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THE USE OF CARBON-14 IN A STUDY OF THE WAGNER REARRANGEMENT

A Doctoral Thesis

Submitted to

THE UNIVERSITY OF FLORIDA

Ben M. Benjamin

Date Issued

JUN 5 1959

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PREFACE

This report is reproduced from a thesis submitted to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The report describes research which was carried out in the Organic Group, Chemistry Division of the Oak Ridge National Laboratory under the direction of Dr. Clair J. Collins. This research was supported by the Graduate Fellowship program sponsored by the Oak Ridge Institute of Nuclear Studies. The fellowship program was guided by a committee consisting of Dr. George B. Butler, Department of Chemistry, University of Florida; Dr. Clair J. Collins, Chemistry Division, Oak Ridge National Laboratory; Dr. L. P. Zill, Biology Division, Oak Ridge National Laboratory; and Dr. Marion T. Clark, Oak Ridge Institute of Nuclear Studies.

The thesis from which this report was taken was approved for the University of Florida by a committee consisting of Dr. George B. Butler, Dr. A. H. Gropp, Dr. C. E. Reid, Dr. T. W. Stearns, and Dr. Mack Tyner.

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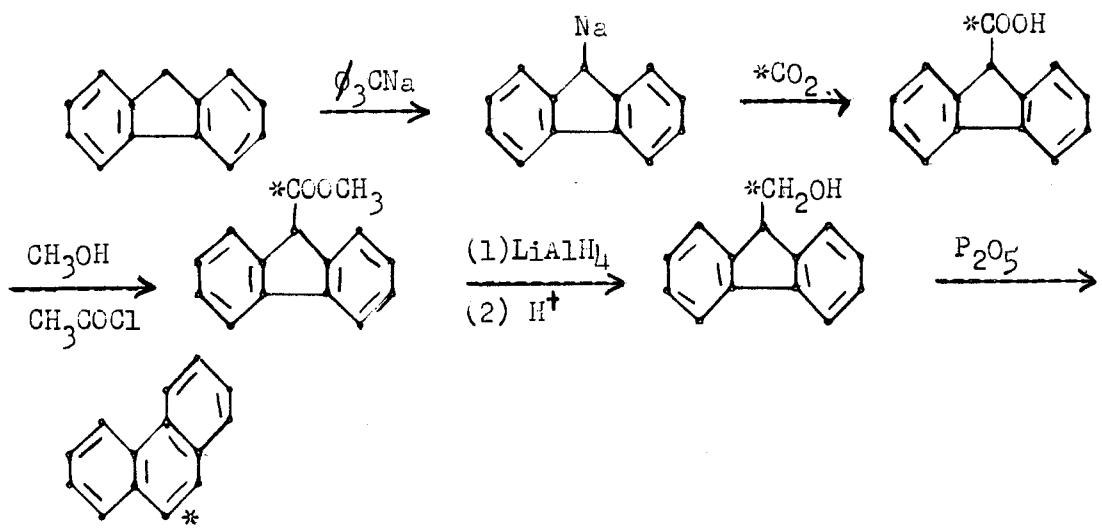
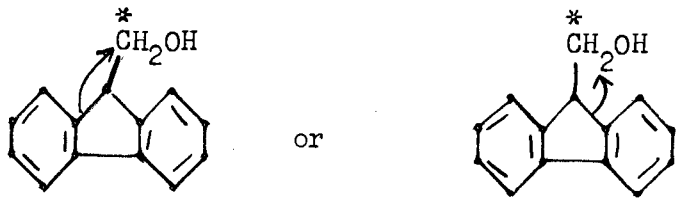
INTRODUCTION

The synthesis of phenanthrene through the Wagner rearrangement of 9-fluorenylcarbinol was reported by Brown and Bleustein[1] in 1940. Eight years later Collins[2] used the procedure to incorporate the radioactive isotope, carbon-14, into this aromatic polynuclear hydrocarbon. Collins prepared phenanthrene-9-C^{14} from 9-fluorenyl-(carbinol-C^{14}) and reported a new synthesis of the latter compound. The following is a schematic diagram of the reactions involved. The asterisk(*) denotes the position of the radioactive carbon.

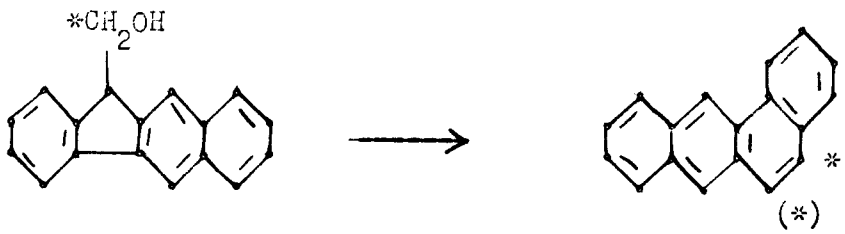


Although rearrangement may proceed by migration of either side of the biphenylene nucleus as indicated by the arrows, the phenanthrene is



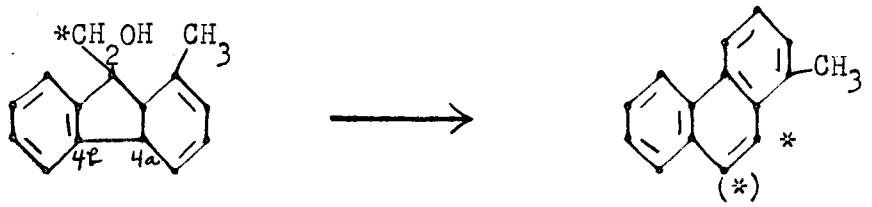
labeled in only one position because the molecule is symmetrical and the 9- and 10-positions are equivalent.

In 1951 Collins, Burr and Hess[3] extended this synthesis to the preparation of carbon-14 labeled benz[a]anthracene through the dehydration rearrangement of 2,3-benzo-9-fluorenyl(carbinol-C^{14}):

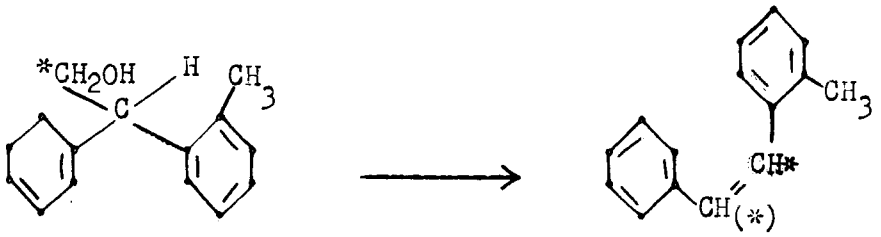


Since the structures of both the carbinol and the hydrocarbon are unsymmetrical, the rearrangement might have proceeded unequally in the two possible ways. A degradative scheme was devised and employed to locate the radioactivity, which was found to be distributed between the 5- and 6- positions in the ratio 48: 52. This difference was thought at that time to be too small to be assigned a significance in the rearrangement tendencies of the carbinol. The experimental results, however, are interesting since they suggest the possibility that certain substituent groups could have a directive influence in the rearrangement of substituted 9-fluorenylcarbinols.

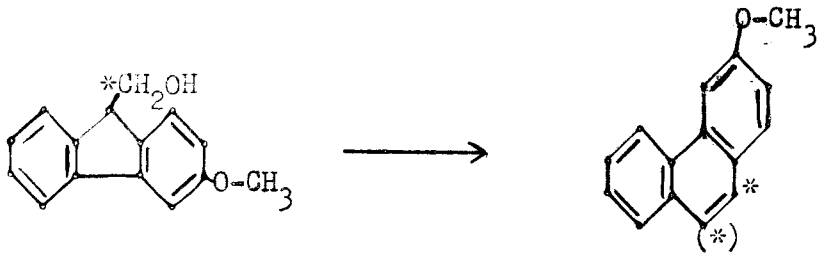
The first objective, therefore, of the research reported here was to study the rearrangement of 1-methyl-9-fluorenyl(carbinol-C^{14}).



By determination of the carbon-14 distribution in the product, 1-methylphenanthrene-9-10-C_1^{14}, it was proposed to examine the directive and steric effects of the o-methyl group. Comparison of these data with the results of the rearrangement of 2-phenyl-2(o-tolyl)ethanol-1-C^{14}, should then allow a quantitative estimate of the effect on the Wagner rearrangement of the biphenylene bond (4a-4b) bond.



A second objective was to examine the influence, on the rearrangement, of such strongly directing groups as p-methoxy by studying the dehydration of 3-methoxy-9-fluorenyl(carbinol-C^{14}).

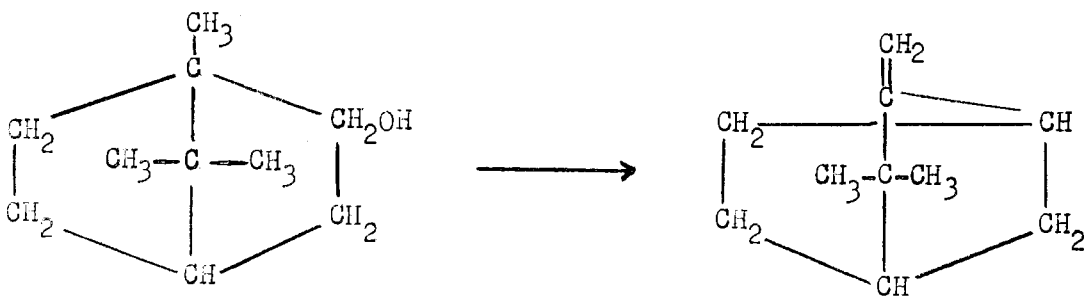


A third objective was to extend the application of this synthetic method of incorporating carbon-14 into aromatic polynuclear hydrocarbons.

The fourth objective was to demonstrate the application of carbon-14 in tracing the course of organic rearrangements.

HISTORICAL NOTES

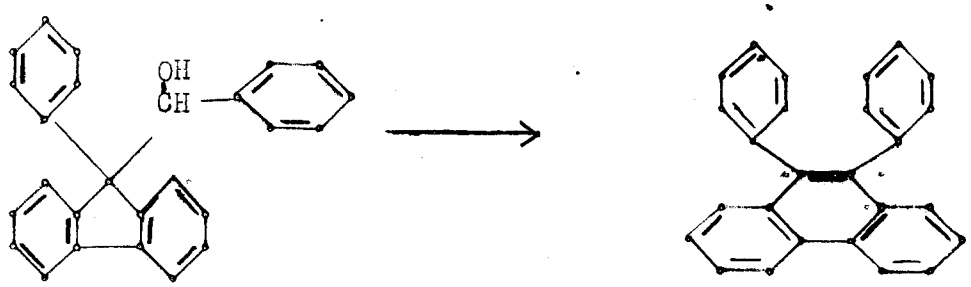
The history of the rearrangement which now bears Wagner's name begins in the last quarter of the nineteenth century. Confusing observations were being recorded in the terpene field by chemists of that time who were obtaining unexpected reaction products when they subjected certain of these terpene alcohols to dehydrating conditions. It was not until 1899 when Georg Wagner published his first paper (4) on the isoborneol-comphene rearrangement that some of this confusion was relieved. Wagner treated isoborneol with a dehydrating agent and isolated as a product a hydrocarbon, camphene, possessing a new carbon skeleton. This transformation Wagner formulated as follows:



Isoborneol Camphene

The reaction, involving a change in ring size, is quite general, and has been known since that time as the Wagner rearrangement.

Meerwein added materially to the scope of the Wagner rearrangement in a series of papers in the early 1900's. He studied changes in rather simple ring systems[5][6][7], including ring expansions from five to six and from six to seven members, and ring contractions from six to five members. Bachmann[8] and Brown and Bleustein[1] also reported very interesting examples of the rearrangement.



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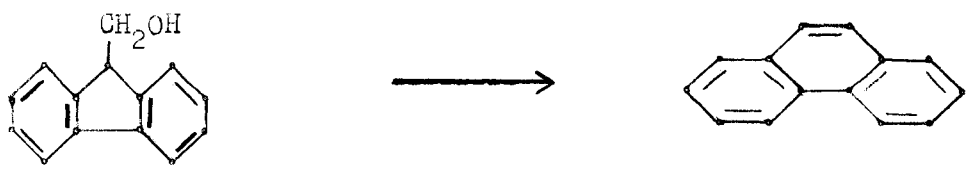
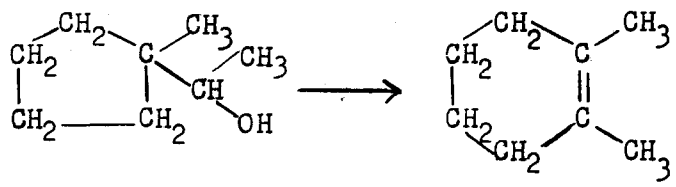


(Ref. 1)

Some of the reaction products result from rearrangements not involving changes in ring size. These structural changes have been caused by the migration of alkyl groups such as methyl (CH_3-), and these changes are occasionally called Meerwein rearrangements. Examples involving the migration of groups other than methyl are taken from the work of Bachmann[8] and Levy[9].



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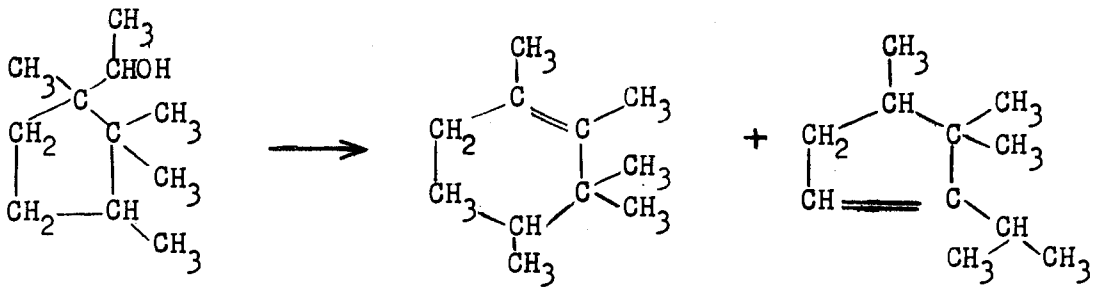

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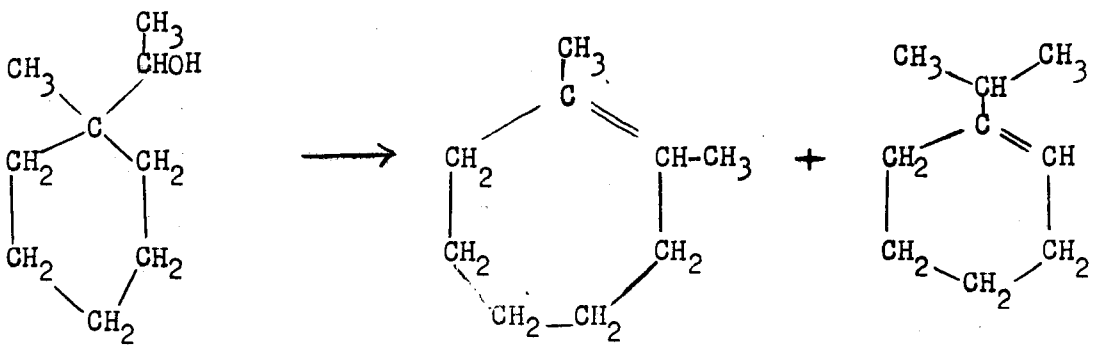

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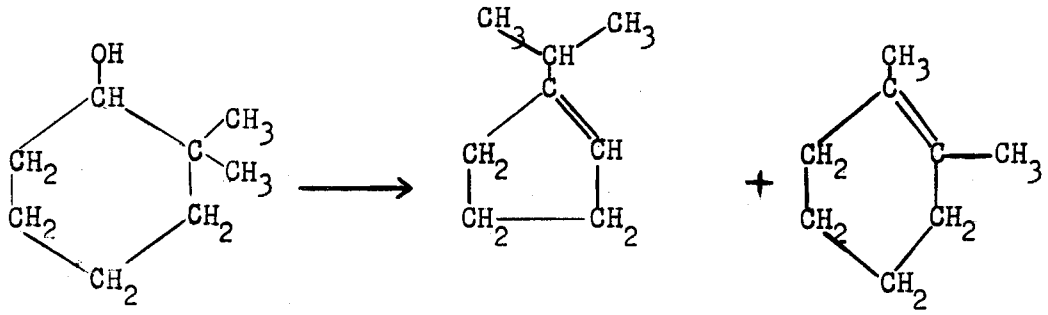

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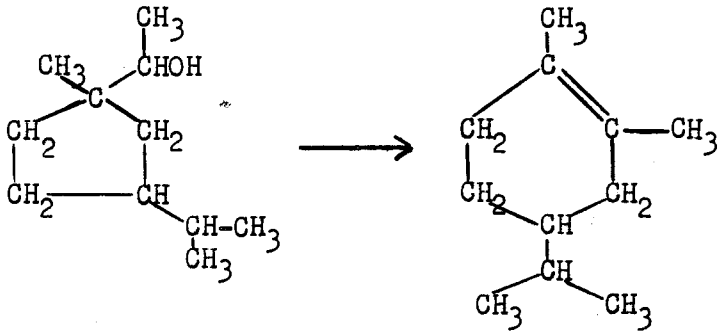

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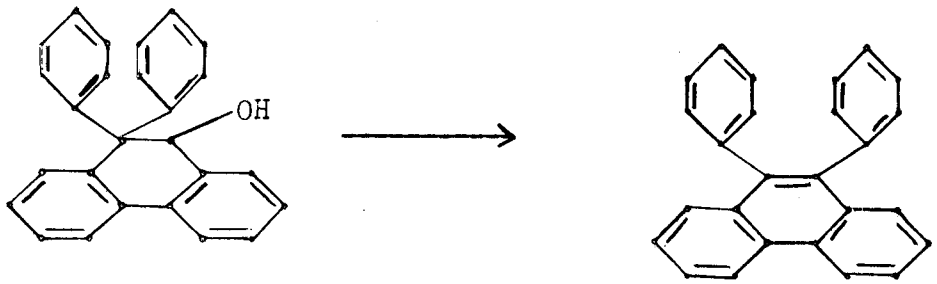

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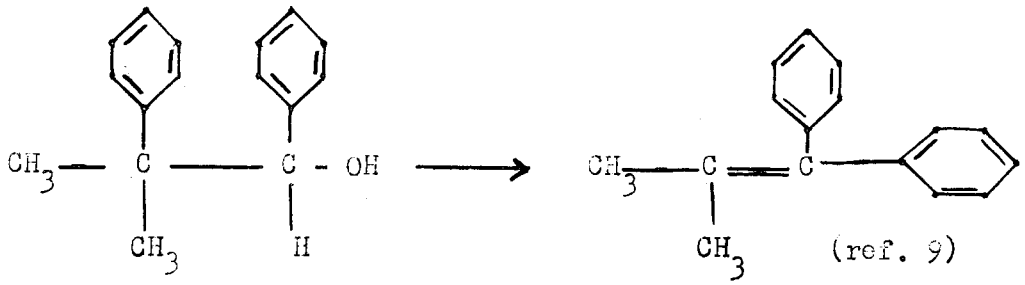

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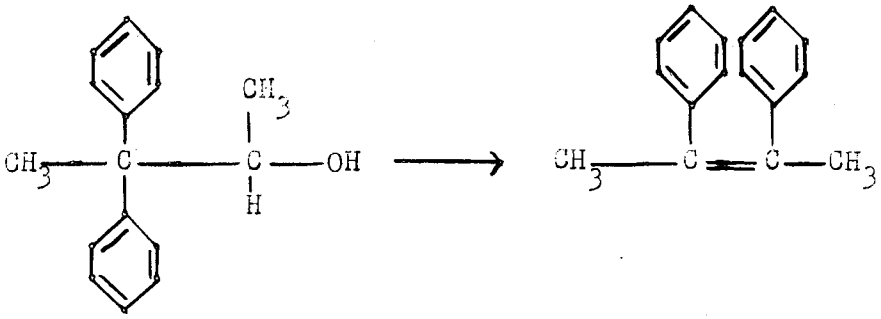
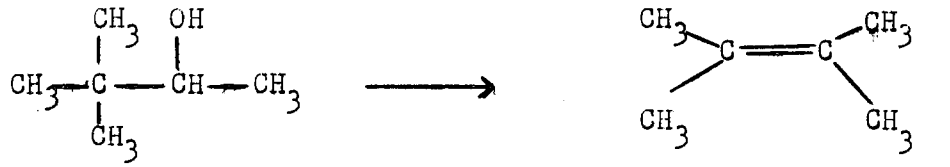


(ref. 9)

Meerwein, in studying the isoborneol-camphene rearrangement compared it with the transformation of methyl(*t*-butyl) carbinol in which tetramethylethylene is formed. This is perhaps one of the simplest examples of the rearrangement. Changes which involve both



Methyl-(*t*-butyl) carbinol Tetramethylethylene

a ring and a methyl group have been called Nametkin rearrangements, although some authors prefer to apply the name "Wagner-Meerwein rearrangement" to all the above examples.

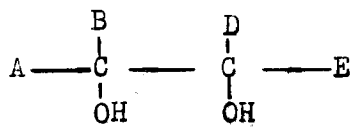
Much information concerning the Wagner rearrangement has been gained through its analogy to the pinacol rearrangement*, a reaction observed by Fittig (11) in 1860. The pinacol rearrangement can be represented by the following equation:

Pinacol Pinacolone

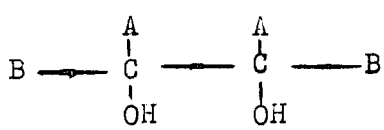
*For a discussion of the pinacol rearrangement and leading references see Ref. (13), (14), and (15).

The analogy was first noticed by Tiffeneau[12] who introduced the word "retropinacol"* and applied this term to the rearrangement of compounds resembling methyl-(t-butyl)carbinol.

If the pinacols substituted with different groups in the molecule are exposed to conditions which cause rearrangement, several products resulting from migration of the different groups are theoretically possible. Which, however, of the four groups, A, B, D, or E, in the following pinacol will migrate?



Bachmann and co-workers[13][14][15][16] have partially answered this question by gathering data for the rearrangements of a series of symmetrical pinacols.



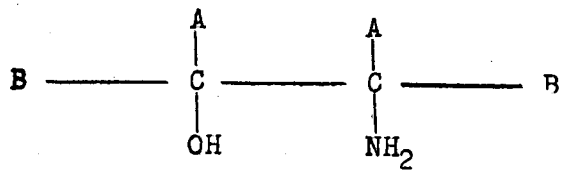
By determining the ratio of the products in the reaction mixtures, it was possible to find out the extent to which various groups migrated. Thus, using this data, the groups were assigned numerical values expressing their migration tendencies and a table of "migratory aptitudes" was compiled. These "migratory aptitudes" could

*The expression "retropinacol rearrangement" has been generally accepted and is used by modern authors such as Whitmore and Wheland as well as the editors of Chemical Abstracts, but it is not used to the exclusion of the term "Wagner rearrangement" with which chemists seem to be more familiar.

be used to predict the amount of migration of each group with unexpected accuracy in symmetrical pinacols not previously studied. The method fails, however, when applied to the rearrangement of unsymmetrical pinacols.

Although chemists were at first impressed with migratory aptitudes, the concept seems to have limited theoretical significance.

For example, the symmetrical pinacols studied by Bachmann have two optically active carbinol carbon positions. These pinacols, therefore, exist as a racemic mixture and a meso form. The spatial relationships of the various groups may differ in each form. Such differences of course, might be expected to influence the extent to which each group migrates. This expectation was found in fact to be valid. Rearrangements of the different forms of o- and m-tolylhydrobenzoins[17], for example, gave different products. Similar results were obtained also for the different forms of p-tolylhydrobenzoin[18]. Curtin and Pollack[19] have obtained data for the rearrangement of the diastereoisomers of 2-aminoalcohols. These, as shown in the formula,

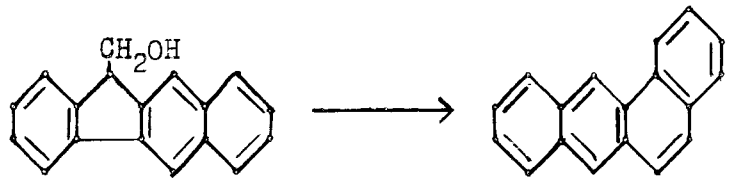


resemble the pinacols very closely. The results of these rearrangements demonstrated conclusively that the tendency of the groups to migrate differs in the various isomers. Smith et al.[20][21] concluded, from data on the Schmidt reaction on substituted benzophenones and acetophenones, that migratory aptitudes did not appear to be an influencing factor in the rearrangement. Smith as well as Szmant and McIntosh[22] thought also that the rearrangement seemed to be affected by steric factors. In applying the Schmidt reaction to substituted diphenylethylenes McEwen[23] and others[24] arrived independently at the conclusion that migratory aptitudes in this series agree qualitatively with those in the pinacol rearrangement.

The conditions under which a rearrangement takes place can also be important in determining the manner in which such a group migrates. Conditions such as the temperature of the reaction, strength and type of the reagent, and characteristics of the group being attacked should be considered. These factors have received attention by Winstein and co-workers[47], but the effects are not yet well understood.

The problem of which group will migrate in the pinacol rearrangement has been mentioned here because the same questions can be asked in the Wagner rearrangement. However, experiments designed to investigate the problem have been made in only one case. Collins, Burr and Hess[3] studied the Wagner rearrange-

ment of 2,3-benz-9-fluorenyl(carbinol-C^{14}) to benzanthracene-5,6-C^{14}_1.



2,3-Benz-9-fluorenylcarbinol Benzathracene

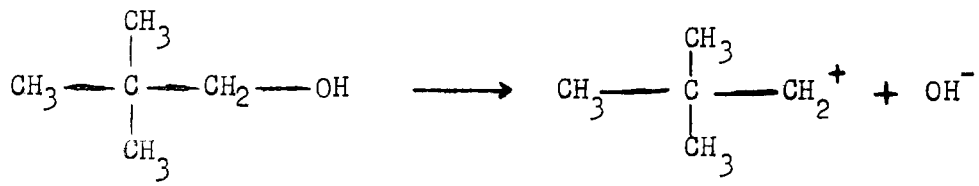
They found that each group migrated almost equally. The experiments of Burr and Ciereszko* on the rearrangement of a series of diarylethanols will give much information concerning the tendency of groups to migrate.

A definite mechanism capable of accounting for all aspects of the Wagner rearrangement has never been written. The reaction has been explained by assuming a variety of intermediates. Among these are intermediates possessing double bonds, cyclopropane rings, bivalent carbon, chelated structures, and true ionic character. Not all these will be discussed because the impossibility of some of them has been demonstrated. Instead the important developments will be outlined.

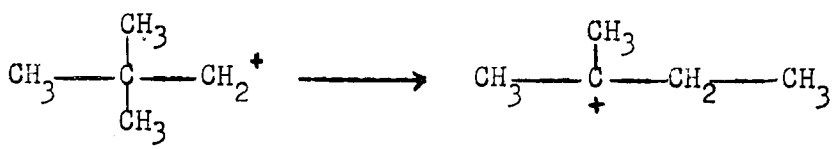
The concept of free carbonium ions as possible intermediates has received rather extensive attention.(25)(26)(27)(28) The formation of such ions can be represented as in the following example:

---

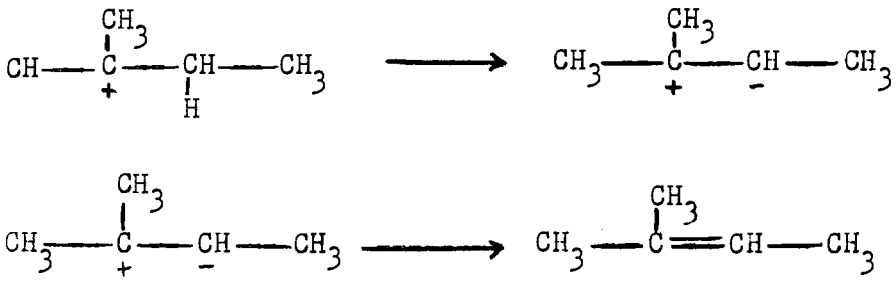
* While this thesis was being written J. G. Burr and L. S. Ciereszko were preparing a paper entitled "Migratory Aptitudes from the Rearrangement of Diarylethanols" for presentation at the Spring Meeting of the American Chemical Society at Milwaukee, March 30, 1952.



In this equation the hydroxyl (-OH) group has been removed from the molecule together with the pair of electrons which bound it to the carbon atom. This carbon is left with a deficiency of electrons and thus it possesses a net positive charge. The primary ion is formulated as a very unstable intermediate which seeks a stable configuration by forcing a methyl group to move from the quaternary carbon to the positively charged carbon.



This explanation implies that the methyl group has migrated with a complete octet of electrons. The result is an ion possessing a rearranged carbon skeleton and a positive charge in a new position. The tertiary carbonium ion formed in this way is said to be more stable than the primary carbonium ion. The process is completed when a hydrogen splits off as a proton and a double bond is formed.



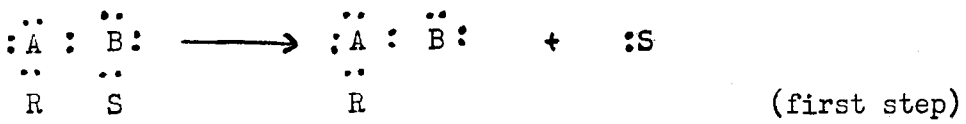
Such mechanisms are doubted now. The activation energy of the rearrangement is not nearly so high as the energy required to break the carbon oxygen bond to form the free carbonium ion*. This step, then, must not be represented correctly. Evidence derived from stereochemical considerations also throws doubt on the formation of a free ion during the rearrangement. This evidence will be presented later.(pp. 18-19).

Probably the most important development toward an understanding of the mechanism was the theory proposed by Whitmore[29] in 1932. A thorough discussion of the theory is found in Wheland's[15] book Advanced Organic Chemistry.

It is customary to represent the reaction in a sequence of steps using the following general symbols:[29]

---

* This statement is based on studies in the quantum theory of reactions as applied by Heitler and London as well as Eyring et al. A brief presentation of the subject can be found in M. J. S. Dewar, The Electronic Theory of Organic Chemistry, Oxford University Press, Amen House, London (1949) pp. 25-30.

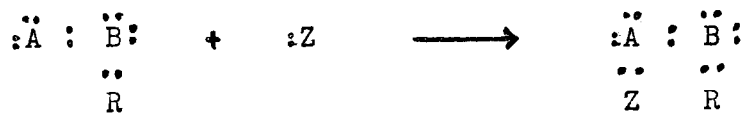


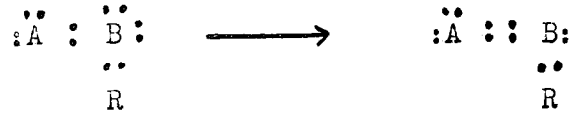
(first step)

In the first step the group :S either splits off spontaneously or is pulled off by interaction with some reagent. As :S leaves, it takes with it the pair of electrons which bound it to the molecule. This results in an unstable intermediate with only six electrons in the valence shell of one of the atoms.

(second step)

In the second step rearrangement takes place. The instability of the intermediate is partially relieved by migration of the group R. Whitmore believed that the two electrons binding R to the molecule moved from A to B and that R moved with them. In the final step one of two things can happen. Either some group :Z in the reaction mixture adds to A, or a further fragment splits off and a double bond is formed.





(third step)

As presented, this mechanism closely resembles the mechanism involving a free carbonium ion. However, Whitmore[29] pointed out that the steps need not occur in the order outlined. Two or all three of the steps may occur at the same time. The strain is then relieved by resonance in the intermediate stages. No free ions are suggested. In fact, Whitmore draws no conclusion regarding the identity of the intermediate stages.

Identification of the intermediate as a true carbonium ion is extremely doubtful from stereochemical considerations. In the rearrangement of optically active carbinols[30][31] a Walden inversion occurs at the carbon atom originally bearing the hydroxyl group. A Walden inversion also occurs at the carbon atom originally bearing the migrating group. Wallis and co-workers* have shown that intramolecular rearrangements of compounds containing asymmetric carbon atoms proceed without optical racemization of the migrating group. Lane and Wallis[33] concluded that optical activity of the migrating group is not only retained during rearrangement but that the group does not suffer a Walden inversion. If true free carbonium ions existed in the above cases, complete racemization might be expected to occur.

Cram and co-workers[34][35] devised systems to study stereochemical transformations occurring at both the carbon atoms to which and from which migration takes place; for example, the acetolysis of the

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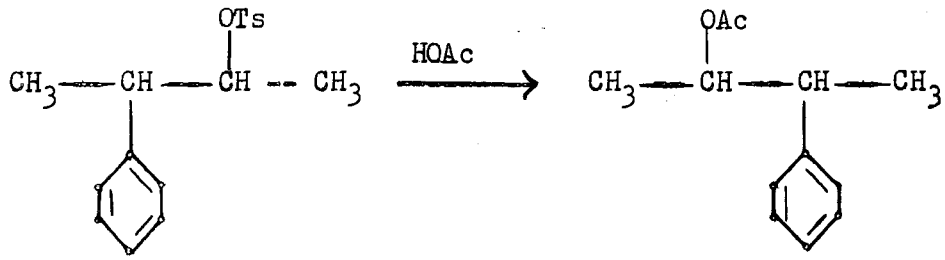
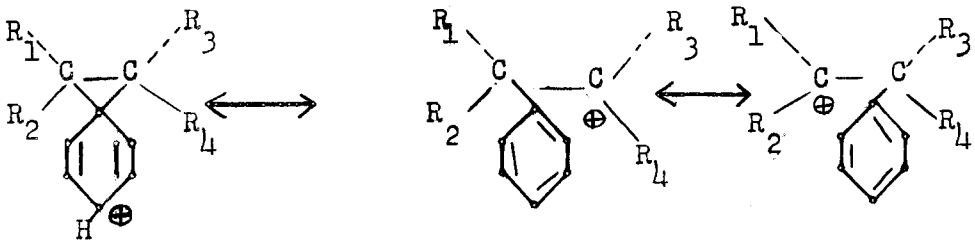
*See ref. (33) for a summary of the literature on this subject.

p-toluenesulfonates of the optically pure stereoisomers of 3-phenyl-2-butanol. The reaction which takes place is



By the use of such systems Cram demonstrated that optical activity was retained at both asymmetric carbon atoms. An inversion occurs at the carbon bearing the oxygen bond when the reaction begins and another inversion occurs at the carbon bearing the phenyl bond during completion of the reaction. The results are interpreted as evidence for an intermediate cyclopropane-like structure. Cram uses the phrase "unequivocally demonstrated the existence of .... a carbocyclic three-membered carbonium ion as an intermediate in a Wagner-Meerwein rearrangement". He writes that the cyclic ion exists as resonance hybrids of the structures shown below:



Whether the intermediate is an ion is subject to discussion. Although Cram's evidence seems to indicate a distinct free intermediate, this does not necessitate its being an ion. The entire reaction may take place all together in a concerted process. The intermediate then could be pictured as a molecule containing all of the reacting entities with the migrating group bound in some way to the two carbon atoms involved. Direct evidence for a concerted mechanism in the Wagner rearrangement is lacking. Concerted mechanisms, however, have been demonstrated in reactions previously thought to occur through ionic intermediates. Swain[36][37] has obtained kinetic evidence for concerted displacement reactions. He investigated the mechanism of the solvolytic displacement of halogens in methyl halides and triphenylmethyl halides. The reaction rates were studied by allowing the reaction to take place in inert solvents containing stoichiometric amounts of the reagents. Thus, the true kinetics of the reactions were obtained and the data indicated a termolecular mechanism. This is related to the Wagner rearrangement in that the group being removed is actually being displaced by the migrating group rather than by some other reagent in the reaction mixture.

The difference between the Wagner rearrangement and solvolytic displacement reactions is thought to involve the degree of freedom of the intermediate rather than the kind of intermediate. This is apparent in the similarity of the mechanism written by Swain for

solvolytic displacement reactions and that written by Winstein[47] for rearrangement reactions. Winstein has reported, in his latest series of papers[47][48][49][50][51], kinetic studies which were designed to determine the degree of participation of various substituent groups in Wagner rearrangements.

Very recently Ronald F. Brown and coworkers have studied the pinacol rearrangements of cis- and trans- 1,2-diphenyl-1,2-acenaphthenediol[72] in a variety of solvents. These authors have concluded that the transition-state complexes in these rearrangements can best be formulated as free carbonium ions rather than as the carbocyclic (or π-complex) intermediates of Cram[34][35] and Lane and Wallis[33].

It is obvious from this discussion of the history of the Wagner rearrangement that the application of tracer techniques to this very important reaction is capable, at least in theory, of providing us with information which can be obtained in no other way. In the section which follows examples will be discussed which will illustrate how some of this new information has been obtained.

DISCUSSION OF EXPERIMENTAL METHODS AND RESULTS

The Use of Carbon-14

The application of isotopes of carbon to organic chemical research has received increasing attention in the past few years. The increase in the number of papers published on the use of the radioactive isotope, carbon-14, is especially noticeable. Three excellent reviews of the subject have appeared within the last two years. One [38] deals with synthetic accomplishments, and the other two [39][40] with the study of reaction mechanisms.

Carbon-14 is now available in sufficient quantities that it need no longer be considered a curiosity. Many compounds labeled with carbon-14 are obtainable commercially and the number and variety of these compounds are constantly being augmented.

The incorporation of carbon-14 into an organic compound renders the compound a valuable tool for studying reactions. For example, it can be considered as putting a label on a particular carbon atom in the compound. Then, when the compound has been submitted to various reactions, the position of this carbon atom can be traced by means of its label. The technique of finding the position of the labeled atom is accomplished, when using carbon-14, by degradation of the molecule and assay of the degradation products for the amount of radioactivity in them. Such a procedure is essential to studying some

reactions. For example, it is possible for some reactions to take place by two different clearly defined paths to give the same product. If the starting material is labeled in the proper position with carbon-14, the path of the reaction can be determined by the position of the label in the product. This is, in fact, the case in the research reported here. Without the use of carbon-14 or one of the other isotopes of carbon these studies could not have been made.

Laboratory Techniques

The use of carbon-14 in the laboratory presents a number of problems not ordinarily met in other organic research. Experiments must be carried out in such a way that none of the material used is allowed to come into contact with laboratory personnel. During the course of the research reported in this thesis, reaction mixtures were placed in completely closed glass apparatus, and the apparatus was set up in well-ventilated hoods. The practice of using shielding with radioactive materials is unnecessary with carbon-14 since the beta-ray emitted is extremely weak. It has a range of about 6 cm. in air, and it can not penetrate the walls of ordinary glass apparatus. It is not necessary to avoid handling the glass apparatus containing the radioactive carbon provided care is exercised in preventing outside contamination.

The common starting material for preparing all carbon-14 labeled organic compounds is barium carbonate-C^{14}* from which carbon-C^{14} dioxide

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* Barium carbonate-C^{14} and sodium cyanide-C^{14}, derived from barium carbonate-C^{14}, used in this research were obtained from Operations Division, Oak Ridge National Laboratory.

may be obtained. This necessitated lengthy and time-consuming procedures to obtain the compounds desired. In carrying out this research a considerable amount of time was spent on non-radioactive model experiments in order to become familiar with the techniques involved. In this way the yields could be improved and the characteristics of the reactions and compounds could be determined before using the expensive radioactive material. This was done not only in consideration of economy but also to avoid having unfortunate accidents with the radioactive compounds.

Special apparatus was used only when working with a high level of activity or when working with gaseous or volatile compounds. Diagrams of the high-vacuum line, continuous extraction apparatus, and pipetting device with descriptions of their use, are in the experimental section. When working with compounds of low activity, ordinary apparatus was satisfactory. It was found very convenient, however, to use the continuous extraction apparatus for a large number of reactions thereby avoiding yield losses which frequently occur in normal laboratory procedures for transferring materials. Final purification of solid compounds for analysis was carried out by the usual methods of crystallization and filtration.

Glass apparatus which had been used for high level of radioactivity was cleaned, before subsequent use, by immersing it in sulfuric acid, which had been heated to 180°, until all organic matter was decomposed. Compounds were thereby protected from changes in radioactivity owing to contamination from the apparatus.

In a series of reactions, the purity of the products could usually be determined by their millimolar radioactivities provided no dilution had occurred. Solids, of course, are easier to work with than liquids; therefore, liquid compounds were converted to solid derivatives before purification and assay.

Carbon-14 Assay Methods

A number of carbon-14 assay methods have been described[41]. The most convenient, accurate, and reproducible method known at present is the one using the Vibrating Reed Electrometer[42][43]* for measuring the ionization current of gaseous carbon-C^{14} dioxide. The radioactive organic sample to be assayed is usually converted to carbon-C^{14} dioxide by wet combustion. The wet combustion method, which is an adaptation of the procedure employed by Van Slyke, Folch, and Plazin[44] for biological samples, is described by Neville[45]. Other adaptations of the method are also described[46]. Its main advantages over dry combustion with oxygen, and other methods[41], are the rapidity with which a determination can be carried out and the simplicity of manipulating the apparatus. Wet combustions have been applied successfully with various designs of the combustion apparatus. A design of one variation of the combustion apparatus and an explanation of its use are given in the experimental section.

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* Vibrating Reed Electrometers and ionization chambers can be purchased from the Applied Physics Corporation, Pasadena, California.

General Remarks

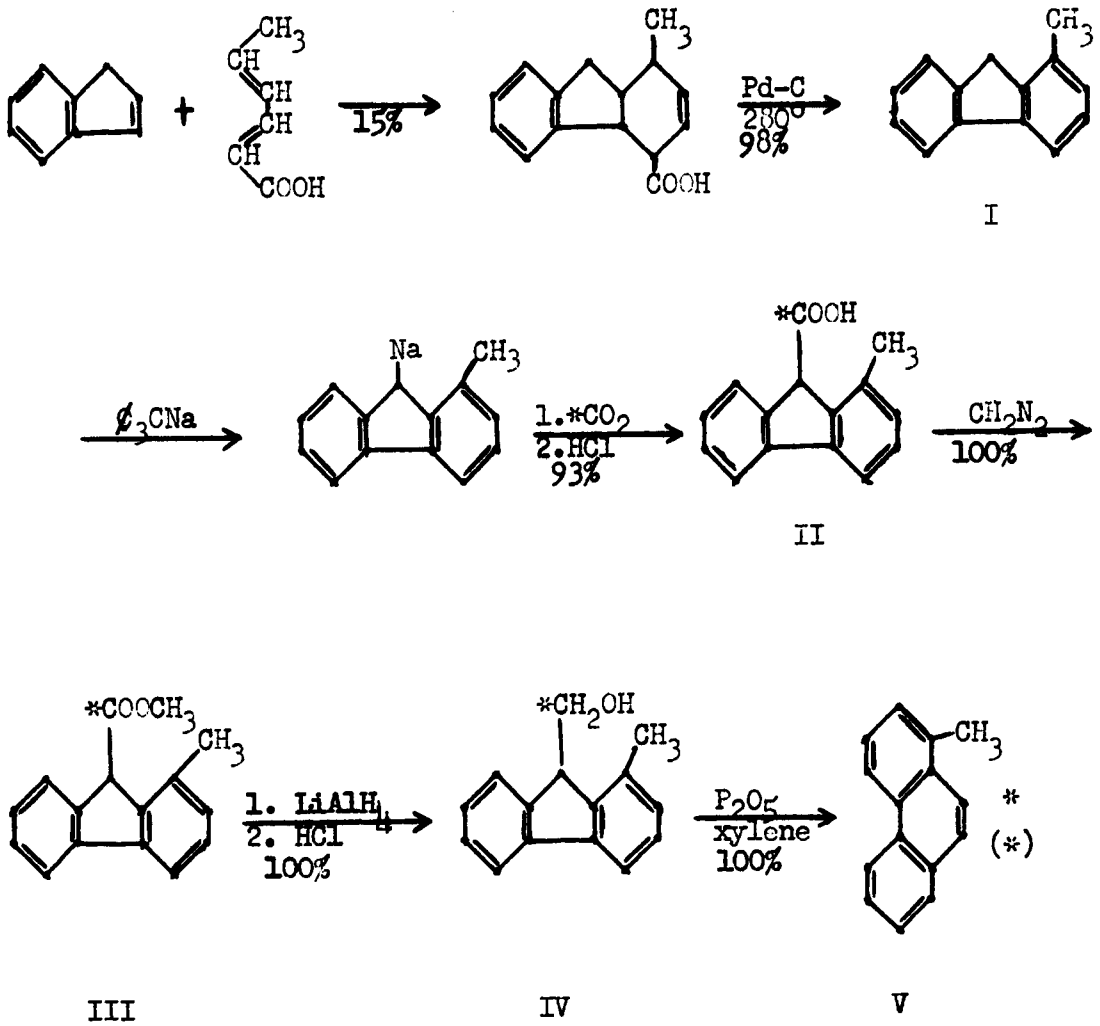
Though the procedures were carefully worked out with non-radioactive material, only the procedures involving the radioactive compounds will be described in the experimental section. The descriptions of the procedures are sufficiently detailed to permit their accurate repetition.

Because of the lengths of the chemical names of some of the compounds, each compound will be assigned a Roman numeral. These numerals will be used in the flow sheets and in the discussion wherever their use will not sacrifice clarity.

Rearrangement of 1-Methyl-9-fluorenyl(carbinol-C^{14})

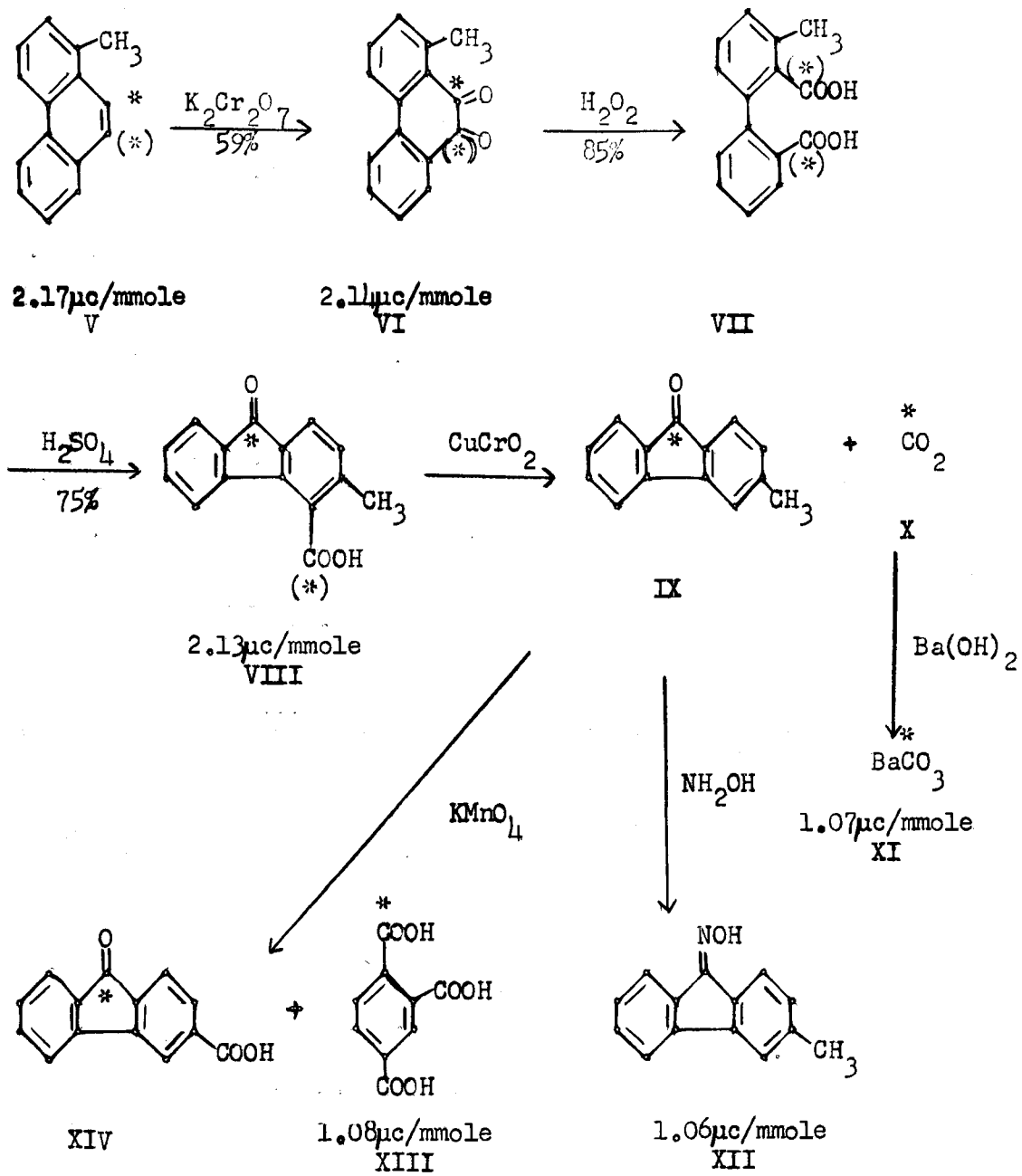
A schematic diagram of the procedures used to prepare and rearrange 1-methyl-9-fluorenyl(carbinol-C^{14}) [IV] is given in Flow Sheet I on the following page. Reagents and yields are recorded. The rearrangement of the carbinol IV was carried out with phosphorous pentoxide in boiling xylene to give 1-methylphenanthrene-9,10-C_1^{14} [V] . The scheme used for the degradation of V is outlined in Flow Sheet II. The degradative scheme was designed to separate into different molecules the carbon atoms originally in the 9- and 10- positions of V. Yields and millimolar activities of the compounds are recorded.

In compounds V, VI, VII, and VIII two carbon atoms are marked with an asterisk, one asterisk being enclosed by parentheses. This is explained in the following way: The rearrangement of the carbinol IV



FLOW SHEET I

Synthesis and Rearrangement of 1-Methyl-9-fluorenyl-(carbinol-C^{14})



FLOW SHEET II

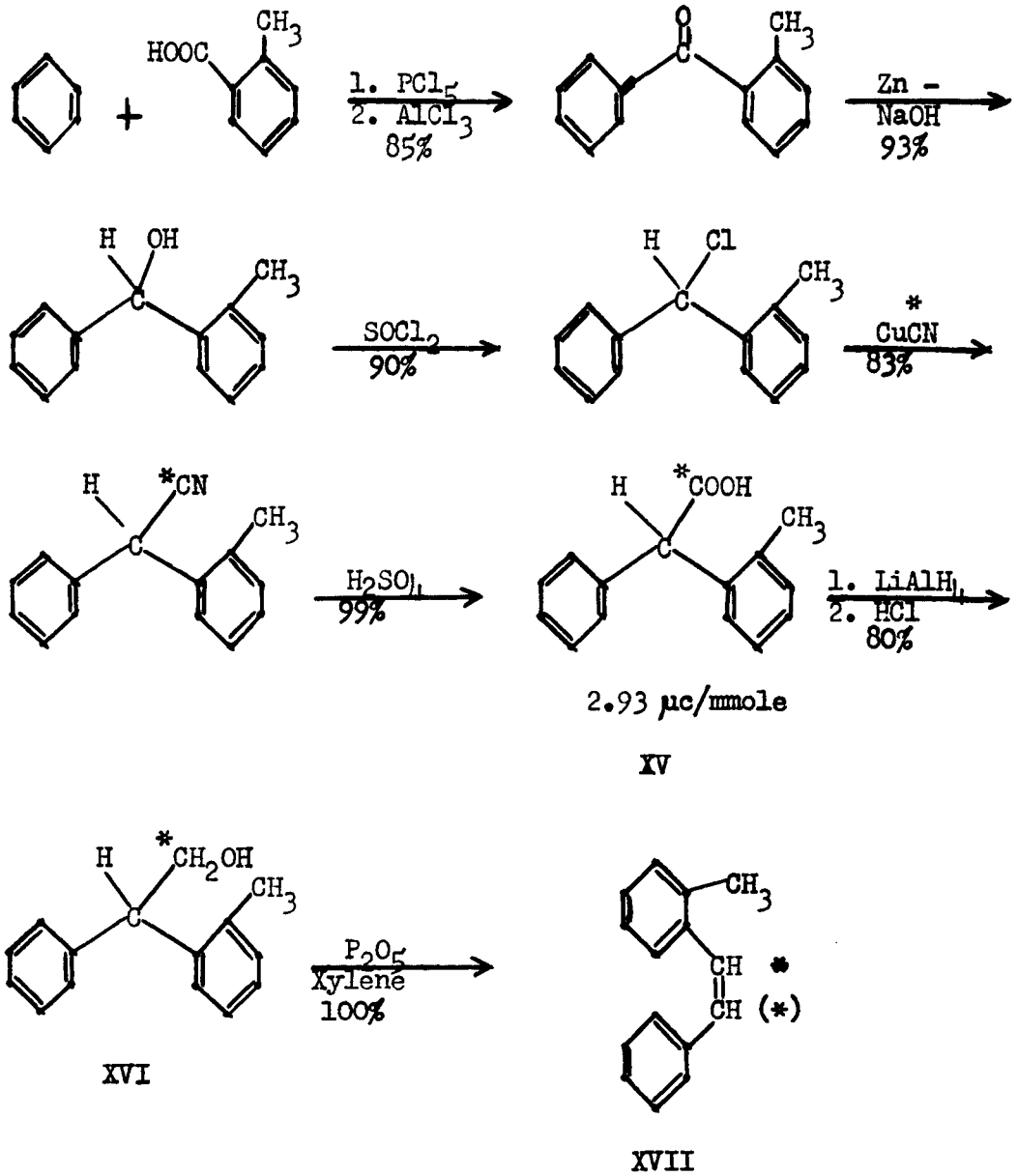
Degradation of 1-Methylphenanthrene-9,10-C_1^{14}

has taken place by migration of both the phenylene and the o-tolylene groups. Therefore, compound V and its descendent compounds, VI, VII, and VIII, consist of mixtures of molecules each one of which is labeled in only one of the two positions marked.

The three labeled compounds, 1-methylphenanthrenequinone [VI], 3-methyl-diphenyl-2,2'-dicarboxylic acid [VII], and 3-methylfluorenone-4-carboxylic acid [VIII], contain the carbon atoms from both the 9- and 10-positions of V. Decarboxylation of VIII removes from it, as carbon dioxide-C^{14} [X], the carbon atom originally present in position 10 of compound V. The radioactivity of the 3-methylfluorene-9-C^{14}-one [IX], then, represents the carbon-14 originally in the 9-position of V. The carbon dioxide-C^{14} [X] was assayed as barium carbonate-C^{14} [XI]. A portion of compound IX was oxidized to trimellitic acid-C^{14} [XIII] and a second portion was converted to the oxime XII. It is obvious from the activities of XI, XII, and XIII, 1.07, 1.08, and 1.06 microcuries per millimole of carbon-14, respectively, that in the rearrangement of the carbinol IV, the phenylene and o-tolylene groups migrated with equal frequency.

Rearrangement of 2-Phenyl-2-(o-tolyl)ethanol-1-C^{14}

The synthetic method employed in the preparation and rearrangement of 2-phenyl-2-(o-tolyl)ethanol-1-C^{14} [XVI] is outlined in Flow Sheet III. Upon rearrangement of XVI, labeled o-methylstilbene [XVII] was formed. This



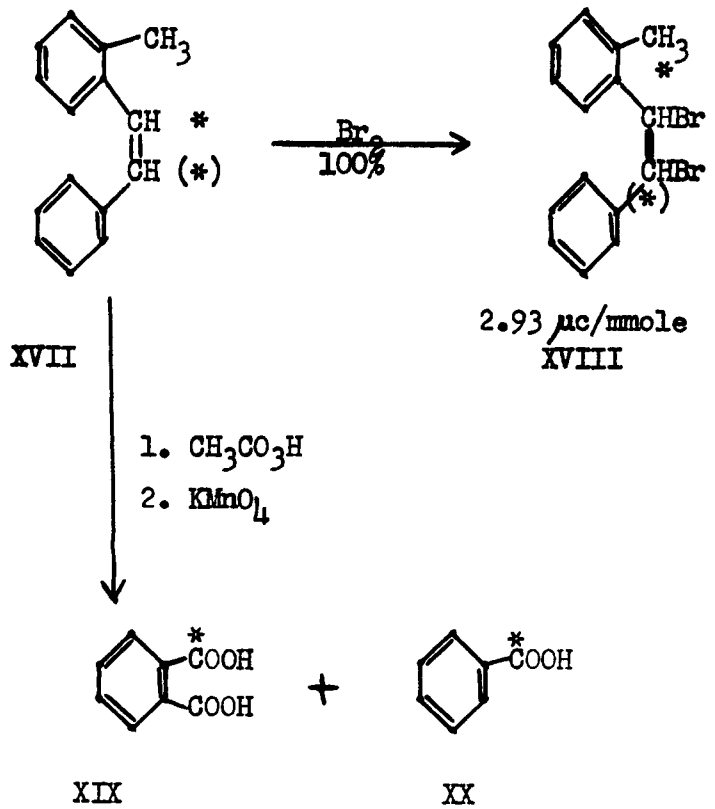
FLOW SHEET III

Preparation and Rearrangement of 2-Phenyl-2-(o-tolyl)-ethanol-C^{14}

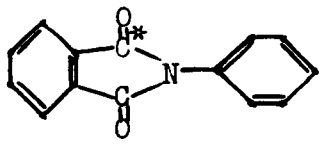
compound is an oil and, therefore, was converted to labeled o-methylstilbene dibromide [XVIII] for assay. The bromination step and degradative steps are shown in Flow Sheet IV. The radioactive o-methylstilbene [XVII] was oxidized in two steps to a mixture of benzoic acid-C^{14} [XX] and phthalic acid-C^{14} [XIX]. The origin of the benzoic acid-C^{14} is uncertain and its activity is not significant. Phthalic acid-C^{14} [XIX] which originates in the tolyl group of the carbinol XVI and the methyl stilbene XVII was assayed as phthalanil [XXI]. The data from the assays of XV, XVIII, and XXI indicates that the ratio of migration of the phenyl and o-tolyl groups of carbinol XVI is 55:45, respectively.

Rearrangement of 3-Methoxy-9-fluorenyl(carbinol-C^{14})

The preparation of 3-methoxy-9-fluorenyl(carbinol-C^{14}) [XXV] is outlined in Flow Sheet V; the rearrangement of XXV and degradation of the 3-methoxyphenanthrene-9,10-C_1^{14} [XXVI] derived from it are outlined in Flow Sheet VI. The methoxy group of XXVI was split by interaction with hydriodic acid to give 3-hydroxyphenanthrene-9,10-C_1^{14} [XXVII]. Oxidation of XXVII gave phthalic acid-C^{14} [XXVIII] which was converted to phthalic dianilide [XXIX] for assay. The radioactivity of XXIX, 0.03 microcuries of carbon-14 per millimole, represents the carbon-14 originally present in the 9-position of XXVI. Therefore, the ratio of the migration of the methoxyphenylene and the phenylene groups of XXV is 98:2.



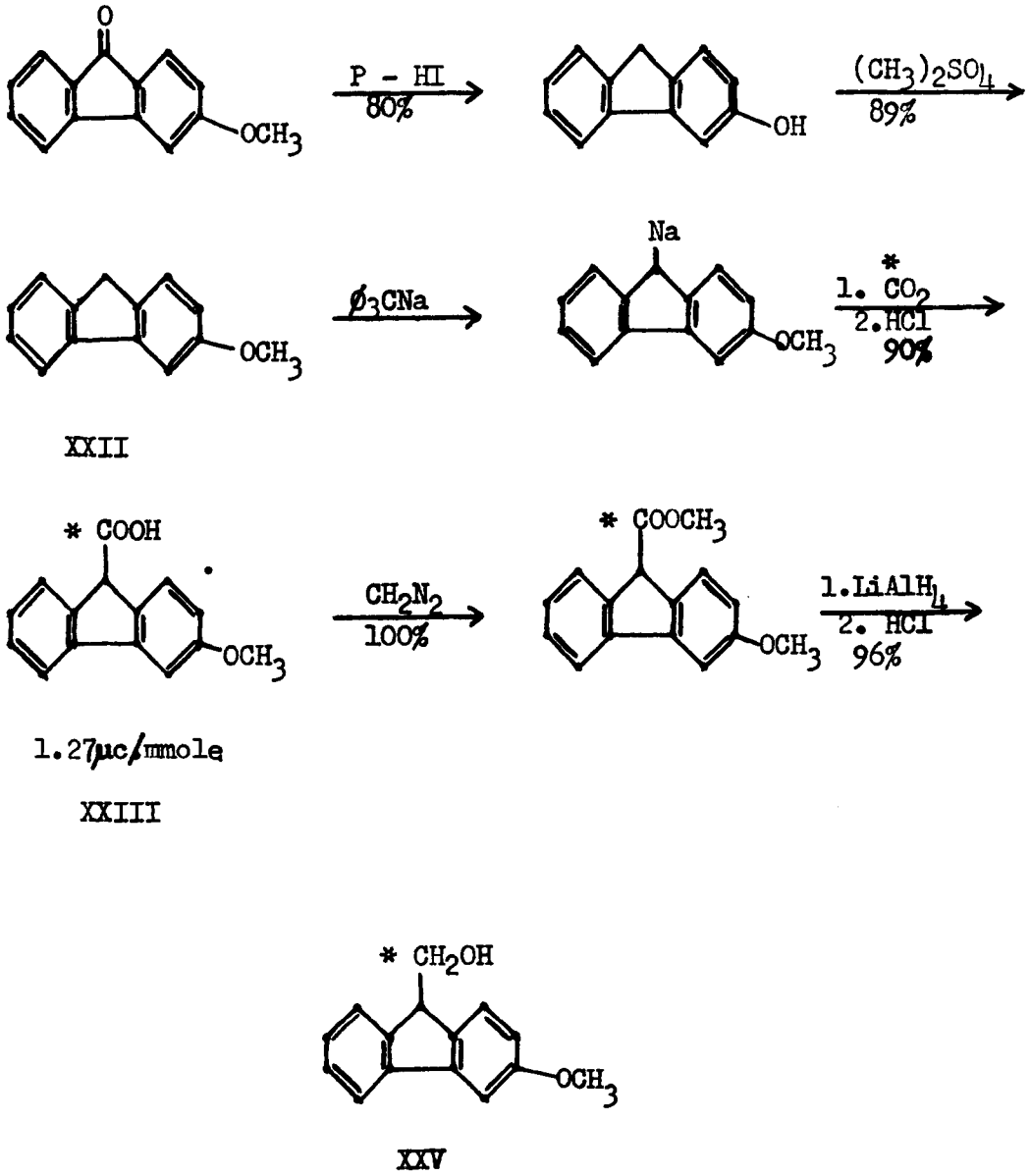
Aniline



1.32µc/mmole
XXI

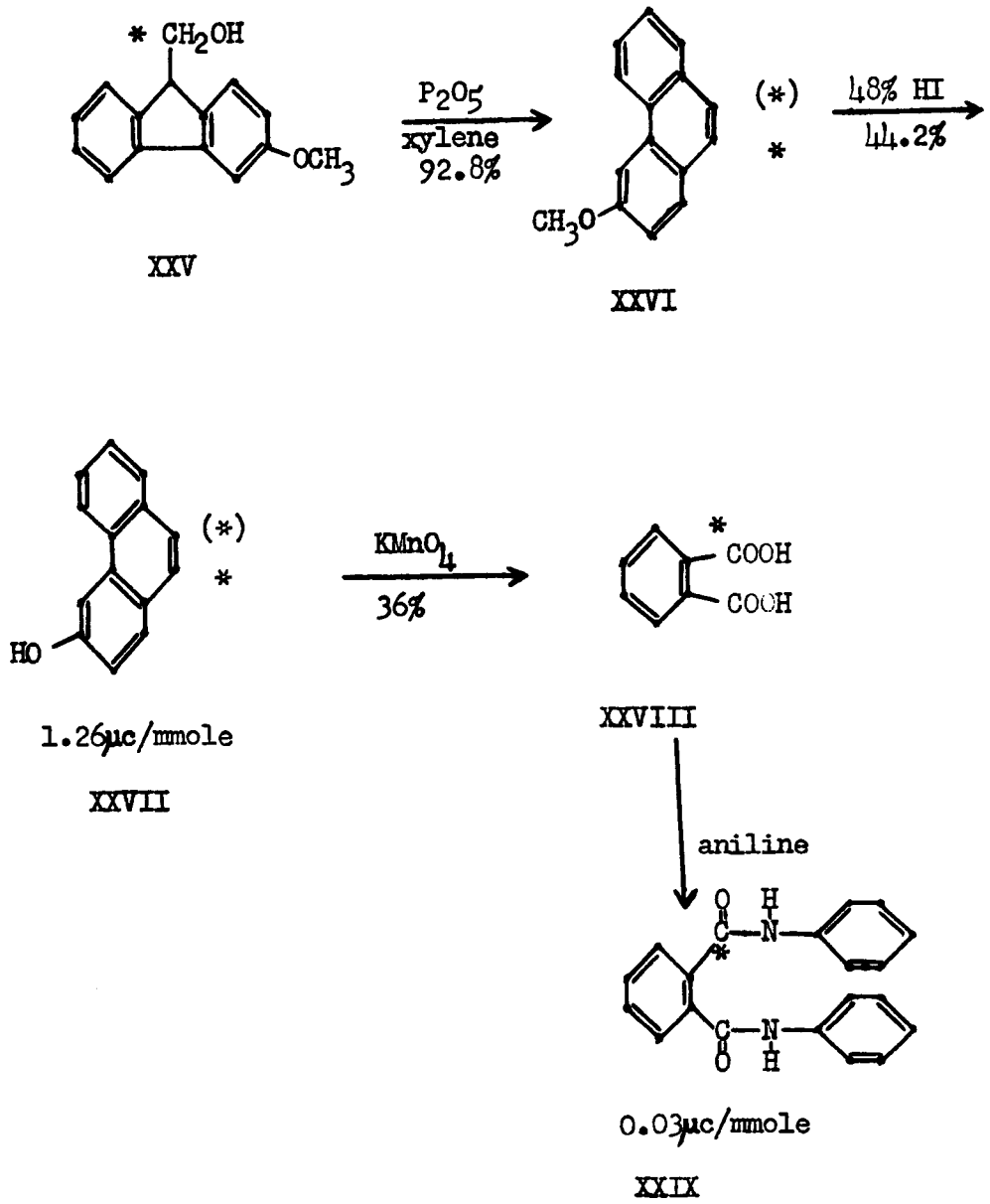
FLOW SHEET IV

Degradation of o-Methylstilbene-α,α'-C_1^{14}



FLOW SHEET V

Preparation of 3-Methoxy-9-fluorenyl-(carbinol-C^{14})



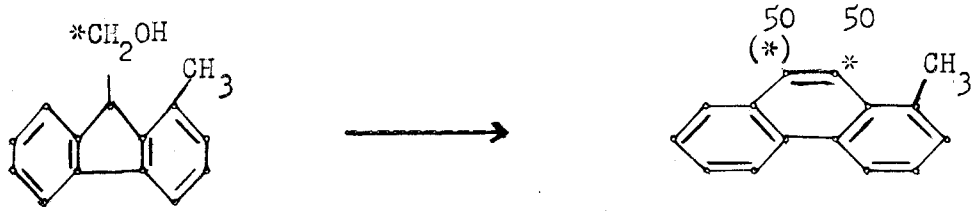
FLOW SHEET VI

Rearrangement of 3-Methoxy-9-fluorenyl-(carbinol-C^{14}) and Degradation of 3-Methoxyphenanthrene-9,10-C^{14}_1

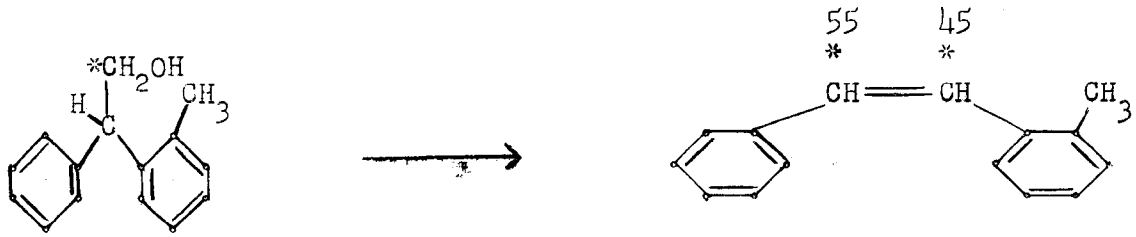
THEORETICAL DISCUSSION

Research Reported in This Dissertation

Upon treatment of 1-methyl-9-fluorenyl(carbinol-C^{14}) [IV] with a dehydrating agent the rearranged product, 1-methylphenanthrene-9,10-C_1^{14} [V], contains equal amounts of carbon-14 in both the 9- and 10-positions. This equal distribution of carbon-14 indicates that the phenylene and o-tolylene groups in IV migrate in the ratio of 50: 50. Comparing this data with the ratio of migration of the phenyl and o-tolyl groups, 55: 45, when 2-phenyl-2-(o-tolyl)ethanol-1-C^{14} [XVI] is rearranged gives a quantitative estimate of the effect of the biphenylene bond in IV.



IV V

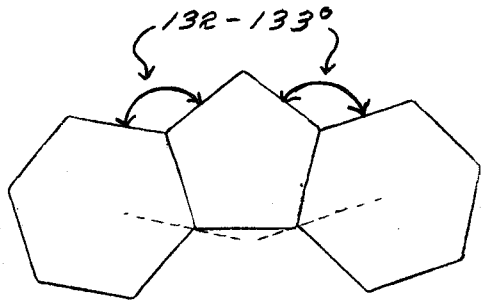


XVI XVII

The difference in the two ratios is clearly beyond the limit of error inherent in the carbon-14 assay method; however, the difference is so small that it alone is not completely definitive of the effects taking place. Nevertheless, in view of other evidence of co-workers in the laboratory, the data will be interpreted as a consequence of a steric effect of the o-methyl substituent.

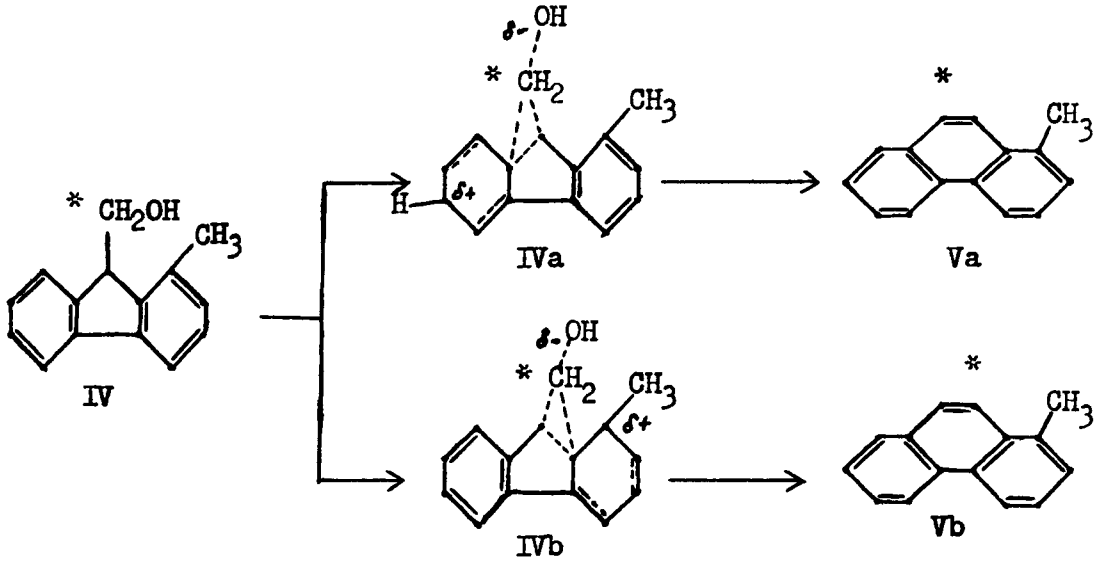
Inspection of a Fisher-Hirschfelder molecular model of XVI reveals that there is considerable steric interaction between the methyl substituent and the carbinol portion, as well as other portions, of the molecule. This steric interference prevents, to a large extent, the tolyl group from rotating about the bond connecting it to the central carbon atom while the phenyl group is more free to rotate. The phenyl group, therefore, can assume more positions favorable to migration than can the o-tolyl group.

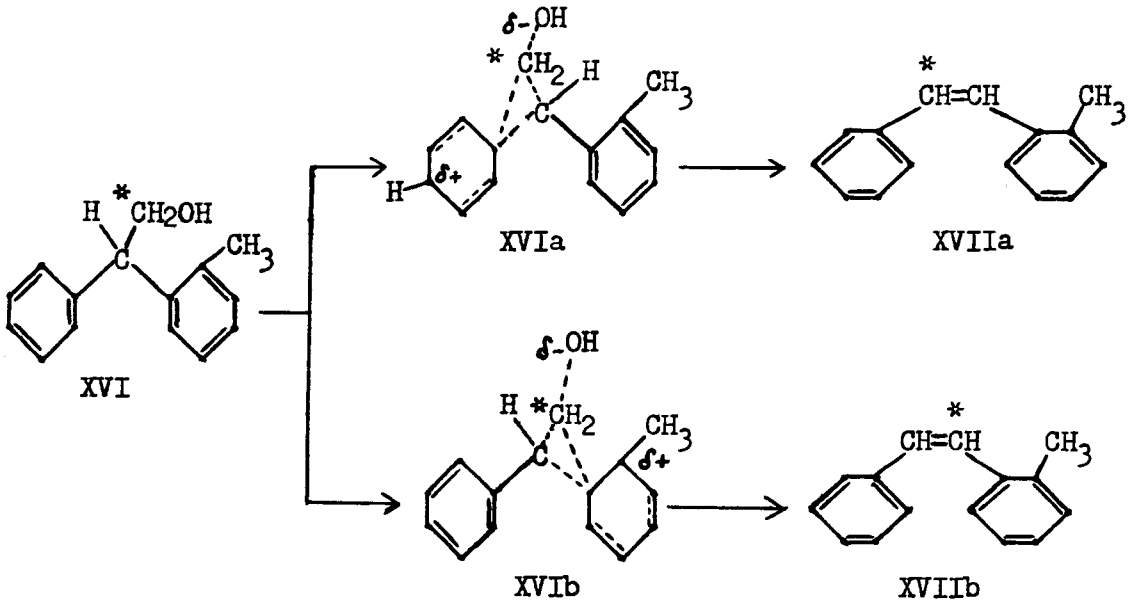
In 1-methyl-9-fluorenyl(carbinol-C^{14}) [IV] the phenylene and o-tolylene groups cannot rotate because they are held in a fixed position by the biphenylene bond. Also, as a consequence of the presence of the five membered ring, which is nearly a regular pentagon (73) the normal valence angles (120°) of the benzene rings are distorted by 12°-13° (73).



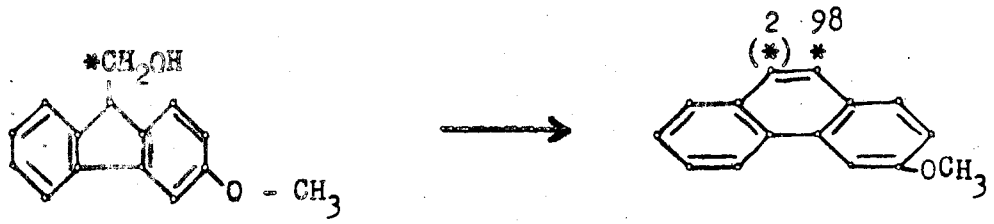
This distortion of the valence bond angles holds the o-methyl group far enough away from the carbinol group to reduce steric interaction between these two groups. In molecular models of the carbinol IV the steric interaction between the methyl and carbinol groups appears to be neglibible and the rearrangement of IV can proceed without the steric effect which is present in carbinol XVI.

The intermediate structures of the rearrangement process are formulated as being similar to the transition states written by Cram and Swain[36]. While the hydroxyl group is being removed, a three-carbon cyclic structure is being formed by the migrating group and the carbon atoms from which and to which migration is taking place. This is in agreement with the concept of a push-pull mechanism in which the migrating phenyl group aids in removal of the hydroxyl group. No restriction is placed on the degree to which the old bonds are broken while the new ones are being formed. This undoubtedly depends on the nature of the substituent groups. By formulating the mechanism in this way, the rearrangements are represented as proceeding by two paths, one involving tolyl, or tolylene, migration and the other involving phenyl, or phenylene, migration. Whereas the intermediate XVIa is less important than XVIb because of the steric effect of the methyl group, the absence of a similar steric effect in IV gives equal importance to IVa and IVb.


δ- OH
* CH2
CH3
H
δ+
IVa
Va
* CH2OH
CH3
IV
δ- OH
* CH2
CH3
δ+
IVb
Vb


δ- OH
* CH2 H
CH3
C
H
δ+
XVIa
* CH=CH
CH3
XVIIa
H * CH2OH
C
CH3
XVI
δ- OH
H * CH2
C
CH3
δ+
XVIb
* CH=CH
CH3
XVIIb

In the rearrangement reaction of 3-methoxy-9-fluorenyl(carbinol-C^{14}) [XXV] the p-methoxyphenylene and phenylene groups were found to migrate in the ratio of 98:2. There is, of course, no chance at all for steric interaction



XXV XXVI

between the carbinol group of XXV and other parts of the fluorene molecule. The only effect, therefore, which influences the course of the rearrangement of XXV is the directive, or electron releasing, effect of the p-methoxy group. If the transition state structures for this arrangement are written in a manner similar to the transition state on page 38 , it is apparent that the intermediate structure XXVa is more important than XXVb in the formation of the final product XXVI.

Other Related Research

There are additional data to support the evidence that the methyl group of IV has negligible steric effect on the course of the rearrangement. 11H-Benzo[a]fluorene-11-methanol-C^{14} has been shown to rearrange* under dehydrating conditions with the phenylene and α- naphthalene

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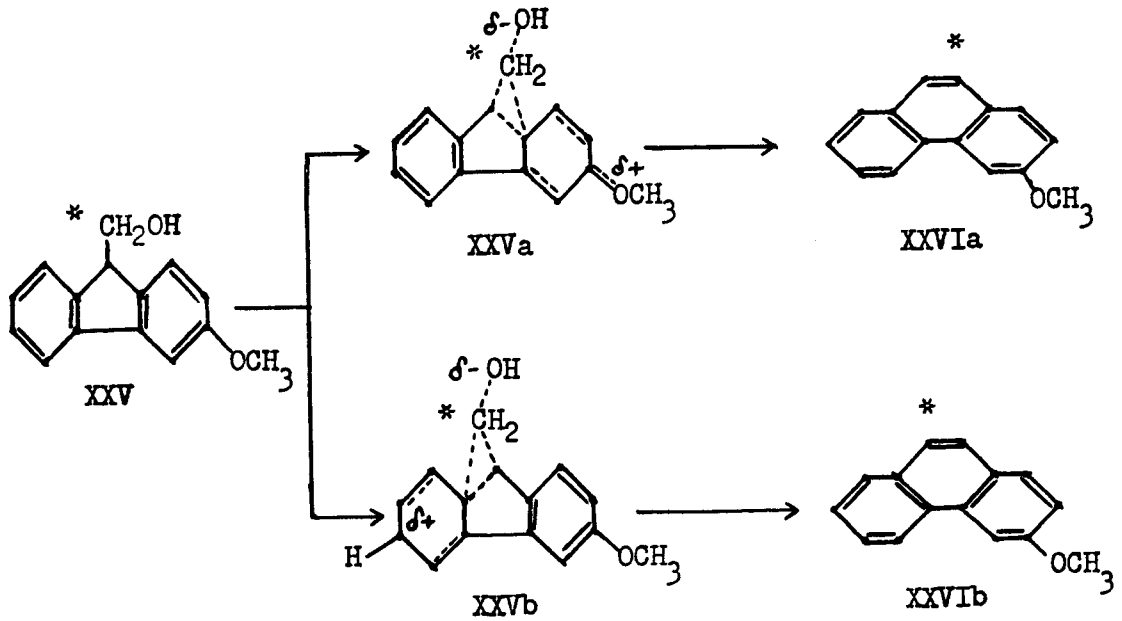
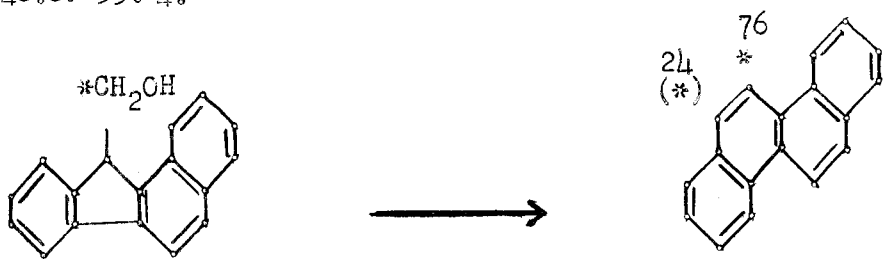
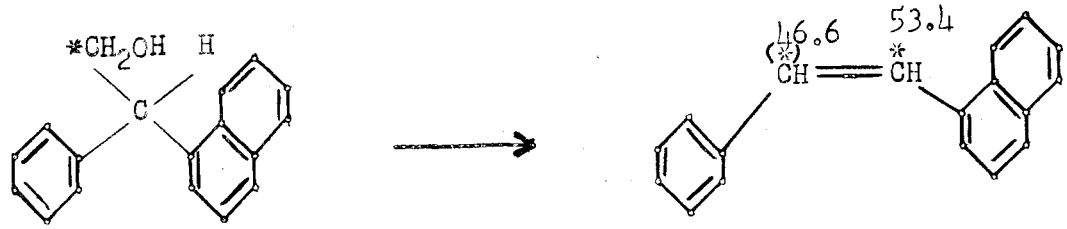
* Data were kindly supplied by C. J. Collins, G. M. Toffel, A. R. Jones, and D. N. Hess before its publication.


δ- OH
* CH2
δ+
OCH3
XXVa
*
OCH3
XXVIa
* CH2OH
OCH3
XXV
δ- OH
* CH2
δ+
H
OCH3
XXVb
*
OCH3
XXVIb

groups migrating in the ratio of 24:76. In the latter compound there is no steric interaction between the carbinol group and the hydrogen in the 1-position. In the similarly constituted 2-phenyl-2-(α-naphthyl)-ethanol-1-C^{14} [XXXII] which lacks the biphenylene bond, steric interaction is apparent and the ratio of migration of phenyl to α-naphthyl is 46.6: 53.4.



XXX XXXI



XXXII XXXIII

By comparing these data with the data on the rearrangement of 1-methyl-9-fluorenyl(carbinol-C^{14}) [IV] and 2-phenyl-2-(o-tolyl)ethanol-1-C^{14} [XVI], it is apparent that the lack of steric effects in the 1-substituted fluorenylcarbinols has resulted in qualitatively similar difference in migrational preferences of the substituted groups.

The dehydration rearrangement of 2-phenyl-2-(p-anisyl)ethanol-1-C^{14} [XXXIV] * proceeds with p-methoxyphenyl and phenyl migrating in the ratio of 96:4, respectively.

XXXIV XXXV

These data, when compared to the ratio of 98:2 for p-methoxyphenylene and phenylene migration in 3-methoxy-9-fluorenyl(carbinol-C^{14}) [XXV], indicate that the effect of the p-methoxy group is nearly the same in the two rearrangements. Steric interactions with the carbinol groups are lacking in both XXV and XXXIV. Also, it is unlikely that biphenylene resonance is important in the rearrangement of compounds like XXV which are substituted in the 3-position with strongly directing groups.

Suggestions for Future Research

The assumption has been made so far that the inductive effect of the methyl group is the same in IV and XVI. If the inductive effect

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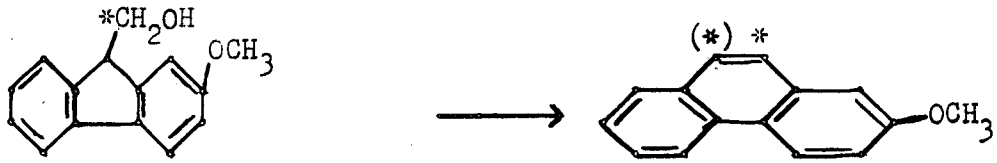
* J. G. Burr and L. S. Ciereszko kindly supplied their data on the rearrangements of 2-phenyl-2-(α-naphthyl)ethanol-1-C^{14} and 2-phenyl-2-(p-anisyl)ethanol-1-C^{14} before its publication.

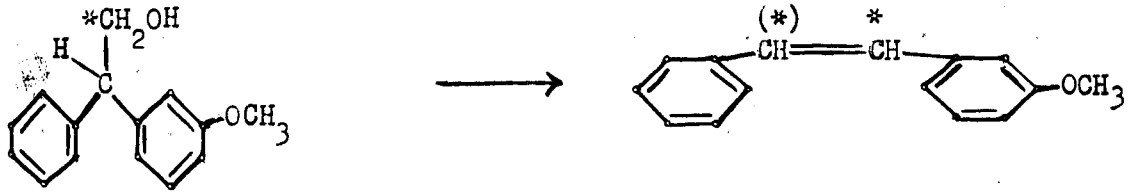
alone were operating during the rearrangement of XVI, the result might be expected to be the same as for the rearrangement of 2-phenyl-2-(p-tolyl) ethanol-1-C^{14} in which Burr and Ciereszko found the ratio of tolyl to phenyl migration to be 66:34. Reasoning similarly for carbinol IV, since steric interference between the methyl and carbinol groups has been shown to be negligible, one might be led to expect preferential tolylene migration. Any such tendency, however, derived from the weakly directing properties of the methyl group is probably nullified by biphenylene resonance. An interesting future project will be the investigation of this postulate by determining the course of the rearrangement of 3-methyl-9-fluorenyl(carbinol-C^{14}) and comparing the ratio of phenylene to p-tolylene migrations with the ratio of phenyl to p-tolyl migration in the rearrangement of 2-phenyl-2(p-tolyl)-ethanol-1-C^{14}. By this approach to the subject of which group will migrate in rearrangement reactions,it has been possible to separate the steric effect of neighboring substituent groups from the effect of their electron releasing ability.

The available data is consistent with the interpretation that the o-methyl group in 1-methyl-9-fluorenyl(carbinol-C^{14}) exerts a negligible steric effect during dehydration-rearrangement of the carbinol. By placing a group much larger than methyl, t-butyl for example, in the 1-position, it would be possible to study the rearrangement of a substituted 9-fluorenyl carbinol in which steric interaction with the carbinol group might be important. This, therefore, is suggested as

another future extension of the research reported here. Still other future experiments should include a study of the rearrangement of 2-methoxy-9-fluorenyl(carbinol) [XXXVI] and comparison of the results with the rearrangement of 2-phenyl-2-(m-methoxyphenyl)ethanol-1-C^{14} [XXXVIII].

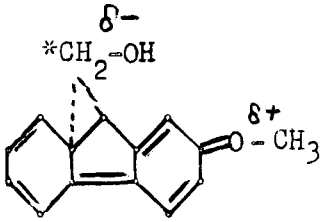


XXXVI XXXVII



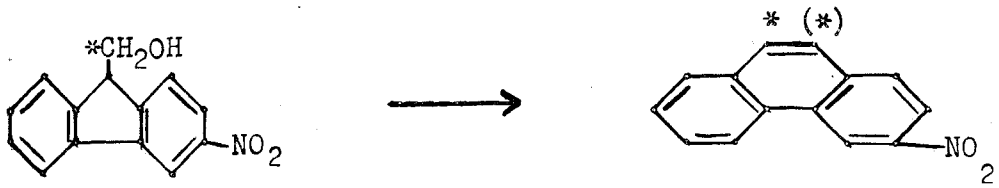
XXXVIII XXXIX

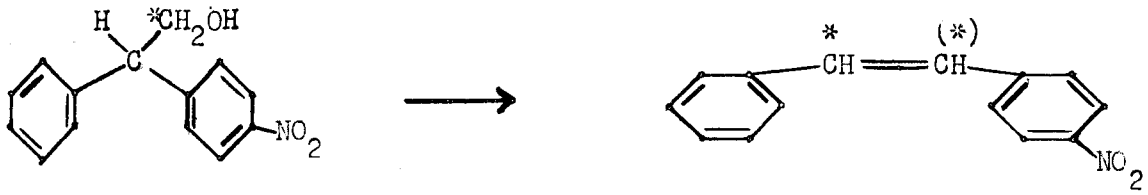
Information concerning the extent of biphenylene resonance in XXXVI and the importance of structures such as XXXVIa could be obtained by determining and comparing the distribution of carbon-14 in the products XXXVII and XXXIX.



XXXVIa

As a final suggestion, it would be interesting to determine the effect of a nitro substituent by studying the following two rearrangement reactions:





SUMMARY

As was pointed out in the Historical Notes, chemists have, for many years, been attempting to assign values to various aryl and alkyl groups which would be a measure of the tendency of these groups to migrate when the compounds of which they are a part are subjected to conditions which cause rearrangement. These values, which have been called "migratory aptitudes" have been used with some success by earlier workers[18][73] who were studying the pinacol and amino-alcohol rearrangements, since it was possible in some cases for them to predict the course of new pinacol and amino-alcohol rearrangements. Such predictions, however, were based upon results which for the following reasons were not always valid:

(1) The products isolated were not always the only products present in the reaction mixture, nor even always the principal products[74].

(2) Many of the substituted glycols and amino-alcohols studied contained two asymmetric centers and thus could exist in two diastereoisomeric forms. It has been shown[19][78][79][80] that such diastereoisomers may rearrange with migration of totally different groups.

(3) In unsymmetrical pinacols the two hydroxyl groups are bound to their respective carbons with different strengths[74] depending on the properties of the other groups attached to the

carbon atoms. The products of the rearrangements of these pinacols depends on the strength of the two carbon-oxygen bonds as well as the abilities of the groups to migrate. The latter factors were circumvented in some of the classical work on symmetrical pinacols[16][19][75].

(4) The degree of participation of the migrating group in removing the hydroxyl ion may vary with different solvents[54] and different compounds[72][76] as well as different strengths of the catalysts and different temperatures of the reactions[77].

Recently McEwen and Smith[21] have extended the concept of migratory aptitudes to include the Schmidt reaction, and McEwen[81] has related his values to the Hammett equation. McEwen's work appears to be the first in which migration ratios have been determined uncomplicated by any possible effect due to stereospecificity. His work suffers, however, in that his migration ratios are based upon yield determinations of two products, and in most cases the two products represent a material yield of approximately only 50 percent.

Although the two ratios 50:50, in the rearrangement of IV, and 55: 45, in the rearrangement of XVI, were too near the same to be considered definitive evidence for a steric effect, the specific accomplishments recorded in this dissertation are as follows:

(1) The method reported gives migration ratios with an accuracy of $\pm$ 1% . Only one product is formed in the crucial reaction, and this product is formed in essentially quantitative yield.

The other complications (2),(3),(4) mentioned above are eliminated.

(2) The effect of the biphenylene bond has been demonstrated quantitatively in the rearrangement of 1-methyl-9-fluorenyl-(carbinol-C^{14}) and the effect of the methoxy group has been demonstrated in the rearrangement of 3-methoxy-9-fluorenyl-(carbinol-C^{14}).

(3) The synthetic method of incorporating carbon-14 into polynuclear aromatic hydrocarbons has been extended to the preparation of 1-methylphenanthrene-9,10-C_1^{14} and 3-methoxyphenanthrene-9,10-C_1^{14}.

(4) The application of carbon-14 in determining the course of reactions and determining migration ratios has been demonstrated.

EXPERIMENTAL SECTION

Special Equipment

The high vacuum line illustrated in Fig. I is a versatile apparatus which was designed for carrying out several different types of reactions. The use of the vacuum line for the carbonation of organo-sodium compounds is described here. The reaction flask and continuous ether extraction apparatus, Fig. II, and the device, Fig. III, for pipetting triphenylmethylsodium were designed for use with the vacuum line in carbonation experiments so that none of the material is exposed to moisture or oxygen of the air before the reaction is completed. The general procedure which was followed in the carbonation reactions reported in this dissertation is described below.

Pure carbon-C^{14} dioxide is prepared from barium carbonate-C^{14}. A quantity of the radioactive barium carbonate is weighed into the flask a (Fig. I) and enough water is added to make a thin slurry. A magnetic stirring bar is placed in the flask which is then secured by springs in the position indicated in the diagram. A large excess of 48% perchloric acid solution is put into the reservoir b and the cap c is secured in position by springs. After the apparatus is swept from d through l with a stream of pure helium - stopcock m is closed - at the rate of about one bubble per second, the perchloric acid is slowly added to the slurry in a. As the carbon-C^{14} dioxide

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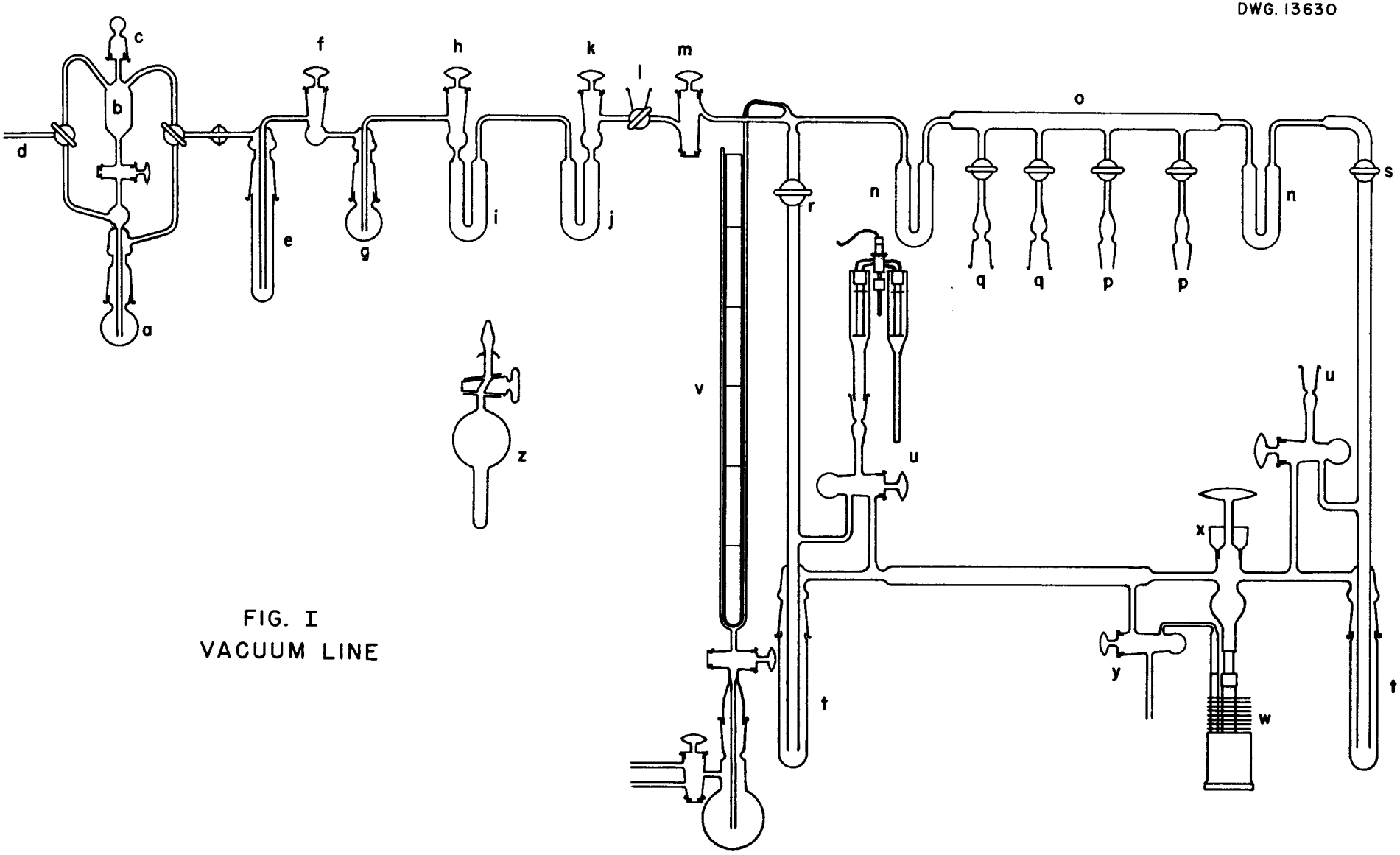

FIG. I
VACUUM LINE

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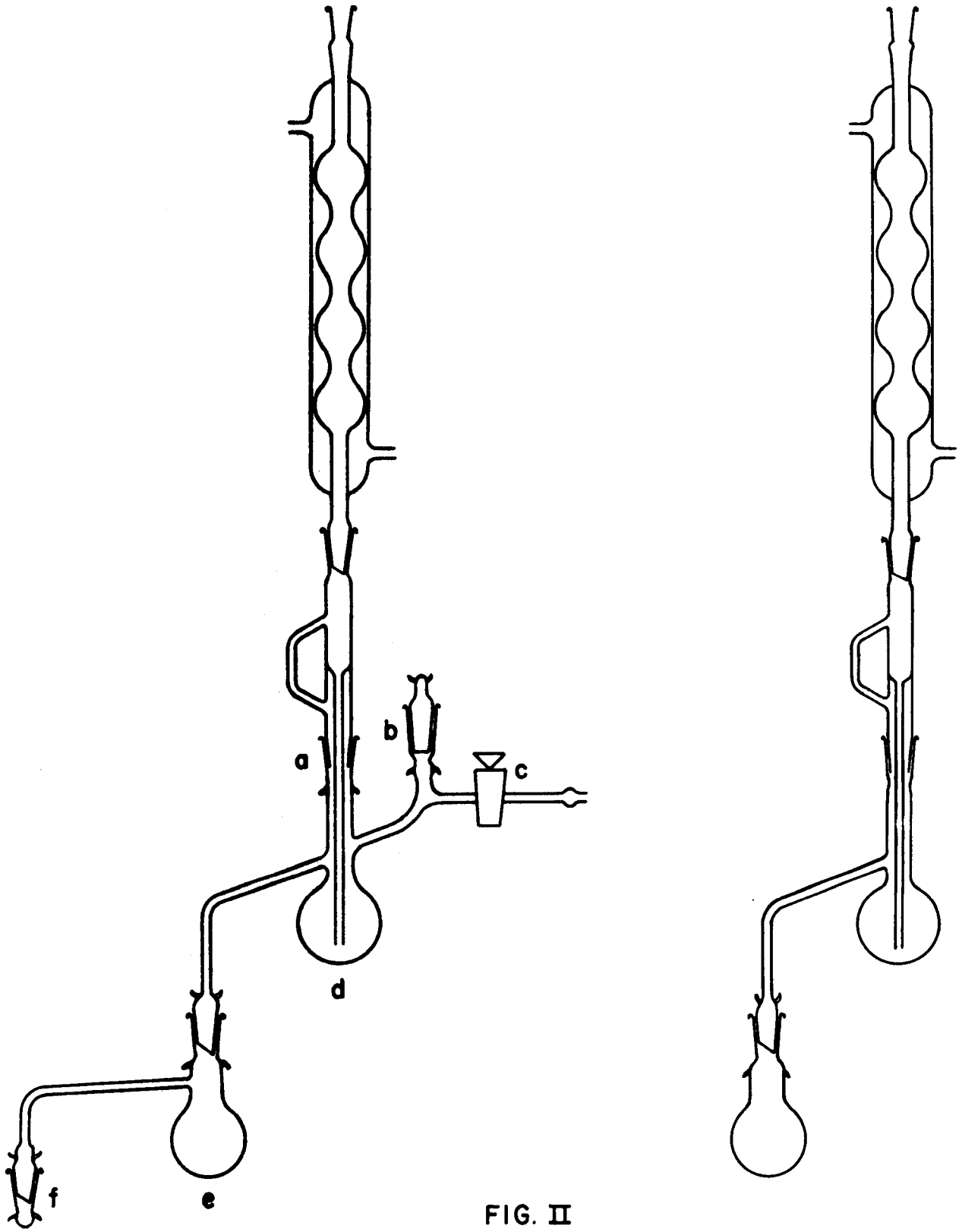

FIG. II

REACTION FLASKS AND ETHER EXTRACTION APPARATUS

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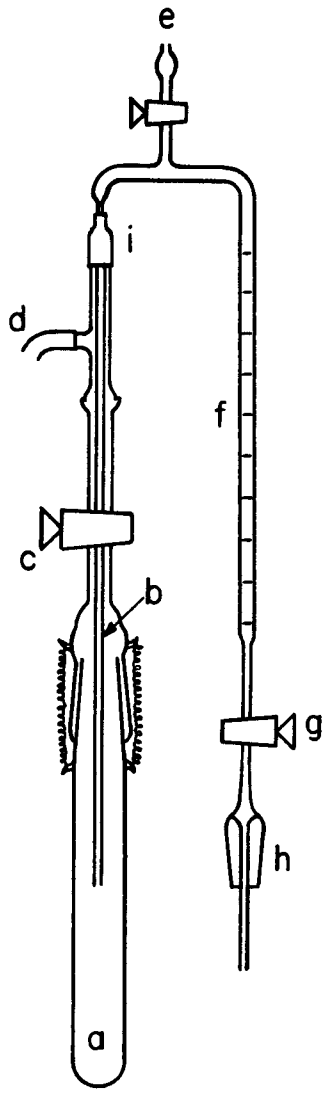

FIG. III

TRIPHENYLMETHYL SODIUM TUBE
AND PIPETTE

is formed, it is swept out of the flask along with the helium and is frozen into the liquid nitrogen traps i and j. Most of the water vapor is removed in the cold trap e, which is held at Dry Ice temperature, and the final traces of water vapor are removed by Drierite in g. When the barium carbonate-C^{14} is completely decomposed, the solution in flask a is heated almost to boiling, and the apparatus is swept with helium for an additional fifteen minutes.

While the carbon-C^{14} dioxide is being generated, the manifold of the vacuum line o is evacuated to a pressure below 1 micron as measured with a Pirani Gauge connected to a system at u. The evacuation is accomplished through an efficient forepump connected at y and an oil diffusion pump w. Trap t is surrounded by liquid nitrogen to protect the pumping system from condensable material which may be removed from the manifold.

When the generation of carbon-C^{14} dioxide is complete, stopcock h is closed and the stopcock at l is turned to isolate the system from the atmosphere. Stopcock m is then opened and the traps i and j are evacuated. When the pressure is below one micron, stopcock r is closed and the liquid nitrogen baths surrounding traps i and j are removed. Trap n is then surrounded by a liquid nitrogen bath causing the $C^{14}O_2$ to distil from i and j into n where it can be stored for a short time. If the $C^{14}O_2$ is to be stored overnight or longer, the gas storage flask z is evacuated at q and the carbon-C^{14} dioxide is distilled into

it. An aliquot of carbon dioxide can conveniently be taken from z when the gas is needed for a reaction.

The remainder of the apparatus is now assembled. First a dry sample of the hydrocarbon to be metalated and carbonated is placed in the reaction flask d (Fig. II) along with a magnetic stirring bar. The joint b of the reaction flask is attached to joint p of the vacuum line. Then joint h of the pipetting device (Fig. III) is connected to a of the reaction flask. All the air in the pipetting and reaction apparatus is swept out completely with helium. The triphenylmethylsodium solution is forced by helium pressure from tube a (Fig. III) into the pipette f from which a measured quantity of the solution can be titrated into the reaction flask d (Fig. II) while the contents of the flask are stirred. After allowing sufficient time for the triphenylmethylsodium to react with the compound to be carbonated (color change), all material in the reaction flask are frozen by raising a liquid nitrogen bath about the flask. The flask is then evacuated. With stopcocks m, r, and s, (Fig. II) closed, carbon-C^{14} dioxide is measured from z into the manifold o and its pressure, as indicated by the manometer v, and temperature are recorded. The carbon dioxide is distilled into the reaction flask which is then warmed to - 60° by a Dry Ice-tetrachloroethane bath and the reaction is allowed to proceed to completion at that temperature. The reaction flask is half filled with water and, after the extraction apparatus as illustrated in Fig. II is assembled, triphenylmethane is

removed from the mixture by continuous ether extraction for two hours. The contents of the flask d are then acidified with dilute hydrochloric acid and the organic acid, which at first separates as a white precipitate, is transferred to flask e by continuous ether extraction.

The acid can be esterified or reduced directly without removing it from flask e. If the acid is esterified, the ester can be reduced in the same flask and can be separated from by-products by continuous extraction methods. In a typical experiment, for example, the acid resulting from the carbonation reaction is esterified with an excess of diazomethane in ether solution. The ether is removed by evaporation in a current of air and the ester residue is dried in a vacuum desiccator over phosphorus pentoxide. The ester is dissolved in dry ether and an ether solution of lithium aluminum hydride is added. When reaction is complete, the solution is treated with water and dilute hydrochloric acid and the resulting alcohol is transferred to a flask similar to e (Fig. II) by continuous ether extraction. As the series of reactions is extended, the method of continuous ether extraction is used wherever possible to transfer the product from one flask to another. This procedure was used, unless stated otherwise, in the syntheses described in the following sections.

Carbon-14 Assay Procedure

Organic compounds which were to be analyzed for radioactivity were converted to carbon-C^{14} dioxide by wet combustion in the apparatus illustrated in Figure IV. This apparatus was adapted by D. N. Hess from the design of Neville[45]. The oxidizing solution[44] was prepared by mixing 3.8 g. of potassium iodate, 19 g. of chromium trioxide, 125 ml. of 85% phosphoric acid, and 250 ml. of 20% fuming sulfuric acid. If the heat of solution was not sufficient to cause the solids to dissolve, the solution was heated on the hotplate to 150° and swirled inside the container.

A 5-10 mg. sample of the radioactive organic compound to be assayed was accurately weighed in a platinum boat and was placed in the combustion flask i (Fig. IV) where it was mixed with approximately 100 mg. of potassium iodate. The ionization chamber a which had previously been swept with non-radioactive carbon dioxide and evacuated at position e, was placed in position b. When the stopcock at h was opened, mercury below the fritted glass disk at c prevented the vacuum in the chamber from being broken. About 10 ml. of the combustion solution was run into the combustion flask i from reservoir h. The combustion flask was then heated with a free flame until all organic matter in it was decomposed.

After combustion of the sample was complete, non-radioactive carbon dioxide was allowed to sweep through the apparatus until the

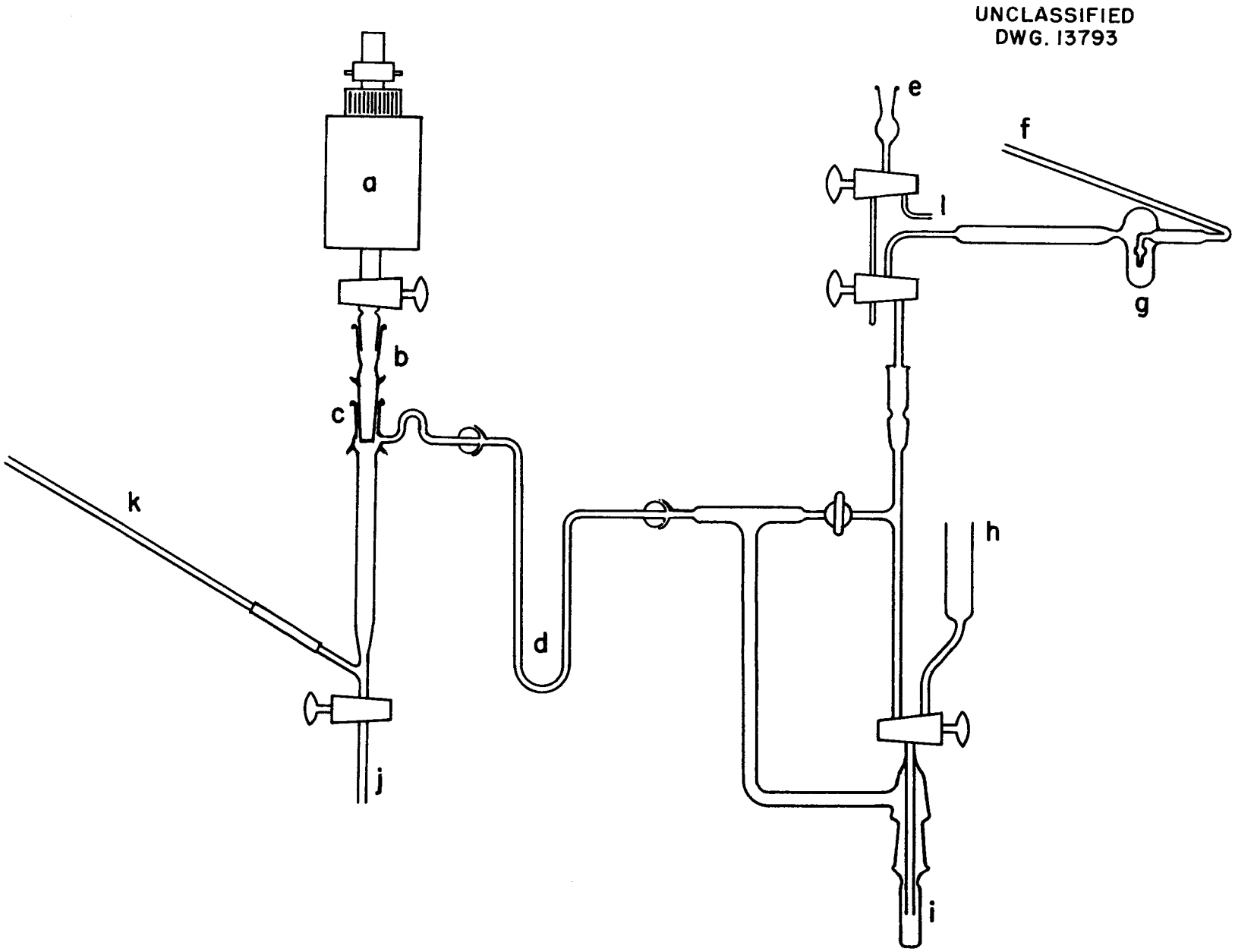

FIG. IV

CARBON-14 ASSAY LINE

ionization chamber reached atmospheric pressure. The ionization chamber was then placed in the appropriate position on the Vibrating Reed Electrometer and the ion current of the carbon-14 dioxide was determined by the rate of drift method. The following formula was used to convert ion current to microcuries per millimole:

$$\mu c/\text{mmole} = \frac{C\ E}{t\ D\ f\ \text{mmole}}$$

c = capacitance of the electrometer (17.23×10^{-12} farads)

E = scale reading in volts (0.6992 on the 1000 millivolt scale).

t = time of scale travel in seconds.

D = disintegrations per second per μc (3.7×10^{4})

f = a factor which depends on changes in instrument from day to day. This factor is obtained from the rate of drift caused by a standard reference ionization chamber. The standard reference ionization chamber was calibrated against $C^{14}O_2$ prepared from a known quantity of Bureau of Standards sodium carbonate-C^{14}.

The factor f may be calculated by the equation $f = \frac{C\ E}{t\ D\ \mu c}$

when the time t is obtained for the scale travel caused by the ion current of the standard reference ionization chamber. The constants C and E for the Vibrating Reed Electrometer were determined by O. K. Neville and A. J. Weinberger, both of Oak Ridge National Laboratory, who also prepared and calibrated the standard reference ionization chamber.

Experimental Procedures*

Triphenylmethylsodium. - An adaptation of the procedure of Bachmann and Wiselogl[55] was used. Two 18 x 150 mm. Pyrex test tubes were broken into 1-5 mm. pieces and placed in the tube a (Fig. III). Five grams of triphenylchloromethane was placed in the tube and two grams of freshly prepared sodium sand was washed into the tube with 80 ml. of anhydrous ether. The tube was capped and shaken vigorously by hand until a red color began to appear around the sodium particles (7-15 min.) at which time the tube was plunged into an ice bath where it was allowed to remain until the vigorous reaction had subsided and the entire ether solution had turned deep red. The tube was then shaken mechanically for three hours. The concentration of triphenylmethylsodium, determined by titrating a 1-2 ml. aliquot with standard acid, was found to vary only slightly from 0.20 normal in several preparations.

1-Methylfluorene [I]. - This compound was prepared in approximately 15% yield by the Diels-Alder reaction between sorbic acid and freshly distilled indene according to the procedure of Deno[56].

1-Methyl-9-fluorenecarboxylic-C^{14} Acid [II]. This acid was prepared from 1.10 g. of 1-methylfluorene(6.11 mmole), 28 ml. of triphenylmetylsodium solution (5.60 mmole), and 6.20 mmoles of carbon-C^{14} dioxide using

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* Melting points are uncorrected. Carbon and hydrogen analyses were performed by Dr. H. W. Galbraith, Knoxville, Tennessee.

the vacuum line and extraction apparatus as described on pages 49 - 55. A 93.3% yield (1.16 g.) of the acid was isolated. The acid was crystallized three times from benzene; m. p. 222.5-3.0°.

Anal. Calcd. for $C_{15}H_{12}O_2$; C, 80.3; H, 5.40. Found: C, 79.9; H, 5.36.

Methyl 1-Methyl-9-fluorenecarboxylate-C_1^{14} [III]. - The ester (1.13 g.) was prepared from 1.076 g. of the acid II and excess dizaomethane in the solution. A pure sample was obtained by crystallization of the ester seven times from cyclohexane; m. p. 95.0 - 6.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.92. Found: C, 80.2; H, 5.57.

1-Methyl-9-fluorenyl(carbinol-C^{14}) [IV]. - The ester III (0.966 g.) was reduced with excess lithium aluminum hydride in dry ether. The carbinol IV (0.865 g.) was isolated in quantitative yield and was purified by four crystallizations from cyclohexane; m. p. 85.5 - 6.4°.

Anal. Calcd. for $C_{15}H_{14}O$; C, 85.7; H, 6.71. Found: C, 85.9; H, 6.62.

1-Methylphenanthrene-9,10-C_1^{14} [V]. - To a solution of 0.567 g. of the carbinol IV in 20 ml. of xylene was added 4 g. of phosphorus pentoxide. The mixture was heated under a reflux condenser for one-half hour. The yield (0.531 g.) of crude yellow product, obtained after washing the xylene solution with alkali and concentrating the solution, was quantitative. The material was purified by dissolving it in benzene, passing the benzene solution through a short alumina column, and evaporating the benzene. The solid residue was crystallized twice from ethanol (Norite); m.p. 119.5 - 20.5. Pschorr[57] gives m. p. 121°. When this material was

mixed with an authentic sample prepared by the Haworth synthesis,[58] the melting point was not depressed.

High Level Synthesis of 1-Methylphenanthrene-9,10-C_1^{14} [V]. - The above procedure was used to prepare 5.17 millimoles (75.4% of the theoretical based on carbon-C^{14} dioxide of specific activity 2.85 mc/mmole) of V. Purification was performed only on the final product, and the intermediate compounds were not isolated. For the degradative procedures 7.16 mg. of the labeled 1-methylphenanthrene so obtained was mixed with 5450 mg. of non-radioactive 1-methylphenanthrene. The diluted compound was crystallized from ethanol and assayed.

Anal. 2.17 Microcuries of carbon-14 per millimole of diluted V.

1-Methylphenanthrenequinone-9,10-C_1^{14} [VI]. - Potassium dichromate (5 g.) was added to a solution of 1.03 g. of V in 20 ml. of acetic acid. The mixture was heated under a reflux condenser for five hours. Dilute hydrochloric acid was added and the quinone along with some acetic acid was removed by continuous extraction with ether. When the solvents had been evaporated in a current of air, 0.842 g. (59%) of impure quinone remained. The product was crystallized from acetone; m. p. 196°.
Lit.[57] 196° .

Anal. 2.14 Microcuries of carbon-14 per millimole of VI.

3-Methyldiphenyl-2,2'-dicarboxylic-C^{14} Acid [VII]. - The acid was obtained as a crude product in 85% yield (267 mg.) by oxidizing 285 mg. of the quinone VI in 15 ml. of acetic acid with 2 ml. of 30% hydrogen peroxide.

The solution was heated under a reflux condenser for two hours and was allowed to stand at room temperature for twelve hours. Acetic acid was removed in a current of air on the steam bath. The acid residue was taken up in sodium bicarbonate solution and non-acidic material was removed by continuous extraction with ether. The aqueous solution was acidified and the organic acid was removed by continuous extraction with ether. The acid was purified by crystallization from chloroform; m. p. 190-191°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.3; H, 4.72; Neutral Equivalent, 128. Found: C, 70.1; H, 4.72; Neutral Equivalent, 131.

3-Methylfluorene-9-C^{14}-one-4-carboxylic Acid and 3-Methylfluorene-9-one-4-Carboxylic-C^{14} Acid*[VIII].- A solution of 106 mg. of VII in 15 ml. of 96% sulfuric acid was stirred at room temperature with a magnetic bar for twenty-one hours. The acid was poured onto ice and the yellow solid which separated was extracted with ether. The residue which remained after the ether was evaporated was taken up in sodium bicarbonate solution and the solution was treated with Norite. The yellow solid was precipitated with dilute acid and was removed by filtration. It was crystallized from benzene; m. p. 206°. The yield was 76 mg. (77% of the theoretical).

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.23. Found: C, 75.0; H, 4.29.

2.13 Microcuries of carbon-14 per millimole of VIII.

3-Methylfluorene-9-C^{14}-one [IX]. - Decarboxylation was effected by heating

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* This substance [VIII] is a mixture, each labeled species of which contains carbon-14 in only one of the two possible positions.

under a reflux condenser 63 mg. of VIII in 15 ml. of freshly distilled quinoline with 50 mg. of copper chromite catalyst for about forty five minutes. During this time the apparatus was swept continuously with helium. The carbon-C^{14} dioxide [X] was caught in a barium hydroxide trap. The barium carbonate-C^{14} [XI] was washed with water and then washed twice with acetone, and dried (yield 49.3 mg).

Anal. 1.07 Microcuries of carbon-14 per millimole of XI.

The quinoline solution was added to dilute hydrochloric acid and this solution was extracted with ether. The ether layer was shaken first with dilute acid, then with dilute base, and the ether was finally evaporated. The orange residue (69 mg.) could not be caused to crystallize. It was converted to the oxime XII which was crystallized from cyclohexane seven times; m. p. 185°. A mixed melting point with the oxime prepared from an authentic sample of 3-methylfluorene [59] was not depressed.

Anal. Calcd. for $C_{14}H_{12}NO$: C, 80.4; H, 5.30.

Found: C, 80.0; H, 5.38, 1.06 Microcuries of carbon-14 per millimole of XII.

Oxidation of 3-Methylfluorene-9-C^{14}-one. - A portion of the impure fluorenone IX was oxidized by heating it under a reflux condenser with 230 mg. of potassium permanganate in 40 ml. of water for one hour. Two acids were isolated from the oxidation mixture. The water insoluble portion was yellow; m. p. 280°. During a non-radioactive preparation this material was identified as fluorenone-3-carboxylic acid (Lit. [60] m. p. 286).

A larger quantity (18 mg.) of water soluble acid XIII was isolated; m. p. 195-200. The m. p. of an analytical sample was 206°. This was identified as trimellitic acid.

Anal. Calcd. for $C_9C_6O_6$: C, 51.4; H, 2.86. Neutral.

Equivalent, 70.0. Found: C, 51.6; H, 2.92. Neutral

Equivalent, 70.8. 1.08 Microcuries of carbon-14 per millimole of XIII.

<u>2-Phenyl-2(o-tolyl)acetonitrile-1-C^{14}</u>. - 2-Methylbenzophenone[61] was reduced[62] to 2-methybenzohydrol[63]. A mixture of 22.2 g. of 2-methylbenzohydrol and 17 g. of thionyl chloride in 25 ml. of benzene was heated at reflux temperature for fifteen minutes. The benzene was removed by evaporation at reduced pressure and the residue was distilled at 0.06 - 0.08 mm.; B. P. 85-87°. 2-Methylbenzohydrylchloride[64] (21.6 g.) was obtained in 90% yield. A mixture of 25.76 g. of 2-methylbenzohydrylchloride and 7.19 g. of cuprous cyanide-C^{14} (prepared by the method of Barber[65]) was heated on an oil bath for an hour at 250°. The nitrile was washed out of the residue with acetone. After evaporation of the acetone, the impure nitrile was distilled at reduced pressure; b. p. 109-110° at 0.06-0.08 mm. The yield was 13.6 g. (83% of the theoretical based on the radioactive cuprous cyanide).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.9; H, 6.32.

Found: C, 86.8; H, 6.20.

2-Phenyl-2-(o-tolyl)acetic-1-C^{14} Acid [XV]. - This acid (35 g.) was obtained in almost quantitative yield when 2-phenyl-2-(o-tolyl)acetonitrile-1-C^{14} (3.4 g.) was hydrolyzed in 70% sulfuric acid by heating the vigorously stirred mixture under a reflux condenser for two hours. The acid was crystallized six times from cyclohexane; m. p. 96 - 97.6°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24.

Found: C, 79.2; H, 6.02. 2.93 Microcuries of carbon-14 per millimole of XV.

2-Phenyl-2-(o-tolyl)ethanol-1-C^{14} [XVI]. - The acid XV (2 g.) was reduced with excess lithium aluminum hydride in anhydrous ether by heating the solution to the boiling point for one-half hour. The solution was hydrolyzed and the carbinol XVI (1.5 g.) was isolated in 80% yield. It was crystallized five times from cyclohexane; m. p. 58.5-59.0°.

Anal. Calcd. for $C_{15}H_{16}O$; C, 84.9; H, 7.60.

Found: C, 85.3; H, 7.46.

2-Methylstilbene-α,α'-C_1^{14} [XVII] and 2-Methylstilbene-α,α'-C_1^{14}-dibromide [XVIII]. - The carbinol XVI (1.5 g) was dissolved in xylene. Phosphorus pentoxide (5 g.) was added and the mixture was heated under a reflux condenser for one-half hour. After adding water and concentrating the xylene solution, the oily stilbene XVII was isolated in quantitative yield (1.5 g.). A portion was heated with bromine in carbon tetrachloride solution for one hour. The dibromide XVIII was isolated and crystallized from isopropyl alcohol; m. p. 160°. (Lit.[66] 159°).

Anal. 2.93 Microcuries of carbon-14 per millimole of XVIII.

Oxidation of 2-Methylstilbene-α,α'-C^{14}. - The oxidation was effected in two steps. An acetic acid solution of 1.2 g. of VII was heated under a reflux condenser with 4 ml. of 40% peracetic acid. All solvents were removed with a current of air. To the solid residue was added 50 ml. of water and 4 g. of potassium permanganate. The mixture was heated with boiling for an hour. Excess permanganate was decomposed with ethanol. The manganese dioxide was removed by filtration and was washed with dilute base. The basic solution was extracted with ether. The aqueous solution was acidified and was extracted continuously with ether for six hours. When the ether was evaporated, a crystalline residue remained. It was washed with chloroform and crystallized from acetone-chloroform mixture (yield 70.5 mg.) The phthalic acid was converted to phthalanil [XXI] by heating it with aniline. The phthalanil was crystallized from ethanol; m. p. 206-7°.

Anal. 1.32 microcuries of carbon-14 per millimole of XXI.

3-Methoxyfluorene. - 3-Methoxyfluorenone, which was prepared by the procedure of Ullmann and Blair (67), was reduced to 3-hydroxyfluorene with red phosphorus and hydrochloric acid according to Lothrop's (68) method. 3-Hydroxyfluorene (13.5 g.) was dissolved in 40 ml. of 10% sodium hydroxide solution to which 15 g. of dimethylsulfate was added. The reaction mixture was stirred at room temperature for three hours. The oily organic layer was extracted with ether and the ether was evaporated in a current of air. The residue of 3-methoxyfluorene

was crystallized twice from ligroin; m. p. 101.0-1.5°. The yield was 13 g. (89%).

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.7; H, 6.17. Found: C, 85.5; H, 6.33.

3-Methoxy-9-fluorenecarboxylic-C^{14} Acid [XXIII]. - A 90% yield (1.21 g.) of the acid XXIII was obtained when 1.1 g. of 3-methoxyfluorene was treated with 28 ml. of triphenylmethylsodium solution and 0.056 mole of carbon-C^{14} dioxide. The acid was crystallized twice from toluene; m. p. 190.3-1.2°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.04

Found: C, 74.8; H, 5.14 . 1.27 Microcuries of carbon-14 per millimole of XXIII.

Methyl 3-Methoxy-9-fluorenecarboxylate-C^{14} [XXIV]. - Esterification of the acid XXIII was accomplished by treating 0.718 g. of it with an excess of diazomethane in ether. A quantitative yield (0.780 g.) of the ester XXIV was obtained. It was crystallized from ether; m. p. 108-9°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.55.

Found: C, 75.5; H, 5.40.

3-Methoxy-9-fluorenyl(carbinol-C^{14}) [XXV] - Reduction of the ester XXIV was effected by treating 0.758 g. of it with excess lithium aluminum hydride in anhydrous ether solution. The carbinol XXV (0.652 g.) was isolated in 96% yield. It was oily and a solid sample could not be obtained.

A derivative for analysis was prepared by treating 0.1 g. of the carbinol with 0.5 ml. α - naphthylisocyanate and heating the mixture on the steam bath for five minutes. The α -naphthylurethane of carbinol XXV (0.12 g.) was extracted with chloroform and crystallized three times

from chloroform-cyclohexane mixture; m. p. 136.5-7.5°.

Anal. Calcd. for $C_{26}H_{21}NO_3$: C, 79.0; H, 5.35.

Found: C, 78.9; H, 5.45.

3-Methoxyphenanthrene-9,10-C^{14} [XXVI]. - To a solution of the carbinol XXV (0.652 g.) in 15 ml. of xylene was added 4 g. phosphorus pentoxide. The mixture was heated at reflux temperature for fifteen minutes. Water was added to the reaction mixture and the xylene solution was concentrated. A 93.5% yield (0.556 g.) of oily XXVI was isolated. It could not be caused to solidify.

3-Hydroxyphenanthrene-9,10-C_1^{14} [XXVII]. - The oily 3-methoxyphenanthrene [XXVI] (0.556 g.) was heated under a reflux condenser with 20 ml. of 55% hydriodic acid for two hours. The organic material was extracted with ether. The ether solution was then extracted twice with 20 ml. of 4% sodium hydroxide solution to which a trace of sodium thiosulfate had been added. Upon acidification of the basic solution, a white flocculent precipitate of XXVII separated. This was extracted with ether and crystallized from light petroleum ether; m. p. 120-121. (Lit.[69] 118-9°; [20] 122-23°). The yield was 0.229 g. (44.2%). A mixed melting point of XXVII with a sample of 3-hydroxyphenanthrene prepared by the method of May and Mosettig[71] was not depressed.

Anal. 1.25 Microcuries of carbon-14 per millimole of XXVII.

Oxidation of 3-Hydroxyphenanthrene-9,10-C^{14}_{1}. - A mixture of XXVII (0.354 g.) and potassium permanganate (2.5 g.) in 40 ml. of water was heated at reflux temperature for one hour. Excess potassium permanganate was decomposed with ethanol. The manganese dioxide was separated from the aqueous solution and was washed with 10 ml. of dilute sodium hydroxide. The basic solution was acidified and extracted continuously with ether for twenty-four hours. After evaporating the ether, the crystalline residue remaining was washed with chloroform. Impure phthalic acid [XXVIII] (0.105 g.) remained. This was converted to phthalic dianilide [XXIX] and crystallized three times from ethanol; m. p. 150-1°.

Anal. 0.03 Microcuries of carbon-14 per millimole of XXIX.

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