino derivative by saponification in 10%

alcoholic potassium hydroxide. A product melting at 230-233° was obtained by this method. The nitro derivative could also be reduced with iron and hydrochloric acid in ethanol, but the resulting amine melted at 218-224°. Recrystallization of this material did not raise the melting point. However, acetylation afforded the same acetylamino derivative. Usually the latter was prepared in one step from the nitrospirane by reduction with tin in glacial acetic acid and recrystallized from dioxane to give fine needles m.p. 266-269°.



The dinitration of 9,9'-spirobifluorene was carried out essentially as the mononitration except that the reaction time was lengthened to one and one half hours. Reduction of this dinitro derivative to the diamine was best carried out with iron and hydrochloric acid in ethanol. The product could be isolated by precipitating the iron with concentrated sodium hydroxide in alcohol solution, filtering the hot mixture and recovering the diamine from the filtrate. Alternatively the iron could be bound in a tartrate complex and the amine

precipitated in aqueous ammonia. The latter method was preferable for larger batches, but the former gave a purer material. The diamine could be recrystallized from benzene with one molecule of solvent of crystallization.

Previous to any attempt at resolution of the monoamine, which might or might not be resolvable according to the spatial configuration of fluorene, it was imperative to resolve the diamine, which ought to be resolvable in any case. The latter problem therefore was attacked first. It was found that the salt of the diamine with d-camphorsulfonic acid formed an intractable oil in ethanol or ethyl acetate. When d-tartaric acid was used as resolving agent the amine was recovered, showing that no salt formation had taken place. Woodward and Doering (52) had used d-dibenzoyltartaric acid successfully. The latter resolving agent had the advantage of being soluble in benzene which was also a good solvent for the diamine. However the resulting salt formed a gel which could not be made to crystallize. While it is possible that this diamine actually exhibits such behavior with various resolving agents in diverse solvents, it is also quite plausible that traces of impurities (or even appreciable amounts) are responsible for the failure to resolve a compound which according to theory should be resolvable. It was noticed that when tartaric or camphorsulphonic acids were used the solutions soon discolored and often became green or brown in color. This might indicate that the amine oxidized and hence lost its basicity,

i.e. its power to form salts. This would explain why the diamine could not be resolved and why the compound was not recovered quantitatively. In view of the failure in resolution of this disubstituted spirobifluorene, work on the monoamine would have been meaningless and was therefore abandoned.

The sulfonic acid group was another convenient handle for a resolution which could be introduced into the hydrocarbon in a one step synthesis. 9,9'-Spirobifluorene remains unchanged upon standing at room temperature with concentrated sulfuric acid or chlorosulfonic acid with or without solvent. Concentrated sulfuric acid at temperatures above 100° does react slowly; at higher temperatures the reaction is more rapid. The product of such a reaction always is the disulfonic acid. The monosulfonated product could never be isolated. When only part of the hydrocarbon had reacted, the product still was the disulfonic acid. The same explanation already given for the nitration holds in this case. It was hoped, however, that by using chlorosulfonic acid in chloroform a monsulfonation could be achieved, since that reagent can be used in exact equivalent amounts and other conditions can be controlled very closely. It was found that a reaction took place only at the boiling point of the solvent. The product then was an approximately equivalent amount of the disulfonic acid and unsulfonated product. Thus monosulfonation could not be achieved. The disulfonic acid was somewhat hygroscopic. It could be recrystallized from dioxane from which the acid separated with

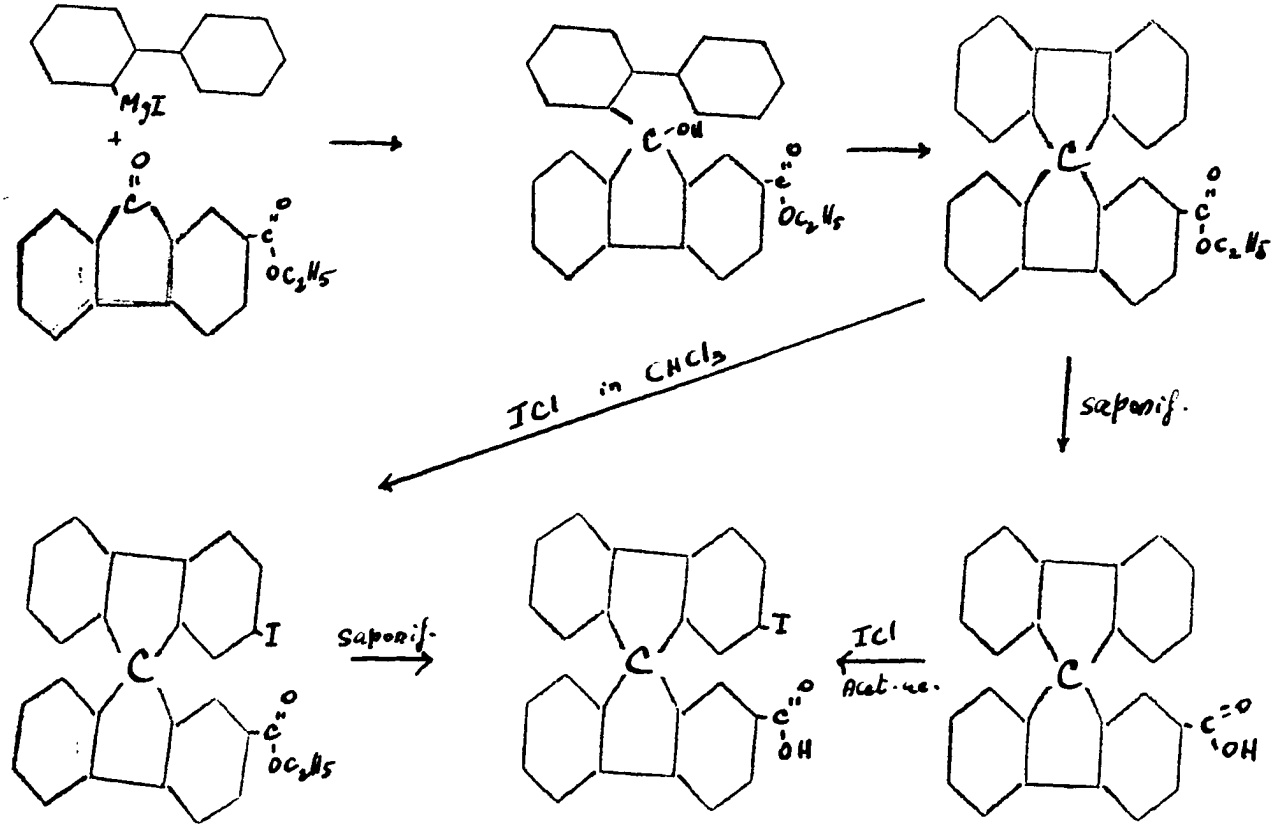
two molecules of solvent of crystallization. The dipotassium salt, prepared in rather concentrated solution, could be crystallized from water.

Since the disulfonic acid was available readily, resolution of this compound with brucine and strychnine was undertaken. The former resolving agent formed difficultly crystallizable salts. However, a partial resolution was obtained. With strychnine no clear cut separation into two equivalent amounts of diastereoisomeric salts resulted. Several fractions were collected and worked up separately. This afforded some samples of resolved spirobifluorenedisulfonic acid all of which were characterized by a positive rotation. An identical phenomenon was noticed when the strychnine salt of the disulfonic acid was prepared from the potassium disulfonate and strychnine sulfate and recrystallized subsequently from water and ethanol. It is not understood at present why no negative rotations were observed in the resolved acids. The very important fact for the purpose of this dissertation is that a resolution was achieved at all. This showed that 9,9'-spirobifluorene follows the rule that a properly disubstituted spirane should be resolvable. If now it could be demonstrated that the monosubstituted spirobifluorene was, or was not, as it may be resolvable, the spatial configuration of fluorene itself would be clearly established.

Since the spirobifluorene monosulfonic acid could not be prepared and the amine was not suitable an entirely new

approach was selected. It was felt that a carboxyl group might be more useful for a resolution. A precedent for this was that Ray and Kreiser-Weisburger (6) resolved 9-hydroxy-fluorene-2-carboxylic acid while Bennett and Noyes (14) were unable to resolve 2,9-diaminofluorene.

However there is no easy direct method for the introduction of the carboxy grouping. But when the synthesis of spirobifluorene was modified somewhat, the spirobifluorene carboxylic acid was obtained in yields comparable to those in the synthesis of the hydrocarbon. The various steps are outlined below:



In the first step the Grignard reagent was reacted with a keto ester. It was desired to bring about a selective reaction at the keto group without affecting the ester grouping. In general a keto group is more active than the ester, hence it would react first if there were only a limited quantity of the Grignard reagent. This is particularly so for the fluorenone derivative, where the keto group is activated by the adjacent biphenylene system. In order to produce a still more favorable ratio of the reactivities of the two functional groupings, the ethyl ester was used rather than the previously known methyl ester. The latter actually is more polar than the former and therefore might react with a Grignard reagent to a greater extent. This assumption was not verified experimentally although it is sound from a theoretical point of view. The Grignard was dropped slowly into a well stirred solution of the keto ester so that the latter always was in excess. Equimolar amounts of ester and 2-iodobiphenyl were used. Since the formation of the Grignard reagent was not 100% complete, the ester was in excess even toward the end of the reaction. The addition complex was insoluble in the benzene ether mixture; this fact might also have contributed to prevent the ester group from reacting. All these favorable circumstances afforded 9-hydroxy-9-(2'biphenyl)-2-carbethoxyfluorene in yields very similar (about 70%) to those obtained when no ester grouping was present.

The cyclization of the tertiary alcohol caused no difficulties. The reaction was much less violent than when

the hydrocarbon itself was produced, perhaps because the resulting ester was soluble in acetic acid. It will be remembered that the hydrocarbon crystallized out during the preparation with evolution of a large amount of heat.

The 2-carbethoxy-9,9'-spirobifluorene upon saponification in 10% ethanolic potassium hydroxide yielded the ccarboxylic acid after acidification. The acid crystallized from glacial acetic acid in brilliant white needles melting at 356° (block).

Thus the 9,9'-spirobifluorene-2-carboxylic acid was available as a monosubstituted spirane. Although a failure to resolve this compound would be meaningful in view of the resolution of the disulfonic acid discussed previously, it was felt that two more closely related compounds should be examined in this manner. The conclusions reached would then be on a firmer experimental basis. Two such compounds would be the 9,9'-spirobifluorene-2-carboxylic acid and the 2'-iodo-9,9'-spirobifluorene-2-carboxylic acid obtained from the former by iodination. If the iodo derivative could be resolved and the uniodinated compound could not, it would constitute striking experimental evidence for planar fluorene. If both could be separated into their optical antipodes, fluorene would certainly be folded.

Accordingly, efforts were made to iodinate the spirane carboxylic acid. In view of the large amount of acetic acid required to dissolve the spirane carboxylic acid, it was

out of the question to use equimolar amounts of the spirane acid and iodine monochloride. A preliminary experiment in which a six fold excess of iodine chloride was used resulted in a nearly theoretical increase in weight. However a titration in acetone (which in this case gave very approximate results) showed the compound isolated after recrystallization to be low in iodine. A larger batch was run with a ten fold excess of iodine chloride.

The resulting material after recrystallizing once was used for a resolution with strychnine. Although this resolution was not clear cut insofar as it did not yield two portions of equal weight of the two diastereoisomeric salts, the various fractions crystallized readily from absolute ethanol. Since the fractions of salts obtained after recrystallization had different specific rotations, they were decomposed separately. The resulting samples of the free iodospirane acid were all optically active. Nevertheless, there was no smooth transition from the most negative fraction to the most positive one. One salt gave a positive rotating acid, the next one negative, then again positive, etc. At the time there was no explanation for this behavior.

A sample of the iodo acid originally used for the resolution was recrystallized several times and analyzed. The iodine found was about 22% whereas theory requires 26.1%. It was recrystallized a few more times and analyzed again. The per cent of iodine found was even lower, 19.1%. Therefore,

the impurities were concentrated during the crystallizations. The sample used for the resolution probably contained a higher percentage of the iodo acid than the analyzed one since it had been crystallized only once. However, the impurities present (probably uniodinated acid) interfered with the proper crystallization of the strychnine salt by serving as centers of crystallization for both diastereoisomers. Even so, as mentioned above (and described in the experimental part) a resolution was achieved.

Further efforts to obtain the pure iodo acid by iodinating 2-carbethoxy-9,9'-spirobifluorene in chloroform were made. It was thought that the ester might yield better results because concentrated solutions could be used. Exactly equimolar amounts of the reagents facilitated control of the reaction. It was found, however, that equivalent amounts of iodine monochloride and ester resulted in incomplete reaction. The separation of pure substances from the reaction mixture was not feasible because of similar solubility relationships. When an excess of iodine monochloride was employed, the mixture could not be separated either. However, a small amount of a substance which had reached a constant melting point at 190-193° was isolated. The analysis was high for a monoiodo derivative and somewhat low for a diiodo compound. Apparently the iodination reaction produced mixtures which could not be separated by crystallization.

The resolution of the 2'-iodo-9,9'-spirobifluorene-2-carboxylic acid probably would have been easier and more clear

cut if the pure compound had been available. Nevertheless for the purposes of this work it was sufficient to demonstrate that the compound was resolvable, even if this was done on a slightly impure compound.

The 9,9'-spirobifluorene-2-carboxylic acid was the crucial monosubstituted spirobifluorene derivative in this work. If it could be resolved, it would indicate a folded structure for fluorene; if it could not the planar configuration would certainly be favored. The acid formed a beautifully crystalline salt with strychnine in absolute ethanol solution. Several fractions of this salt were obtained. All of them had a melting point of 238-240°. Their specific rotations in acetone were all in the neighborhood of -37°. Although the properties of the various salt fractions were very similar, they were decomposed separately to give the corresponding fractions of the free acid. None of these showed any signs of optical activity. The conclusion must be drawn that fluorene has a planar structure. The experimental work thus confirms the theoretical evidence.

Part III

EXPERIMENTAL DETAILS

A. 2-Iodobiphenyl.

In a 5 l. round bottom flask there were placed 169.2 g. (1 mole) of 2-aminobiphenyl (Eastman Kodak technical) and 390 ml. of water. Concentrated sulfuric acid (65 ml. or 1.2 moles) was added all at once while the amine suspension was mechanically stirred. The mixture was heated to the boiling point. A reddish-tan solution resulted. The flame was removed and the flask lowered into a pail, which then was filled with a chipped ice-salt mixture. Mechanical stirring was maintained and the temperature lowering observed carefully. When the solution reached 30°, about 1000 g. of finely chipped ice was added to the flask as quickly as possible with good stirring. The amine sulfate precipitated all at once in a pink slush, which had to be broken up by the stirrer before the next step. When the inside temperature was around 0° (never above 5°) a solution of 69 g. (1 mole) of sodium nitrite in 140 ml. of water was slowly dropped in over a period of about one hour. The solid went into solution as the reaction progressed. Occasionally a handful of ice was added to control the temperature. Then 20 ml. (0.37 mole) of concentrated sulfuric acid diluted with some ice was added and the solution stirred for one half hour. Ten grams of urea was introduced and stirring continued for three fourths of an hour

to remove the excess nitrous acid. A solution of 199.2 g. (1.2 mole) of potassium iodide in 200 ml. of water was added all at once and the mixture was stirred for about two hours, then allowed to stand overnight. The water layer was decanted and discarded. (During one run it was extracted with ether; an insignificant amount of the product was recovered.) The heavy oil was placed in a separatory funnel and washed successively with dilute sodium hydrogen sulfite and about five portions of water. During the latter part of this operation emulsions sometimes formed at the phase boundary. As much as possible of the brown oil was collected and ether added to the separatory funnel. Finally the oil and ether fractions were combined and dried over drierite. The ether was distilled off on a steam bath. The oil was fractionally vacuum distilled, collecting a small dark colored fore-run. The main fraction was light yellow and distilled at 142°/4-5 mm or 152°/6-7 mm. Toward the end the distillate darkened again; this fraction was collected separately. The fore-and afterruns were usually added to subsequent batches. The center fraction was used for the subsequent steps. It generally weighed about 200 g. (70% yield).

B. 9-(2-Biphenyl)-9-fluorenol.

Ten grams of magnesium was placed in a 2 l. three necked round bottom flask equipped with a mercury-sealed stirrer, reflux condenser (drierite tube) and a 500 ml. dropping funnel. A glas-col heater with variac was used.

The system was heated while a dry air stream was slowly sucked through it for two hours. After cooling 300 ml. of anhydrous ether (recently distilled from sodium) was added and heated to the boiling point. The stirrer was started and 71 ml. (0.4 mole) of 2-iodobiphenyl dissolved in 200 ml. anhydrous ether dropped in. After a few minutes the ether turned cloudy indicating that the reaction had started. The heater was disconnected and the iodobiphenyl added at such a rate that good reflux was maintained (approximately 45 minutes required). Then the mixture was refluxed another hour. In the meantime 72 g. of fluorenone was dissolved in 100 ml. of benzene (stored over sodium), the solution diluted with 200 ml. anhydrous ether and placed in the dropping funnel. With good stirring the fluorenone solution was added over one and one half hours to the Grignard reagent. A yellow precipitate formed soon after the beginning of the addition. The mixture was refluxed another three hours, cooled and filtered as rapidly as possible. The filter cake was washed several times with ether and pressed as dry as possible. After air-drying for a short time, the yellow granular powder was added to 1500 ml. of water containing 90 g. of ammonium chloride and stirred for about two hours. After filtering the crude material was air-dried overnight. It weighed 95 g. This was dissolved in 350 ml. of benzene and filtered hot into a 2 l. Erlenmeyer flask and reheated to the boiling point. A large funnel was supported by a ring stand and suspended over the

flask in such a manner that vapors could escape readily. One liter of low boiling petroleum ether was added through the funnel all at once. Some of it vaporized in contact with the hot benzene solution (Caution:fires). A few seconds afterwards the material crystallized. After standing and cooling the product was filtered, washed with petroleum ether, and air-dried. The yield of white to lemon platelets, m.p. 168-171° (shrink at 165°), was 75 g.

C. 9,9'-Spirobifluorene

In a 2 l. Erlenmeyer flask 72.5 g of 9-(2-biphenyl)-9-fluorenol was dissolved by heating in 300 ml. of glacial acetic acid. At the boiling point a few drops of concentrated hydrochloric acid were added through the condenser. A few seconds afterwards the boiling of the solution intensified, and a few crystals appeared in the solution. The flame was reduced somewhat to moderate the violence of the reaction. Some acid generally was thrown out the top of the condenser, therefore the latter had to be long and of large diameter. It was important, however, to run the reaction in this manner. If the reaction was moderated as described below, a side reaction occured. After the 9,9'-spirobifluorene had come down in a white crystalline slush, the flame was removed, the mixture swirled and allowed to cool. The product was filtered, washed with acetic acid and pressed as dry as possible, then air dried. The white glistening plates weighed 65.4 g. and melted at 200-202°.

The filtrate when diluted with water to turbidity at the boiling point and allowed to stand afforded another 1.7 g. of product. This was recrystallized from 20 ml. glacial acetic acid using Darco to yield 1.2 g. of material melting also at 200-202°.

D. 2,2-(2,2'-Biphenylene)-3,4,5,6-dibenzopyrane

In a ring closure on a rather large batch of 9-(2-biphenyl)-9-fluorenol (252.5 g.) dissolved in 800 ml. of glacial acetic acid, it was felt advisable to moderate the reaction somewhat. Therefore as soon as 1 ml. of concentrated hydrochloric acid had been added through the top of the condenser the flame was removed. When the first crystals formed and the speed of the reaction increased, the flask was cooled in a cold water bath. This however stopped the reaction. The mixture had to be reheated and after about ten minutes the reaction was completed (usual time no more than one minute from time of addition of hydrochloric acid). The main product was filtered as before. The filtrate upon dilution with water at the boiling point yielded another batch of somewhat less pure 9,9'-spirobifluorene. The filtrate at this point was yellow. It was treated with Darco and distilled down to 100 ml. Upon standing small white needles melting at 241-251° resulted. Successive recrystallizations from 90, 85, 75, 65, 60 and 60 ml. glacial acetic acid afforded 1.1 g. of long brilliant white prismatic needles melting at 261-264°. The crystals turn orange-yellow in concentrated sulfuric acid. A solution in

chloroform takes on a yellow color with chlorosulfonic acid. This would indicate formation of a pyrylium type of compound.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.5; H, 4.82; Mol.Wt., 332,
Found: C, 90.49, 90.49; H, 4.65, 4.51;
Mol. Wt., 346, 337.

E. 2-Nitro-9,9'-spirobifluorene

Six and three tenth grams (0.02 mole) of 9,9'-spirobifluorene was dissolved in 300 ml. of glacial acetic acid by heating. At about 90-100°, 37.8 ml. of concentrated nitric acid (d= 1.42) was added dropwise with mechanical stirring over a period of 3-4 hours and allowed to stand overnight. Then the mixture was refluxed for exactly one half hour with stirring and allowed to stand and cool for two hours. Two and seven tenth grams of light yellow material, m.p. 205-210° were filtered off. The filtrate on standing overnight deposited 0.2. g. of pale yellow small needles melting at 234-235°. The filtrate diluted dropwise with mechanical stirring with 500 ml. of water afforded 3.7 g. of material melting 207-218°. The product obtained first was recrystallized from 60 ml. of glacial acetic acid to give 0.8 g. of pale yellow needles melting at 235-236° (this substance was analyzed). The 3.7 g. obtained later were dissolved in the last mother liquor and after standing overnight yielded 3.5 g., m.p. 227-228°. This could be used in subsequent steps leading to the 2-acetylamino derivative.

Anal. Calcd. for $C_{25}H_{15}O_2N$: N, 3.89.
Found: N, 3.93, 3.91.

F. 2-Acetylamino-9,9'-spirobifluorene

Nine and six tenth grams of impure 2-nitro derivative was dissolved in 80 ml. of glacial acetic acid by heating. Ten grams of tin foil was added and the mixture was refluxed. After about one half hour the solution had turned from yellow to colorless and a white precipitate started forming. After refluxing for two hours, the mixture was filtered hot. The solid (tin and tin acetate) was discarded. The filtrate upon standing overmight yielded a white slush, which was filtered and dried. The white powder (6.4 g.) melting at 250-259° was recrystallized from 30 ml. of dioxane to give 5.1 g. of product, m.p. 266-269°. From the acetic acid filtrate more material was recovered which when crystallized from the dioxane mother liquor yielded another 1.4 g., m.p. 263-267°. The analytical sample melted at 266.5-269°.

Anal. Calcd. for $C_{27}H_{19}ON$: N, 3.76.

Found: N, 3.77, 3.68.

G. 2-Amino-9,9-spirobifluorene

Six and four tenth grams of 2-acetylamino-9,9'-spirobifluorene was suspended in 150 ml. of 95% ethanol containing 15 g. of potassium hydroxide and heated on a steam bath. The mixture was refluxed for a total of three and one half hours, then allowed to cool. The product in the form of nearly colorless plates was filtered and washed with ethanol. It weighed 3.2 g. and melted at 230-232°. A further amount of material could be recovered from the filtrate.

Anal. Calcd. for $C_{25}H_{17}N$: N, 4.24.

Found: N, 4.35, 4.29.

The same compound was also obtained by direct reduction of the nitro derivative as follows: Three and six tenth grams of the impure nitro derivative was finely ground and added to 4.0 g. of iron powder and 75 ml. of 95% ethanol. The mixture was heated to refluxing and 13 ml. of concentrated hydrochloric acid dropped in slowly over a period of one hour. After filtering off the excess iron the filtrate was reduced in volume by one half, then added slowly with stirring to 200 ml. of water. The resulting precipitate was washed with a small amount of dilute hydrochloric acid to remove some yellow color, then with water. It was suspended in dilute ammonia and stirred for two hours, filtered and washed well. The white powder weighing 2.8 g. melted to a dark brown liquid about 210-215° after discoloring above 200°. One and eight tenth grams of this product recrystallized from 18 ml. of benzene yielded 1.0 g. of light gray microcrystals possessing a greenish sheen, melting at 218-224° to a red liquid. The melting point could not be raised by further crystallizations. However, a small sample when acetylated in the conventional manner yielded a product melting at 260-263°. This when recrystallized from dioxane melted at 266° which is the melting point of the 2-acetylamino derivative.

H. 2,2'-Dinitro-9,9'-spirobifluorene

Fifteen and one tenth grams of 9,9-spirobifluorene

was dissolved by heating in 500 ml. of glacial acetic acid in a one liter flask equipped with a reflux condenser and a dropping funnel. At the boiling point a mixture of 150 ml. concentrated nitric and 150 ml. glacial acetic acid was run in over a period of one half hour, then the mixture was refluxed an additional one and one quarter hour. After standing one hour the solution was diluted with an equal volume of water. After several hours the yellow product was filtered and air dried. It weighed 18.3 g. and melted at 220-224°. (In various runs yields were as low as 17 or as high as 20 grams; the melting points sometimes were considerably lower (170-190°)). The material dissolved in 250 ml. of glacial acetic acid after refluxing for one half hour. It was filtered hot and allowed to cool overnight. The resulting yellow needles weighed 12.7 g. and melted at 245-249.5°. The analytical sample was recrystallized three times more ; it melted at 249-250.5°.

Anal. Calcd. for $C_{25}H_{14}O_4N_2$: N, 6.89.

Found: N, 6.91, 6.95.

I. 2,2'-Diamino-9,9'-spirobifluorene

Twelve grams of 2,2'-dinitro-9,9-spirobifluorene was finely ground in a mortar, mixed with 12.0 g. of iron powder and suspended in 350 ml. of 95% ethanol. To the boiling solution 35 ml. of concentrated hydrochloric acid was added dropwise over a period of approximately one half hour. After refluxing for a total of one hour the mixture was filtered hot to remove the excess iron. The ethanolic solution was reheated to the boiling point and with mechanical stirring 35 ml. of

concentrated sodium hydroxide (50% solution) was added. The mixture was refluxed for a short time, then filtered through a hot funnel. The precipitated iron hydroxide was washed three times with hot ethanol, then removed from the funnel and dissolved in 25 ml. of concentrated hydrochloric acid. This solution was diluted with 250 ml. of ethanol and heated to the boiling point. As before the iron hydroxide was precipitated with concentrated sodium hydroxide (25 ml.) and the solution filtered hot, the precipitate washed with hot alcohol and discarded. The combined alcoholic filtrates were diluted with 1000 ml. of water and a few milliliters of ammonia added producing a curdy white precipitate. After drying in vacuo over potassium hydroxide, 9.7 grams of powdery diamine was obtained. This was dissolved in 200 ml. of water containing 6 ml. of concentrated hydrochloric acid, treated with Darco for ten minutes and the free diamine liberated by adding 8 ml. of concentrated ammonia to the ice cold solution. After drying in vacuo 7.9 g. of a white powder melting at 244-248° (around 155° some change to a pasty form, resolidifying near 180° was observed) was obtained.

Anal. Calcd. for $C_{25}H_{18}N_2$: N, 8.10.

Found: N, 8.10, 8.01.

The diamine can be crystallized from benzene in beautiful colorless rectangular prisms with one molecule of solvent of crystallization per molecule of diamine. The melting point of the analytical sample was 246.5-248° with pronounced effervescence at 130° (removal of the benzene of crystallization)

and resolidification around 160-180°.

Anal. Calcd. for $C_{25}H_{18}N_2 \cdot C_6H_6$: N, 6.62.

Found: N, 6.62, 6.51.

Another way of preparing this diamine which avoids the handling of the voluminous precipitates of iron hydroxide was as follows:

Four grams of finely ground 2,2'-dinitro-9,9-spirobifluorene, 4 g. of iron powder and 100 ml. of ethanol were refluxed while 15 ml. concentrated hydrochloric acid was dropped in over one half hour and the mixture refluxed for an additional half hour. The hot suspension was filtered. The green filtrate was added to 400 ml. of water containing 15 ml. of concentrated ammonium hydroxide and 20 grams of potassium sodium tartrate (Rochelle salt), yielding a dark green solution of the iron complex and a white suspension of the diamine. To eliminate some absorbed iron, the filtered precipitate was redissolved in dilute hydrochloric acid, one gram of Rochelle salt added and the solution clarified by stirring at room temperature with Darco (boiling the solution with Darco produced a violet colored solution and dark colored low melting amines). After filtration concentrated ammonium hydroxide was added dropwise to the clear solution with mechanical stirring until precipitation of the product was complete. The white powder was dried in vacuo over KOH. It weighed 3.5 g., shrinking and turning pasty around 155°. Recrystallization from benzene afforded a material identical to that obtained by the previous method. However, traces of iron still seemed to be included in the

crystals, because solutions of the diamine prepared in this manner were less stable to air oxidation then those containing the material prepared by the first method.

J. 2,2'-Diacetylamino-9,9'-spirobifluorene

One and seven tenth grams of 2,2'-diamino-9,9'-spirobifluorene was dissolved in 45 ml. of glacial acetic acid. At the boiling point 1.5 ml. acetic anhydride followed by 5 ml. of glacial acetic acid was dropped in through the condenser. After about 10 minutes a white precipitate appeared. The mixture was refluxed for a total of 20 minutes and allowed to cool. The precipitate was filtered and washed with acetic acid. It weighed 1.3 g. Recrystallized from acetic acid (100 ml.) the resulting brilliant white needles weighed 0.7 g. and melted above 360° on a copper block (presumably below 400°, however).

Anal. Calcd. for $C_{29}H_{22}O_2N_2$: N, 6.52.

Found: N, 6.32, 6.26.

The combined acetic acid mother liquors treated with Darco and distilled down to 25 ml. yielded another 0.7 g. of crystalline product.

K. Attempted resolutions of 2,2'-diamino-9,9'-spirobifluorene

1. With d-camphorsulfonic acid:

Three and five tenth grams of the diamine was dissolved in 350 ml. of ethanol by heating and the hot solution was filtered. Four and six tenth grams of d-camphorsulfonic acid was dissolved in 10 ml. of hot water and the solution filtered. Both solutions were mixed at the boiling point and allowed to cool slowly. Upon standing for two days nothing had crys-

tallized out. Successively 200, 100 and 30 ml. of alcohol were distilled off, allowing the solution to stand at least 24 hours between distillations. A rather heavy oily liquid remained. Thirty milliliters of water was added, the solution filtered hot, another 10 ml. water added at the boiling point and the clear solution allowed to cool slowly. An uncrystallizable oil resulted. The diamine was recovered by adding ammonia to the oil, filtering and washing the recovered product with water.

In another attempt ethyl acetate was used as solvent: d-Camphorsulfonic acid (4.6 g.) was dissolved in 100 ml. of ethyl acetate. The finely powdered diamine (3.5 g.) was added at the boiling point of the solvent; the amount of the latter was progressively increased to 400 ml. to keep all solids in solution. Toward the end an oil separated on the walls of the flask. The clear solution was decanted into a clean flask, but on short boiling more oil was produced. The solution was transferred again repeatedly until no more oil resulted from further boiling. The clear solution was allowed to cool slowly. An oil resulted. Although the separate fractions of oil were allowed to stand for over two weeks, no crystallization occurred.

2. With d-tartaric acid:

Two and eight tenth grams of d-tartaric acid was dissolved in 100 ml. of ethanol. Three and two tenth grams of finely powdered diamine was added progressively at the boiling point of the solvent. An additional 75 ml. of ethanol was added, the mixture refluxed on a water bath for one half hour, fil-

tered hot and allowed to cool very slowly. After standing over the week end a small amount (0.1 g.) of material was collected. The filtrate was distilled down to 50 ml. Upon standing overnight some gummy substance had come out. It was filtered off and triturated on the filter with ether. The resulting solid was dried in vacuo to give 0.6 g. of material (fraction 2). The filtrate when reheated deposited solid matter. It was heated to the boiling point and allowed to cool slowly. The resulting light tan material weighed 0.9 g. The filtrate deposited another 0.05 g. of light tan material when its volume was reduced to about 10 ml. All these fractions were shown to be mainly uncombined diamine by recrystallization from benzene; the recrystallized products melted at 247-249°. The residue obtained after removal of the alcohol was an uncrystallizable oil. It solidified in an ice bath but reverted to an oily stage on attempted filtration.

3. With d-dibenzoyltartaric acid:

This acid was prepared according to the directions given by Butler and Cretcher (53). In this case its use seemed to be of advantage because of its increased solubility in non-polar solvents and its higher molecular weight. Four and three tenth grams of benzene recrystallized diamine (with solvent of crystallization - 0.01 mole) was dissolved in 50 ml. of benzene. Six and seven tenth grams (0.02 mole) of d-dibenzoyltartaric acid was dissolved in 100 ml. of benzene. On mixing the two clear hot solutions a white precipitate formed which did not dissolve on refluxing. Complete solution was secured by addi-

tion of 25 ml. of absolute ethanol. However on cooling and standing no crystallization took place. Seeding was without effect. Therefore 56 ml. of solvent was distilled off and the solution cooled slowly. A jelly like material (no liquid remaining)resulted. Additions of benzene or chloroform and heating did not change the nature of the solid. The jelly was transferred to an evaporating dish and placed in a vacuum desiccator. After two days 9.2 g. of a dirty cream powder remained. It was very soluble in cold methanol, ethanol, acetone, ethyl acetate; soluble in hot benzene, xylene, chlorobenzene producing jellies on cooling and slightly soluble in carbon tetrachloride, chloroform or ether. The material could not be crystallized satisfactorily from any solvent.

L. 9,9'-Spirobifluorene-2,2'-disulfonic acid

Twelve and eight tenth grams of 9,9-spirobifluorene was dissolved in 80 ml. of chloroform in an all glass apparatus (250 ml. round bottom flask, reflux condenser carrying a dropping funnel, and a drying tube) placed on a water bath. At the boiling point 5.4 ml. of chlorosulfonic acid dissolved in 20 ml. of chloroform was dropped in over a period of 75 minutes. About 60 minutes after the start of the reaction, a white precipitate began forming. The mixture was refluxed for a total of three hours. The flask was cooled in an ice bath for 15 minutes, then the precipitate was filtered and washed well with chloroform. It was dried in vacuo over potassium hydroxide and calcium chloride. The light greyish-white powder weighed 17.9 g. and melted at 225° with slight effervescence.

Anal. Calcd. for $C_{25}H_{16}O_6S_2$: S, 13.4.

Found: S, 12.0.

The acid crystallized from dioxane (about 1 ml. of solvent per gram of material) with two molecules of solvent of crystallization. The resulting perfectly white needles melt with decomposition at 250° (turns black) after discoloring somewhat from 230° upward. On the copper block decomposition occurs at 155° (probably removal of solvent of crystallization).

Anal. Calcd. for $C_{25}H_{16}O_6S_2 \cdot 2C_4H_8O_2$: S, 9.81; Equivalent weight, 326.1

Found: S, 10.07, 9.93; Equivalent weight, 327.3, 326.6.

The dipotassium salt was prepared by adding enough solid potassium chloride to a solution of the sulfonic acid to make it about 20% in potassium chloride, heating to the boiling point to obtain complete solution and stirring with cooling for several hours. The white precipitate so obtained is nearly pure. A further amount can be recovered by partially neutralizing the filtrate with solid potassium hydroxide. The salt so obtained can be recrystallized from water in the ratio of 15 g. salt per 80 ml. of water. The analytical sample was recrystallized three times, and dried in an oven at 140° for two hours.

Anal. Calcd. for $C_{25}H_{14}O_6S_2K_2$: K, 14.15.

Found: K, 14.18, 14.07.

The ditoluidine salt was prepared by dissolving equivalent amounts of the disulfonic acid and p-toluidine in water at the boiling point, treating with charcoal, filtering hot and allowing to stand. The yellowish filtrate on standing

deposits long slender light yellow needles. In a capillary tube, the material shrinks somewhat from 250° upward, but has no definite melting point; it decomposes around 300°. On a copper block the substance melts around 290°, blackens at 300°.

Anal. Calcd. for $C_{25}H_{14}O_6S_2.2\ C_7H_9N$: N, 4.05.

Found: N, 4.19.

The sulfonation of the 9,9'-spirobifluorene could also be carried out by stirring 1.0 g. of the hydrocarbon with 5 ml. of concentrated sulfuric acid on a steam bath for one hour, cooling and adding a small piece of ice. The resulting mush was filtered through a sintered glass funnel and washed with a little ice water. The solid was dried in a desiccator in vacuo. As an alternative the reaction could also be carried out at 200° for 20 minutes. However, the excess sulfuric acid could never be removed completely, therefore this method could not be used for preparative purposes. When the product from such a reaction was dissolved in a little hot water and p-toluidine added until there was a slight excess (the latter being removed by treatment with Darco), p-toluidine sulfate crystallized out first as white platelets after a few hours. The filtrate upon standing deposited the slightly yellow slender needles characteristic of the p-toluidine salt of the spirane disulfonic acid described above.

M. Resolution of 9,9'-spirobifluorene-2,2'-disulfonic acid

1. With brucine:

Seven and nine tenth grams (0.02 mole) of brucine was dissolved in 20 ml. of 95% ethanol and the hot solution was

added to a boiling solution of 4.8 g. (0.01 mole) of the disulfonic acid in 40 ml. of water. The clear solution was allowed to cool slowly. After standing in the refrigerator overnight, a white solid had settled out. It was filtered and washed three times with cold water and dried in vacuo. The salt weighed 11.9 g. From the filtrate two successive portions of 0.1 g. and 0.5 g. respectively could be recovered by reducing to dryness.

The main portion (11.9 g.) was recrystallized from 140 ml. of absolute ethanol using Darco to give fractions I (3.2 g.), II (3.1 g.), III (1.0 g.), IV (0.45 g.) and V (0.4 g.). These fractions were again systematically recrystallized from 25 ml. of absolute ethanol to yield another five fractions: Ia (2.6 g.), IIa (3.0 g.), IIIa (0.8 g.), IVa (0.3 g.) and Va (0.5 g.).

The salts were decomposed in a separatory funnel containing 20 ml. of water and 10-15 ml. of chloroform. Enough 6 N sodium hydroxide was added to make the water phase distinctly alkaline. Repeated extractions with chloroform removed the strychnine. The water phase was boiled briefly to remove dissolved chloroform, filtered and the volume measured. The rotations of the resulting solutions were then observed in a 2 dm tube at 28° using yellow light. The results are given in table I.

Table I

Results on Resolution of Disulfonic Acid with Brucine

Fraction	Specific Rotation of Salt	Actual Rotation of Acid in Water
Ia	-22.4°	0.12°
IIa	-22.4°	0.03°
IIIa	-22.4°	0.00° *
IVa	-19.8°	0.00° *
Va	-18.5°	0.00° *

* The amount of optically active material in solution may have been so small that its actual rotation was below the sensitivity of the instrument (0.01°).

2. With strychnine:

Seven grams of 9,9'-spirobifluorene-2,2'-disulfonic acid was dissolved in 125 ml. of absolute ethanol by heating and the solution was filtered. Similarly 9.7 g. of strychnine was dissolved in 100 ml. of chloroform. Both solutions were mixed and allowed to cool slowly. No crystallization had occurred after standing overnight. Therefore 65 ml. of the solvent was distilled off. After standing for six hours in the refrigerator an oil had formed. The solution was decanted carefully through a filter (solution A). The oil was triturated with ether for ten minutes thus yielding a white crystalline solid weighing 12.5 g. (Solid I). The solution A was reduced in volume by

distillation. When about 30 ml. (of 100 ml.) had been removed a heavy white precipitate started forming rapidly. Distillation was stopped and the mixture allowed to cool. A further 3.9 g. of white material (solid II) was thus isolated. The filtrate was taken to dryness on a steam bath to give 0.9 g. of light tan material (solid III).

Solid I was suspended in 300 ml. of 95% ethanol and heated to boiling. Since the solid did not dissolve, 15 ml. of water was added and the mixture refluxed for one half hour, when much of the material had dissolved. The solution was decanted from the solid and reheated, then allowed to stand twenty hours. Brilliant white plates weighing 5.2 g. were obtained. (fraction Ia.) The undissolved portion left above was dissolved in the mother liquor and yielded 2.2 g. of white plates (fraction Ib) after standing overnight. The filtrate upon standing again overnight spontaneously deposited another 1.7 g. of brilliant white crystals (fraction Ic).

Solid II (2.9 g.) was dissolved by refluxing with 100 ml. of 95% ethanol and 15 ml. of water. The solution was allowed to stand overnight. Laminar shiny white plates assembled in rosettes (2.1 g.) (fraction IIa) crystallized out. Upon standing for twenty hours another 0.1 g. of white plates was obtained and added to the main fraction. Reduction in volume of the filtrate by 105 ml. produced no crystalline material upon standing.

Fractions Ia, IIa, Ib, Ic and III were decomposed

by adding sodium hydroxide, and extracting the strychnine with chloroform. The rotations of the resulting solutions were determined (the concentrations of acid were calculated on the basis of the amount of the strychnine salt used) and are tabulated in table II. The solutions were taken to dryness on a steam bath by passing a stream of air over the surface of the liquid. The resulting powder was ground and extracted with absolute ethanol containing enough concentrated hydrochloric acid to give an acid reaction. Under these conditions the free sulfonic acid went into solution while the insoluble Sodium chloride was filtered off. Table II shows the rotations of the ethanolic solutions so obtained. After reduction of the alcoholic solution to a small volume repeated evaporation with water yielded the dry and nearly pure disulfonic acid. Samples of each fraction were weighed accurately on an analytical balance, dissolved in water and the rotations determined. These are given in the last two columns of the table.

Table II

Resolution of Disulfonic Acid with Strychnine

Fraction of Salt	I		II		III	Total
	(12.5 g.)		(3.9 g.)		(0.9 g.)	16.7 g.
Specific Rotation		-27.2°		-30.6°		
Conc. in g/100 ml.		0.257		0.245		
Salt Recrystallized Specific Rotation	Ia	-23.5°	IIa	-21.2°		
	Ib	-19.2°				
	Ic	-27.0°				
Conc. g/100 ml.		0.255 0.313 0.259		0.235		
Crude Acid in Water Specific Rotation		3.82° 1.76° 3.54°		1.6°		5.0°
Conc. g/100 ml.		8.6 4.0 3.5		4.0		1.5
Acid in Alcohol Specific Rotation		-1.1° -0.6° $-.35^{\circ}$		-0.5°		
Conc. g/100 ml.		6.9 4.4 2.8		3.0		
Acid in Water Specific Rotation		3.3° 1.0° 1.8°		1.34°		
Conc. g/100 ml.		6.8 3.0 2.8		3.7		

N. 2-Carbethoxyfluorenone -

In an all glass apparatus 75 g. of fluorenone-2-carboxylic acid (54) was suspended in 800 ml. of thionyl chloride and refluxed for four hours. The condenser was set for downward distillation and the thionyl chloride was removed, first at atmospheric pressure and the last traces with vacuum applied. Absolute ethanol (200 ml.) was added to the yellow solid and the mixture heated under reflux for about one half hour when a mush had formed. Anhydrous benzene (250 ml.) was then added and the mixture was refluxed for one hour, by when nearly all the material had gone into solution. The solution was filtered through a hot funnel, the filtrate reheated to the boiling point and allowed to cool slowly. The long yellow needles that crystallized out were filtered off and washed with ethanol. They weighed 62.2 g. and melted at 139-143°. The filtrate was distilled down to 80 ml. and allowed to stand, thus yielding another 7.1 g. of material melting at 137-139°. Both fractions were combined and recrystallized from 210 ml. of benzene using Darco. This afforded 59.4 g. of long yellow needles, m.p. 140-142.5°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.11; H, 4.77.

Found: C, 76.40, 76.64; H, 4.96, 4.87.

O. 2-Carbethoxy-2-(2-biphenyl)-9-fluorenol

A Grignard reagent was prepared from 36 ml. of 2-iodobiphenyl dissolved in 80 ml. of anhydrous ether and 5.0 g. of magnesium covered with 80 ml. of ether using the procedure given for

9-(2-biphenyl)-9-fluorenol. The Grignard was then diluted with 200 ml. of anhydrous ether. The resulting solution was dropped into a refluxing solution of 50 g. of 2-carbethoxy-fluorenone in 225 ml. of anhydrous benzene over a period of 75 minutes. The yellow suspension was stirred and refluxed for another three hours, then cooled and filtered. The solid was washed well with anhydrous ether and allowed to air dry for a short time. The yellow powdery addition complex was decomposed with 1000 ml. of water containing 100 g. of ammonium chloride by stirring the suspension for two hours. The resulting light yellow solid was filtered and air dried overnight. It weighed 74.2 g. and had a melting range of 155-165°. The crude material was dissolved in 700 ml. of benzene by heating, treated with Darco and at the boiling point 1500 ml. of ligroin (30-60°) was added all at once through a large size funnel so suspended that the vapors initially produced could escape freely. After a few seconds fine leaflets started forming. The mixture was allowed to crystallize in a refrigerator for three hours. Sixty and four tenth grams of nearly colorless plates were collected and washed with ligroin. They melted at 189-192.5°, with shrinking at 185°. The analytical sample was recrystallized in the same manner twice more to yield brilliant white plates, m.p. 193-194.5°.

Anal. Calcd. for $C_{28}H_{22}O_3$: C, 82.7; H, 5.42.

Found: C, 83.1, 82.9; H, 5.11, 5.49.

P. 2-Carbethoxy-9,9'-spirobifluorene-

Three hundred and fifty milliliters of glacial acetic acid was heated to near the boiling point. Sixty grams of recrystallized 2-carbethoxy-9-(2-biphenyl)-2-fluorenol was was added and the mixture was refluxed. The solid went into solution readily. While heating with a low flame, a few drops of concentrated hydrochloric acid were introduced through the condenser. Soon afterwards the boiling of the solution increased somewhat for a few minutes. The solution was refluxed for another five minutes, then Darco was added and boiling continued for 15 minutes. After filtration, the clear solution was added with mechanical stirring to 2 l. of cold water producing a fluffy white precipitate. This was filtered and washed well. The powdery air dried material weighed 54.7 g. and melted gradually around 80-100°. This material could be used for the saponification to yield the acid. A sample was recrystallized successively from ligroin and 95% ethanol. The shiny white prismatic plates melted at 174-177°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.16.

Found: C, 86.15, 86.52; H, 4.98, 5.04.

Q. 9,9'-Spirobifluorene-2-carboxylic acid-

Twenty five and eight tenth grams of crude 2-carbethoxy-9,9-spirobifluorene was added to 235 ml. absolute alcohol containing 25 g. potassium hydroxide and 15 ml. of water. Upon heating the white fluffy material turned yellow and coagulated, then dissolved after short refluxing. The

solution was boiled for 45 minutes, then diluted with 200 ml. of water and refluxed with Darco for 5 minutes and filtered hot. Five hundred ml. of water was added and the solution heated to the boiling point. With mechanical stirring approximately 45 ml. of concentrated hydrochloric acid was dropped in, yielding a white heavy precipitate. It was stirred for 15 minutes, filtered and washed well with water. After oven drying at 130° for two hours, the white powder weighed 22.3 g. and melted around 350° on a copper block. This was crystallized from glacial acetic acid (2300 ml.) using Darco and yielded 18.2 g. of shiny white needles melting at 356° (block).

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.7; H, 4.44

Found: C, 86.92, 86.84; H, 4.37, 4.45.

R. Attempt at resolution of 9,9'-spirobifluorene-2-carboxylic acid

Three and five tenth grams (0.01 mole) of the acid was suspended in 100 ml. of hot acetone. A hot solution of 3.3 g. (0.01 mole) of strychnine in 45 ml. of chloroform was added to the suspension of the acid. The suspension cleared. The solution was filtered hot and distilled down to 30 ml. Upon standing overnight no crystallization had taken place. The solvent was removed in vacuo on a steam bath. Ten ml. of absolute ethanol dissolved the residue readily, but upon standing for a short time a precipitate formed which did not redissolve on heating. Addition of 210 ml. of absolute ethanol and refluxing on a steam bath for six hours caused the solution of most of the solid material. The solution was filtered

hot and allowed to stand for four days (crystallization is very slow). After filtration and washing with absolute ethanol, 5.4 g. of short stubby needles assembled in rosettes were obtained (fraction I). They shrank at 240° turning into a yellow plastic mass with some effervescence. The filtrate was reduced by 160 ml. and allowed to stand for four days. The light tan needles assembled in rosettes (0.6 g.-fraction II) shrank at 238°. The filtrate taken to dryness yielded 0.7 g. (fraction III) of a brown residue, m.p. 225°. Fraction I was recrystallized from 170 ml. of absolute ethanol and gave 4.3 g. (fraction Ia) of needles growing in rosettes, m.p. 239-240° to a paste (on copper block the instantaneous m.p. was 204°). Fraction II was recrystallized from 20 ml. of absolute ethanol affording 0.5 g. of light tan rosettes (fraction II'). This was dissolved in the mother liquor of fraction Ia while the latter was distilled down to about 80 ml. Upon standing 1.3 g. (fraction I^1a) melting at 238-240° resulted. Fraction III was dissolved in mother liquor from fraction II' to yield upon standing 0.2 g.of light tan needles, m.p. 236-239°(fraction IIIa). The filtrate from fraction I^1a was reduced to about 20 ml. and gave 0.2 g. (fraction IVa) of material melting at 233-236°. The mother liquor taken to dryness yielded another 0.2 g. (fraction Va) melting at 220°. Fractions IVa and Va were combined and recrystallized from 10 ml. of absolute ethanol using Darco. Another 0.2 g. (fraction IVa') of fine needles m.p. 238-240° was obtained.

Anal.(fraction Ia) Calcd. for $C_{47}H_{38}O_4N_2 \cdot C_2H_5OH$: C, 79.5; H, 5.95; N, 3.79.

Found: C, 79.34; H, 5.79, 5.61; N, 3.80,3.81.

Fraction Ia (3.5 g.) was dissolved in 270 ml. of acetone, 15 ml. of concentrated hydrochloric acid was added and the solution made up to 1 l. with hot water, producing a white flocculent precipitate, which was filtered and washed well with hot water. The resulting acid weighed 1.8 g. Its solution in acetone was optically inactive. Fraction IIa (1.2 g.) was similarly decomposed using 75 ml. of acetone, 5 ml. of acid and 200 ml. of hot water and yielded 0.6 g. of acid, also optically inactive. Fraction IIIa in 25 ml. of acetone, 2 ml. of acid and 100 ml. of hot water afforded 71 mg. of optically inactive acid. Similarly fraction IV' gave 72 mg. of inactive acid. After recrystallization of the various fractions from glacial acetic acid, the melting point was 356°, i.e. identical with the starting material. Table III will summarize these results.

Table III

Resolution attempt with 0.01 mole, 9,9'-spirobifluorene-2-carboxylic acid and 0.01 mole strychnine in absolute ethanol (rotations in acetone).

Salt Fractions	Recrystallized Fractions	Recrystallized Fraction	Free Acid	Actual Rotation
I (5.4 g.) m.p. 240°	Ia (4.3 g.) m.p. 239-240° $[\alpha]_D$ = -37.2° C = 0.4044		Ia(1.8 g.) m.p. 356°	0.00°
II(0.6 g.) m.p. 238°	IIa (1.3 g.) m.p. 238-240° $[\alpha]_D$ = -37.0° C = 0.5005		IIa(0.6 g.)	0.00°
III(0.7 g.) m.p. 225°	IIIa (0.2 g.) m.p. 236-239° $[\alpha]_D$ = -36.4° C = 0.4980		IIIa(71 mg.)	0.00°
	IVa (0.2 g.) m.p. 233-236° $[\alpha]_D$ = -31.4° C = 0.4780	IV'a (0.2 g.) m.p. 238-240° $[\alpha]_D$ -38.4° C = 0.2935	IVa(72 mg.)	0.00°
	Va (0.2 g.) m.p. 220° $[\alpha]_D$ = -25.4° C = 0.5545			

S. 2'-Iodo-9,9'-spirobifluorene-2-carboxylic acid

In a 2 l. round bottom flask with ground glass joint equipped with a ground glass reflux condenser 12.0 g. of 9,9-spirobifluorene-2-carboxylic acid was dissolved in 1350 ml. of glacial acetic acid by heating. Them 15 ml. of iodine monochloride followed by 20 ml. of acetic anhydride was added and the solution was refluxed for six hours and allowed to stand for two hours. The solvent and the excess iodine monochloride were then distilled off until the volume was about 300 ml. and the distillate light pink. Twice 100 ml. of glacial acetic acid was added and distilled down so as to remove most of the iodine. The mixture was cooled in a cold water bath. The resulting crystalline precipitate was filtered and washed with acetic acid. It weighed 12.2 g. A further amount of material (4.6 g.) could be recovered by diluting the filtrate at the boiling point with water containing a small amount of sodium hydrogen sulfite. The combined fractions were dissolved in 1 l. glacial acetic acid by refluxing for one hour, treated with Darco for 15 minutes and the volume reduced to 400 ml. by distillation. After standing overnight, 10.0 g. of material, m.p. 345°, had crystallized out. Part of this was used in the resolution to be described later. The remainder was recrystallized once from glacial acetic acid and once from xylene, then analyzed. The white granules melted now at 348°.

Anal. Calcd. for $C_{26}H_{15}O_2I$: I, 26.1.

Found: I, 22.20, 22.02.

Since this analysis was rather low, the acid was recrystallized several times from the same solvents as above and analyzed again. The melting point rose to 350-351°.

Found: I, 19.1, 19.3.

Crystallization thus appeared to concentrate the impurity.

An attempt was therefore made to prepare the acid by iodination of 2-carbethoxy-spirobifluorene followed by saponification of the ester.

With mechanical stirring a solution of freshly prepared iodine monochloride (2.0 g. - 0.012 mole) in 3 ml. of dry chloroform was added dropwise to a boiling solution of 3.9 g. (0.010 mole) of 2-carbethoxy-9,9'-spirobifluorene in 10 ml. of chloroform over a period of 20 minutes (micro dropping funnel). The mixture was refluxed for 90 minutes. Some hydrogen chloride was evolved. After cooling the solution was transferred to a separatory funnel by means of 50 ml. chloroform. It was shaken successively with a dilute solution of sodium hydrogen sulfite, sodium hydrogen carbonate and washed several times with water. The light yellow solution was dried over drierite and the solvent removed on a steam bath. The gummy material was dissolved in 40 ml. ethanol, treated with Darco, filtered hot and allowed to cool slowly. A light cream powder weighing 3.2 g. and melting with effervescence around 90° was obtained. This was dissolved in 50 ml. of ethanol containing 5 g. of potassium hydroxide and the solution refluxed for one hour. The mixture was diluted with 200 ml. of water and at the

boiling point acidified with stirring. The resulting acid was oven dried. It weighed 2.5 g. and melted at 345°. This was recrystallized from 240 ml. of xylene using Darco to yield 1.7 g., m.p. 348°. This was again recrystallized twice from 170 and 150 ml. of xylene respectively to afford 1.2 g., m.p. 350°.

Anal. Found: I, 19.3.

Since this result was low again, the conditions were modified as follows: A solution of 2.2 g. (0.0135 mole) of iodine monochloride in 5 ml. of chloroform was added dropwise with mechanical stirring to a boiling solution of 3.2 g. (0.0083 mole) of 2-carbethoxy-9,9'-spirobifluorene in 15 ml. of chloroform over a period of 45 minutes. The mixture was refluxed gently for five and one half hours and allowed to stand overnight. The dark solution was transferred to a separatory funnel with some chloroform and shaken with dilute sodium hydrogen sulfite, sodium hydrogen carbonate and washed several times with water. The chloroform layer was dried over drierite and the solvent removed on a steam bath. To the resulting light yellow semi-fluid paste 160 ml. of absolute methanol was added and the mixture was refluxed for two hours until nearly all solids had gone into solution. The solution was treated with Darco, then 45 ml. of solvent distilled off (slight turbidity). After standing overnight 2.0 g. of light cream powdery material shrinking at 167°, turning pasty at 170° and melting at 181° was obtained. This material on long boiling

dissolved in 310 ml. of methanol. On standing it yielded 0.8 g. of white crystalline powder shrinking at 180° and melting 184-188° with isolated particles remaining solid until the temperature reached 194°. Four successive recrystallizations from ligroin (b.p. 90-120°) (20, 10, 10 and 6 ml.) finally yielded 0.2 g. of microcrystals melting at 190-193° with softening at 189°.

Anal. Calcd. for $C_{28}H_{19}O_2I$: I, 24.8.

$C_{28}H_{18}O_2I_2$: I, 39.7.

Found: I, 32.4.

Although the melting point of this material had been constant over two successive recrystallizations, its analysis indicated it to be a mixture of mono-and diiodo derivative. Working up the mother liquors of the various recrystallizations produced a material melting with effervescence around 90°, similar to that described previously.

T. Resolution of 2'-iodo-9,9'-spirobifluorene-2-carboxylic acid

Four and eight tenth grams of the acid and 3.3 g. of strychnine were refluxed in 200 ml. of 95% ethanol for one and one half hours until all solids had dissolved. The solution was filtered hot, reheated to the boiling point and allowed to stand overnight in the refrigerator. A powdery cream colored solid weighing 1.3 g. (fraction I) was obtained. Exactly 96 ml. of solvent was distilled off and the solution allowed to stand for four hours. Fraction II in form of a powdery nearly white solid weighing 2.0 g. resulted. Reducing the volume by 50 ml.

and standing overnight afforded fraction III as powdery white microcrystals weighing 1.7 g. Removal of 25 ml. of solvent and standing for thirty hours gave fraction IV (0.9 g.). Fraction V weighing 1.4 g. was obtained after distillation of 35 ml. of ethanol and standing for fifty hours. The filtrate taken to dryness produced fraction VI weighing 0.9 g. Systematic recrystallization of these six fractions from 95% ethanol afforded eight fractions. The weight and specific rotation of these fractions in acetone at 28^{0} is given in table IV.

These various salt fractions were decomposed as follows: Each fraction was dissolved in about 10 - 30 ml. of acetone depending on its weight. Concentrated hydrochloric acid (3-5 ml.) was added to the acetone solution. To this acid solution from 60 to 100 ml. of hot water was added carefully (some acetone boils off in the process) whereby the 2'-iodo-9,9-spirobifluorene-2-carboxylic acid precipitated in an easily filterable form. After standing for about 15 minutes, the precipitate was filtered and washed well with hot water to remove all of the strychnine hydrochloride. The various fractions were air-dried and their rotations determined in acetone. The results are given in table IV.

Fraction 5 having the highest positive rotation, was recrystallized by solution in 20 ml. of glacial acetic acid (refluxing for 45 minutes) and standing overnight. Fraction 5a weighing approximately 0.1 g., m.p. 350-351° (block), with a specific rotation of $+16.9^{0}$ (actual rotation $+0.10^{0}$ for 0.0592 g.

dissolved in 20 ml. of acetone) was obtained. The filtrate was diluted at the boiling point with 5 ml. of water. After standing it yielded fractions 5b weighing 0.2 g., m.p. 350-351° (block), with a specific rotation of + 37.9° (actual rotation + 0.19° for 0.0501 g. in 20 ml. of acetone).

Fraction 8 with the highest negative rotation was also recrystallized from 55 ml. of glacial acetic acid to give fraction 8a m.p. 344-45°, $[\alpha]_D$ -14.3° (α -0.09° for 0.0785 g. in 20 ml. of acetone). The filtrate diluted at the boiling point with 18 ml. of water produced fraction 8b, weighing 0.4 g., m.p. 341-42° (block), $[\alpha]_D$ -16.8° (α -0.11° for 0.0785 g. in 20 ml. of acetone).

Table IV

Resolution of 2'-Iodo-9,9'-spirobifluorene-2-carboxylic Acid with Strychnine

Fraction of Salt	Weight Salt	Rotation	Weight of Acid Obtained	Melting Point	Actual Rotation	Specific Rotation
1	0.4 g.	-26.6°	0.25 g.	318°	-0.06°	-7.1°
2	1.3 g.	-26.7°	0.8 g.	328°	-0.05°	-5.1°
3	0.6 g.	-28.1°	0.4 g.	336°	-0.03°	-3.2°
4	0.8 g.	-31.6°	0.5 g.	341°	+0.15°	+15.5°
5	0.6 g.	-18.6°	0.35 g.	350°	+0.28°	+25.5°
6	0.3 g.	-39.8°	0.2 g.	336°	-0.02°	-2.0°
7	0.8 g.	-27.2°	0.5 g.	347°	+0.12°	+15.0°
8	2.1 g.	-51.9°	1.0 g.	344°	-0.18°	-16.8°

Part IV

SUMMARY

A contribution has been made to the elucidation of the spatial configuration of fluorene. A theoretical interpretation of data available in the literature indicated this hydrocarbon to be planar. This finding was corroborated experimentally by a study of the stereochemistry of 9,9'-spirobifluorene. A monosubstituted spirobifluorene could not be separated into optical antipodes, whereas several symmetrically disubstituted spiranes could be resolved.

Part V

BIBLIOGRAPHY

(1) Berthelot, Amm. chim. phys., (4), 12, 222 (1867)

(2) Fittig, Ber., 6, 187 (1873)

(3) Graebe, Ber., 7, 1625 (1874) Ann., 174, 194 (1874)

(4) Kliegl, Ber., 62, 1327 (1929)

(5) E.K. Weisburger, Ph.D. Thesis, Univ. of Cincinnati,(1947)

(6) Ray and Kreiser (Weisburger), J.Am.Chem.Soc., 69,3068 (1947)

(7) Hengstenberg and Mark, Z.Krist., 70, 283 (1929)

(8) Bergmann and Mark, Ber., 62, 750 (1929)

(9) Stuart, "Molekulstruktur" p. 76 (1934) J. Springer, Berlin

(10) Sundarajan, Z. Krist., 93, 238 (1936)

(11) Krishnan and Banerjee, Phil. Trans., 234 A, 265 (1935)

(12) Cook and Iball, Chem. and Ind., 55, 467 (1936)

(13) Iball, Z. Krist., 94, 397 (1936)

(14) Bennett and Noyes, J.Am. Chem.Soc., 52, 3437 (1930)

(15) E.K. Weisburger, Private communication

(16) Pinck and Hilbert, J.Am.Chem.Soc., 59, 8 (1937)

(17) Robertson, Chem.Rev., 16, 417 (1935)
Hendricks, Chem.Rev., 7 , 431 (1930)

(18) Bergmann, Engel and Hoffmann, Z.Phys.Chem., B17, 92 (1932)

(19) Hughes, LeFevre and LeFevre, Chem. and Ind., 55,545,581 (1936)

(20) Hughes, LeFevre and LeFevre, J.Chem.Soc., 1937, 202

(21) Syrkin and Shott-Lvova, Acta Physicochim. U.R.S.R., 19, 379 (1944); C.A. 39, 3710 (1945)

(22) E. Bergmann, "Isomerism and Isomerizations", p.12 (1948) Interscience Publishers, New York

(23) Wheland "Theory of Resonance" p.174, (1944) John Wiley and Sons, New York

(24) Branch and Calvin, "Theory of Organic Chemistry" p.114, (1941) Prentice-Hall, New York

(24) Wheland, Op.Cit., p.69

(25) Adams and Yuan, Chem.Rev., 12, 262 (1933)

(26) Clark and Pickett, J.Am.Chem.Soc., 53, 167 (1931)

(27) Wheland, Op.Cit., p.106

(28) Gilman, "Organic Chemistry" Vol.I, p.136 (1947) John Wiley and Sons, New York

(29) Mills and Nixon, J.Chem.Soc., 1930, 2510

(30) Lothrop, J.Am.Chem.Soc., 61, 2115 (1939)

(31) Bergmann and Berlin, J.Am.Chem.Soc., 62, 316 (1940)

(32) Branch and Calvin, Op.Cit., p.155

(33) Bury, J.Am.Chem.Soc., 57, 2115 (1935)

(34) Gilman, Op. Cit., p. 1786

(35) O'Shaughnessy and Rodebush, J.Am.Chem.Soc., 62, 2906 (1940)

(36) Smakule and Wasserman, Z. physik Chem., A155, 353 (1931)

(37) Ramart-Lucas and Hoch, Bull.Soc.Chim.,(5), 2, 1376 (1935)

(38) Jones, J.Am.Chem.Soc., 67, 2023 (1945)

(39) Jones, J.Am.Chem.Soc., 67, 2130 (1945)

(40) Lewis and Calvin, Chem.Rev., 25, 273 (1939)

(41) Mulliken, et al., J.Am.Chem.Soc., 63, 41, 1770 (1941)

(42) Watson, "Modern Theories of Organic Chemistry" p.97 (1941) Oxford University Press, London

(43) Watson, Op.Cit., p.90

(44) Jones, J.Am.Chem.Soc., 67, 2141 (1941)

(45) Hayashi and Nakayama, J.Soc.Chem.Ind. Japan, (Suppl. binding) 36, 127 B, (1933)

(46) Van't Hoff, "Die Lagerung der Atome im Raum," (1908) Vieweg und Sohn, Braunschweig

(47) Mills and Maitland, J.Chem.Soc., 1936, 987

(48) Perkin and Pope, J.Chem.Soc., 99, 1510 (1911)

(49) Aschan, Ber., 35, 3389 (1902)

(50) Gilman, Op. Cit., p.341

(51) Clarkson and Gomberg, J.Am.Chem.Soc., 52, 2881 (1930)

(52) Woodward and Doering, J.Am.Chem.Soc., 67, 860 (1945)

(53) Butler and Cretcher, J.Am.Chem.Soc., 55, 2605 (1933)

(54) Rieveschl and Ray, Organic Syntheses, 28, 63 (1948) John Wiley and Sons, New York