THE SYNTHESIS AND CYCLIZATION OF SOME NEW KETONES CONTAINING NITROGEN

by

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TO MY WIFE

AND MY PARENTS

ACKNOWLEDGEMENTS

The author would like to express his gratitude to Dr. Frank A. Vingiello without whose continued guidance, interest, and foresight this investigation would not have been possible.

The author also wishes to express his appreciation to his fellow graduate students for their invaluable suggestions during the entire course of the investigation, and to the Chemistry Department for their constant cooperation.

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INTRODUCTION

INTRODUCTION

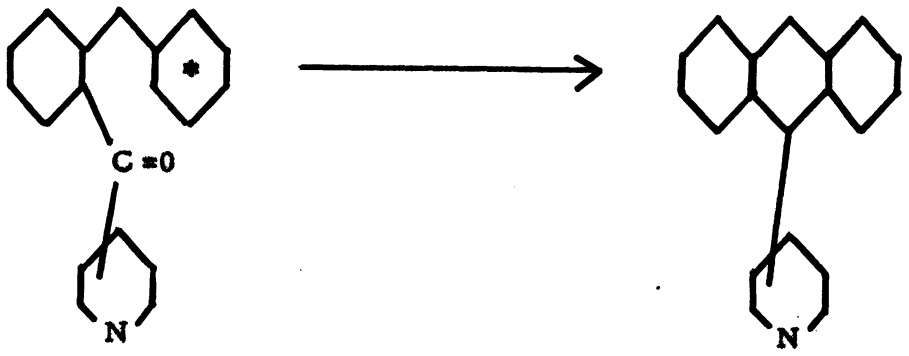
As early as 1930, the substance thought to be responsible for the cancer-producing properties of tars and mineral oils was an aromatic polynuclear hydrocarbon (1).

Since that time, subsequent investigations were primarily concerned with the search for an active carcinogenic substance of known structure.

More recent research has unveiled several considerations to the effect that only certain types of chemical structures possess carcinogenic activity. These structures, primarily polynuclear hydrocarbons, will usually produce tumors at the site of application while the greater percentage of nitrogen-containing carcinogens tend to be more active at a distant site (2).

Considering that the relationship between chemical structure and physiological activity is vague, these indications, although circumstantial, are of such interest as to stimulate further research in the field of nitrogen heterocycles (2).

One objective of this investigation was to prepare pyridyl derivatives of anthracene by synthesizing the three isomeric pyridyl ketones (I) and studying their cyclization to the three corresponding isomeric pyridyl anthracenes (II).



I II

The linkages may be alpha, beta, or gamma.

Another important aspect of this investigation was to study a gravimetric and a spectrophotometric method of determining the rates of cyclization of I ⟶ II. It was thought that the observed values of the various rate constants would be helpful in attempting to postulate a plausible mechanism for the cyclization of the isomeric pyridyl ketones (I) to the isomeric pyridyl anthracenes (II).

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* All rings in all of the structures in this thesis are fully aromatic unless otherwise specified.

HISTORICAL

HISTORICAL

In 1940, Bradsher (3) showed that an aromatic cyclodehydration reaction was effective in preparing polynuclear hydrocarbons from various ketones. Further extensive investigations by Bradsher (4, 5, 6) and Vingiello (7 - 12) followed which utilized substituted o-benzylbenzophenones as a means of synthesizing substituted anthracenes and substituted 2-(naphthylmethyl)-benzophenones to prepare 1, 2-benzanthracene derivatives.

The basic method consisted of heating the ketone in a mixture of hydrobromic and acetic acids for varying periods of time. More recent modifications of the basic technique have employed higher temperatures which necessitated the use of sealed tubes as reaction vessels (8 - 11). Other cyclodehydrating agents, ie. phenyl acid phosphate* (13), sulfuric acid (13), and anhydrous alumina (14, 15) have been used with varied degrees of success.

Although there is no record in the literature of the utilization of the aromatic cyclodehydration reaction in the synthesis of pyridyl derivatives of anthracene of the type II, previous investigations concerning polynuclear heterocyclic systems will be cited.

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*Phenyl acid phosphate was obtained from Virginia-Carolina Chemical Corporation. The acid is a mixture of mono- and dihydrogen phosphate esters containing varying amounts of polyphosphates.

In one of the first literature reports of a pyridyl anthracene derivative, anthracene-1,2:2,3-pyridine (VI), was prepared from alizarin-α-quinoline (V) starting with either 3-nitro-, (IV) or 3-amino-alizarin (III) proceeding via an acid catalyzed Skraup type of ring closure (16, 17, 18) (Chart I).

Many years later while discussing the reactivity of meso - substituted anthracenes, Cook (19) had occasion to prepare 9-benzyl-10-anthranylpyridinium bromide (IX) (Chart II). In this reaction 9-benzyl-anthracene (VII) treated with pyridine perbromide in pyridine yielded 9-benzyl-9,10-dihydroanthraquinyl-9,10-pyridinium dibromide (VIII) which on subsequent reaction with acid or alkaline reagents was converted to IX. As far as this investigator has been able to determine, this study by British workers was the only instance in which the preparation of a 9-, or 10-substituted pyridyl anthracene* has been cited.

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* The numbering system used by Chemical Abstracts for anthracene derivatives is shown below with the example of 9-phenylanthracene.

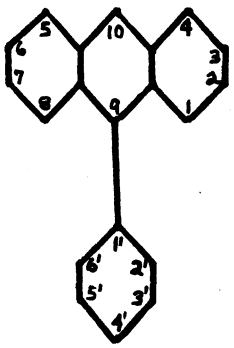
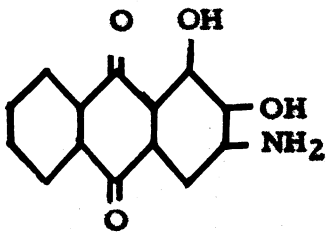
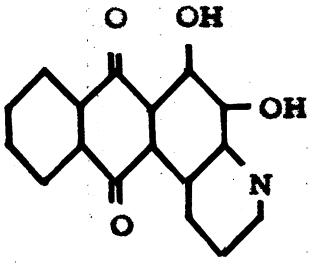


CHART I



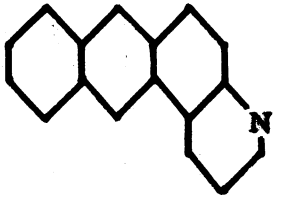
III

nitrobenzene
sulfuric acid
glycerol

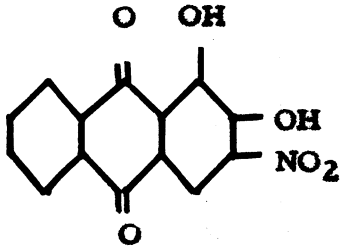


V

Zinc dust
distillation



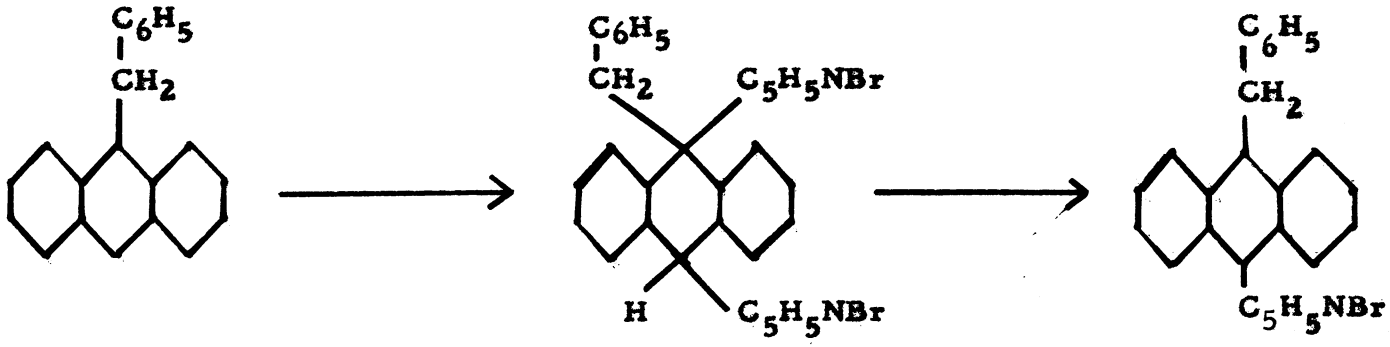
VI



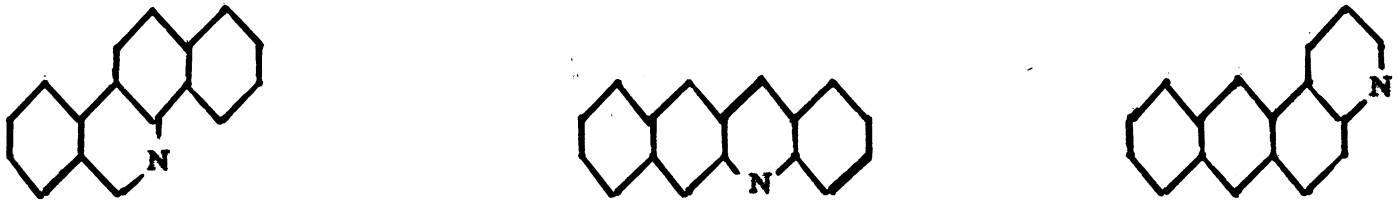
IV

sulfuric acid
glycerol

CHART II



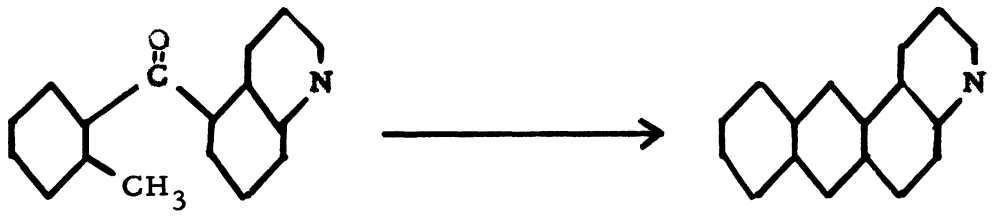
VII VIII IX



X XI XII

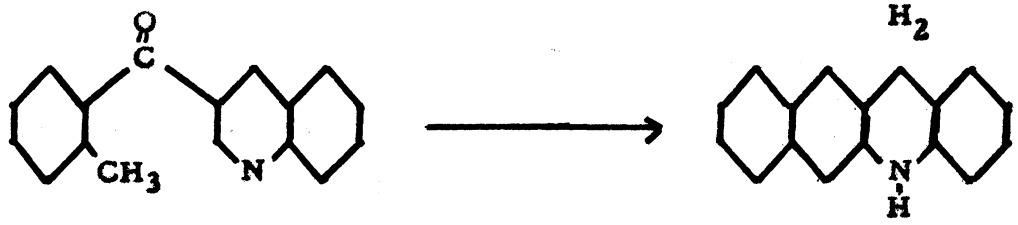
In the last two decades there has been renewed interest in heterocyclic polynuclear systems. Of particular interest to the organic chemist as well as those interested in the relationship of physiological activity to chemical structure have been, for example, compounds related to benzophenanthridine (X), 2, 3-benzacridine (XI), and 4'-aza-1, 2-benzanthracene (XII) (Chart II). It was of interest to note that the syntheses of X, XI, and XII were the first instances of polynuclear heterocyclic systems having been prepared from non-polynuclear precursors (20).

An Elbs reaction has been used to convert various pyridyl ketones to heterocyclic hydrocarbons. The conversion of 5-quinolyl o-tolyl ketone (XIII) to 4'-aza'-1, 2-benzanthracene (XII), although in poor yield, was realized in 1940 (2).



XIII XII

More recently investigators (20) have successfully synthesized various polynuclear hydrocarbons from similar ketones. The conversion of 3-o-toluoylquinoline (XIV) to 5, 10-dihydro-2, 3-benzacridine (XV) is a typical example.



XIV XV

The use of the Elbs reaction for the preparation of hydrocarbons has been a valuable implement in synthetic organic chemistry; however, this high temperature method is somewhat limited in its use due to extensive decomposition which usually accompanies the reaction.

The Bradsher-type aromatic cyclodehydration reaction has also been an outstanding tool for the preparation of substituted hydrocarbons (3 - 15). Preliminary studies on the mechanism of the aromatic cyclodehydration reaction utilizing a quantitative gravimetric technique were undertaken by Bradsher (6), and Vingiello (12). Several years later more exhaustive studies (7, 21) were accomplished and again the isolation of a pure product was a major requirement of the technique. However, the application of this method to the determination of the rate of cyclization of the isomeric pyridyl ketones (I) was only partially successful in producing precise quantitative results.

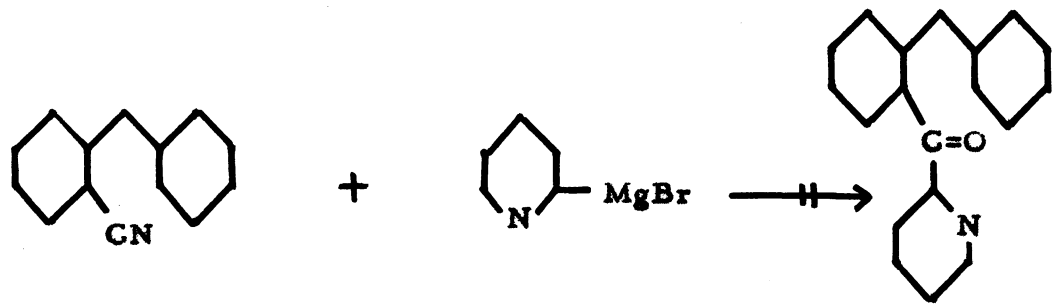
Very recent investigations (22) based on Moffett's (23) spectrophotometric study of the aromatic cyclodehydration reaction proved to be very successful. The scope of this spectrophotometric method has

been expanded, during this investigation, to include the study of the cyclization of the isomeric pyridyl ketones (I) to the isomeric pyridyl anthracenes (II).

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

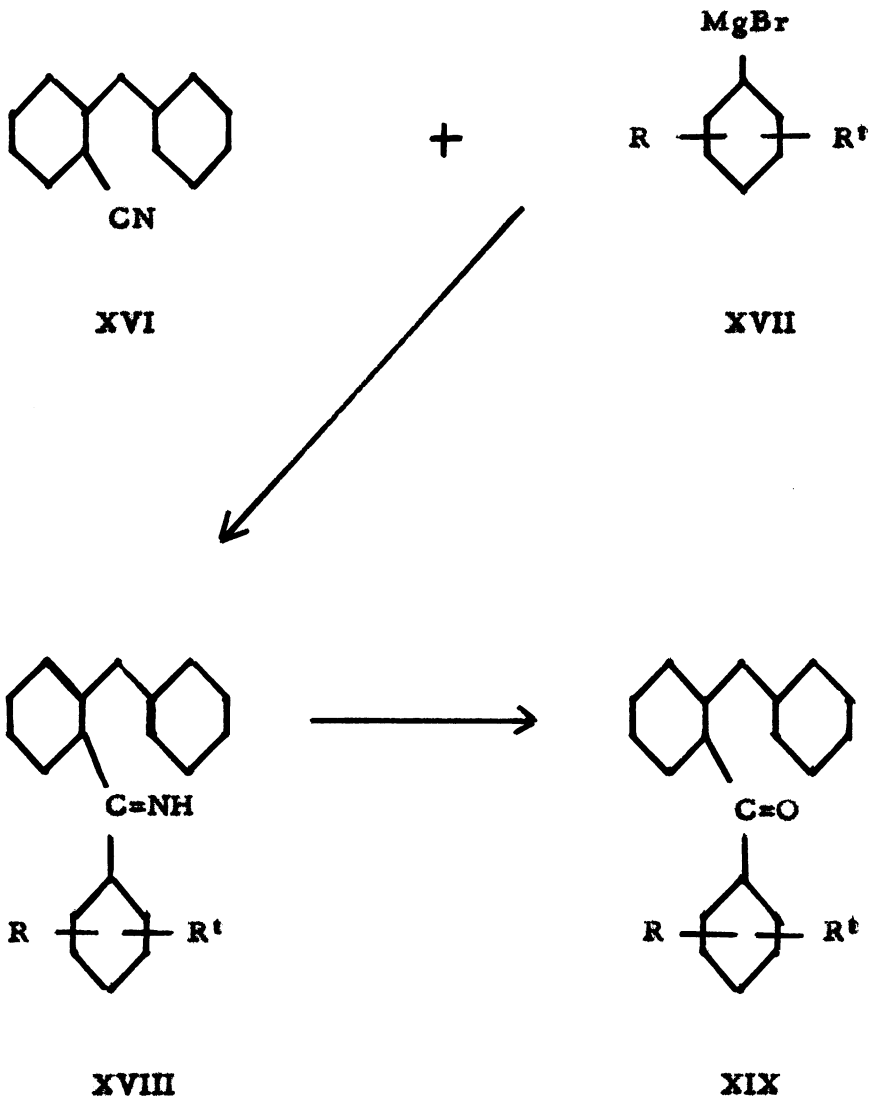
In considering the carbocyclic series (24), substituted o-benzylbenzophenones (XIX) (Chart III) were prepared by allowing the appropriate Grignard reagent (XVII) to react with o-benzylbenzonitrile (XVI), and hydrolyzing the resultant ketimines (XVIII) to the corresponding ketones XIX. Attempts to prepare a pyridyl ketone (XXI) using XVI and a pyridyl Grignard reagent (XX) by this method were unsuccessful.



XVI XX XXI

The preparation of the Grignard reagent (XX) employing the "entrainment" technique (25) appeared to be successful and little difficulty was encountered during the addition of XVI. However, one or two hours of gentle heating produced a dark brown tar. The product was isolated in the usual manner and one of the two fractions obtained yielded an intense red color on treatment with ferrous ion (26). This colorimetric phenomenon might be due to the formation of 2, 2'-dipyridyl (XXII) which has been utilized in the analysis of biologically active

CHART III



XVI XVII

XVIII XIX

R, R' = CH_3

compounds such as vitamin E (27).

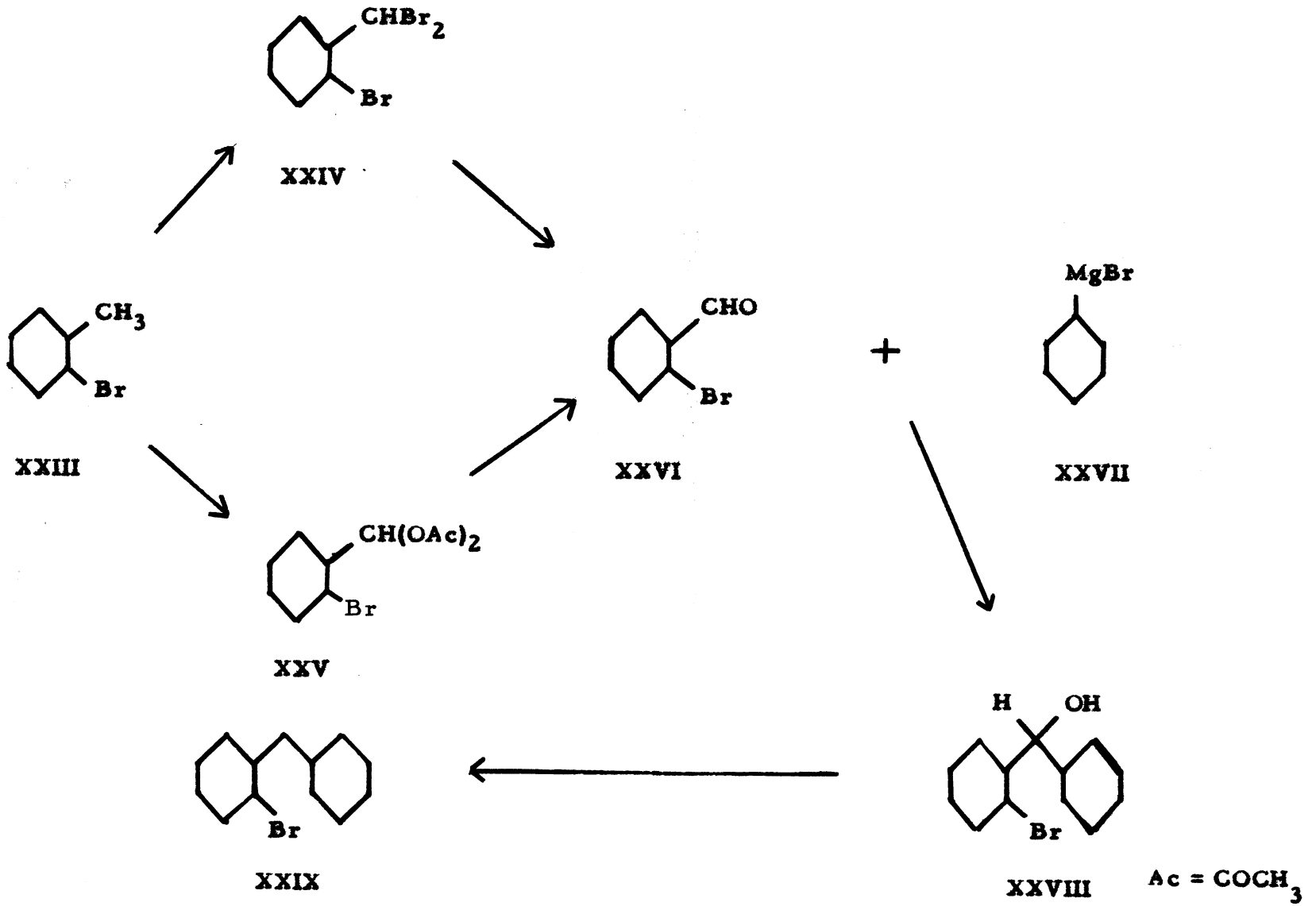
XXII

Considering that the addition of the nitrile (XVI) in the carbocyclic series is a somewhat sluggish reaction, ie. the reaction mixture is usually heated under reflux for relatively long periods of time, and that the pyridyl Grignard reagents are usually only submitted to short reaction times under mild conditions, one may speculate that coupling of the Grignard reagent may have occured during this reaction.

These considerations made the above procedure appear unattractive as a means of preparing ketones of the type I. In order to pursue another synthetic route to I several intermediate products were prepared.

The preparation of o-bromobenzaldehyde (XXVI) was accomplished via two routes starting in each case with o-bromotoluene (XXIII) (Chart IV). The first method (28) consisted in the bromination of XXIII followed by hydrolysis of o-bromobenzalbromide (XXIV) to XXVI. The second technique (29, 30, 31) employed the chromic acid oxidation of XXIII to the diacetate (XXV) which was converted to the aldehyde (XXVI) on hydrochloric

CHART IV



Ac = $COCH_3$

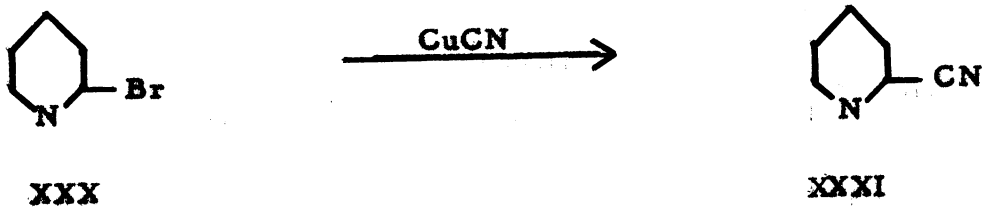
acid hydrolysis.

Although the bromination method was more tedious, it was found to be more applicable for the preparation of large amounts of XXVI since it yielded almost twice as much of the aldehyde (XXVI) (69.5%) as the technique employing chromic acid oxidation (39.1%).

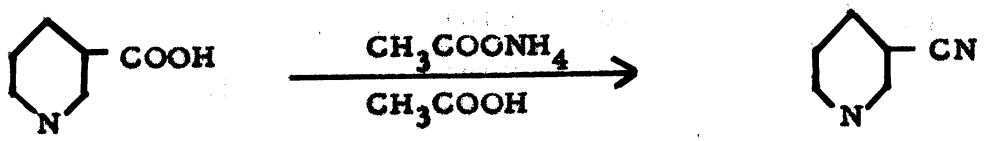
The conversion of XXVI to o-bromodiphenylmethane (XXIX) was accomplished in the usual manner (in 63% yield) by allowing it to react with phenyl magnesium bromide (XXVII), and reducing the resultant compound, o-bromobenzhydrol (XXVIII), with red phosphorous and iodine (Chart IV). No attempt was made to isolate the hydrol since a maximum possible yield of the reduced compound was desired.

Some difficulty was experienced in the preparation of 4-cyanopyridine (XXXVII), while the synthesis of the other isomers, 2-cyano-, (XXXI) and 3-cyanopyridine (XXXIII) were fairly straightforward (Chart V). The esterification of isonicotinic acid (XXXIV) proceeded smoothly, and following the conversion of the ester (XXXV) to isonicotinamide (XXXVI), the nitrile (XXXVII) could not be recovered from the phosphorous pentoxide dehydrating mixture. However, 4-cyanopyridine was subsequently prepared from XXXIV using the same technique (32) which effected the conversion of 3-cyanopyridine (XXXIII) from nicotinic acid (XXXII). A modified von Braun reaction (33) was successful in converting 2-bromopyridine (XXX) to 2-cyanopyridine (XXXI).

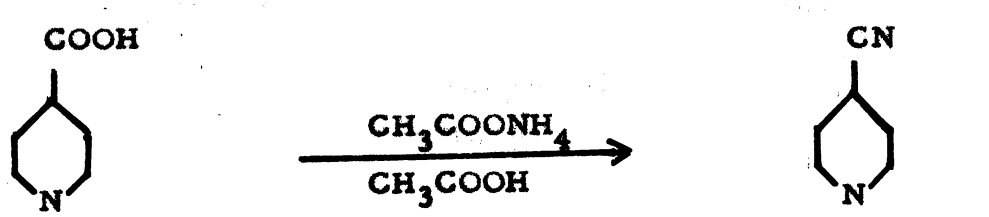
CHART V



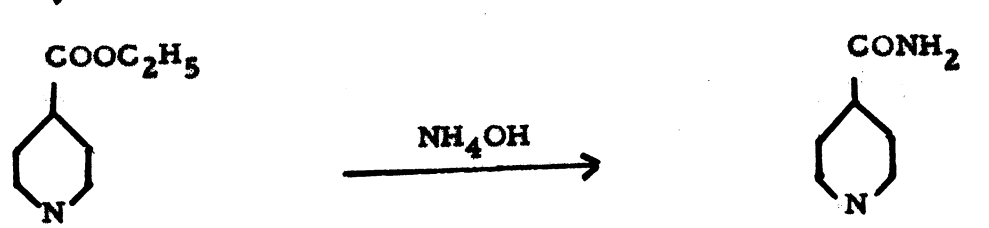
XXX XXXI



XXXII XXXIII



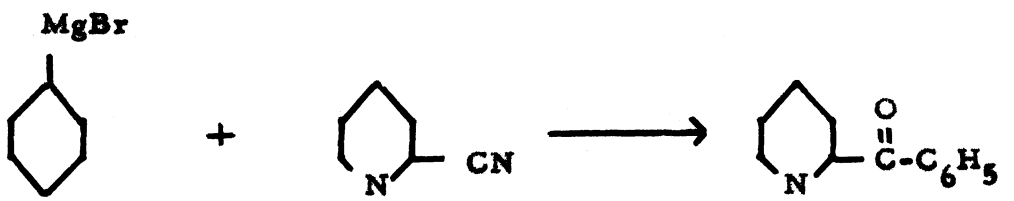
XXXIV XXXVII



XXXV XXXVI

The yields for all of the aforementioned conversions, although somewhat low (averaging 50%), were in the same order of magnitude as those values recorded in the literature.

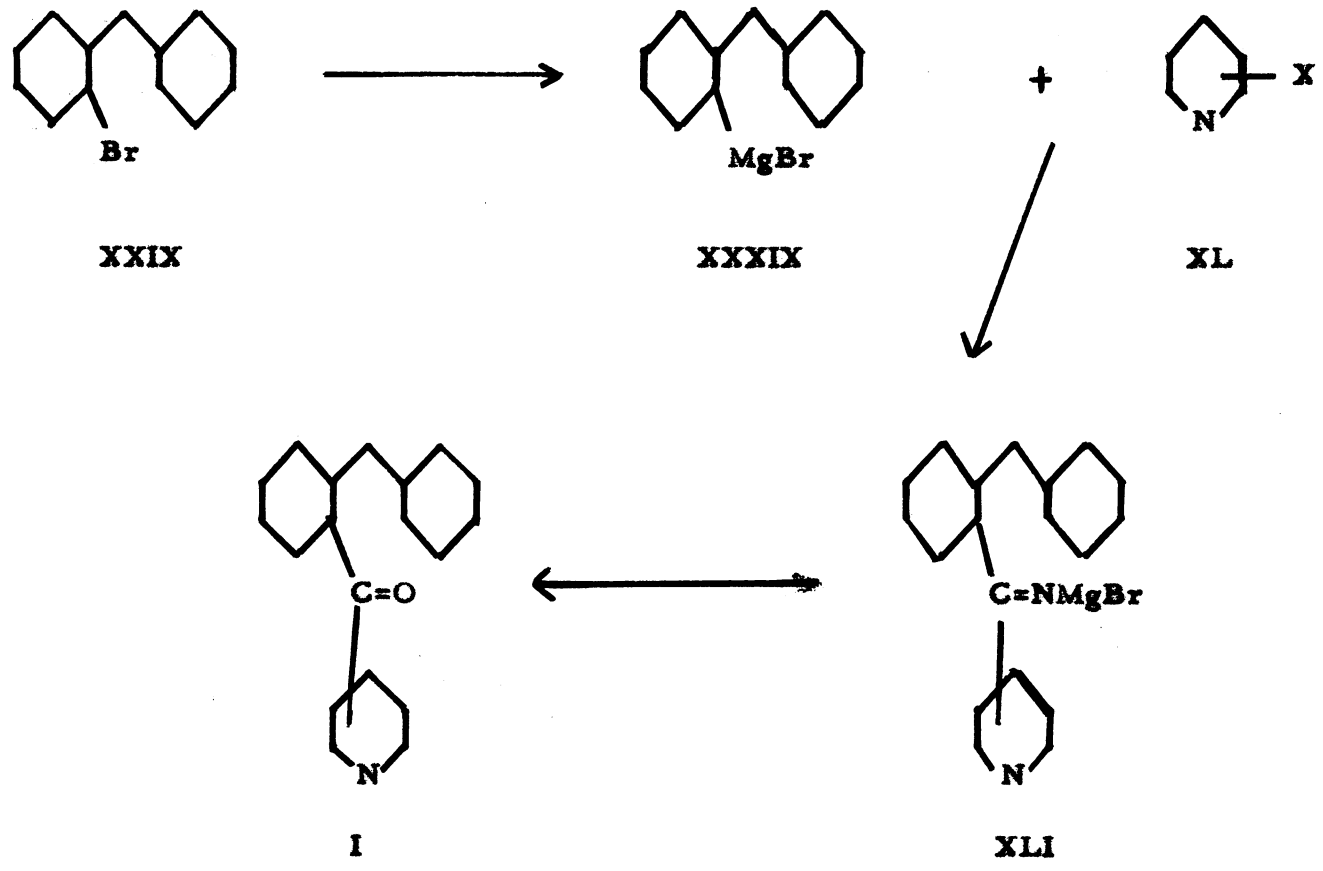
Previous to a study of the interaction of Grignard reagents with cyanopyridines a probing type of reaction was undertaken. The method of Frank and Weatherbee (34) was modified when 2-cyanopyridine (XXXI) was allowed to react with XXVII and a yield of 53% of 2-benzoylpyridine (XXXVIII) somewhat justified the extension of this type of reaction to the preparation of the isomeric pyridyl ketones (I).



XXVII XXXI XXXVIII

The extension of this technique employed the conversion of o-bromodiphenylmethane (XXIX) to its Grignard reagent (XXXIX) followed by treatment with the appropriate cyanopyridine (XL) (Chart VI). Decomposition and hydrolysis of the intermediate (XLI) yielded I. The formation of the Grignard reagent (XXXIX) proceeded smoothly and additional heating of the solution in excess of two hours rarely dissolved the magnesium which remained upon completion of the addition of the

CHART VI



XXIX XXXIX XL

I XLI

X = 2-cyano (XXXI), 3-cyano (XXXIII), or 4-cyano (XXXVII).

bromo compound. The addition of the three isomeric pyridines (XL) was somewhat exothermic in each case and decomposition of the colored complex was straightforward.

The diminished yield of 2-benzylphenyl-3'-pyridyl ketone (XLII) (33%) as compared to 59% for 2-benzylphenyl-2'-pyridyl ketone (XXI) and 52% for 2-benzylphenyl-4'-pyridyl ketone (XLIII) could not be increased by additional heating or use of higher boiling solvents, viz. benzene and toluene.

The utilization of other synthetic routes to ketones of the type I were not investigated. Other methods, ie. Friedel-Crafts reaction would not be as direct as the synthesis employed in this investigation and might possibly lead to a difficult problem of separation and isolation of the products.

All of the isomeric pyridyl ketones (I) were converted to their corresponding hydrocarbons,* 9-(2'-pyridyl)-anthracene (XLIV), 9-(3'-pyridyl)-anthracene (XLV), and 9-(4'-pyridyl)-anthracene (XLVI) in excellent yield. These conversions were accomplished using a mixture of hydrobromic and acetic acids under reflux conditions, and in a sealed tube at elevated temperatures. Other cyclodehydrating reagents,

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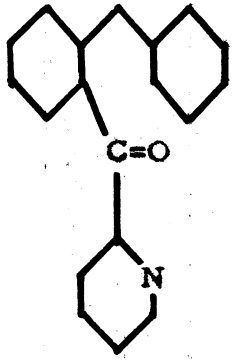
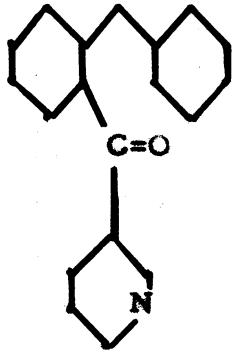
* The structures of all of the isomeric pyridyl anthracenes and all of the isomeric pyridyl ketones were included in Chart VII for reference.

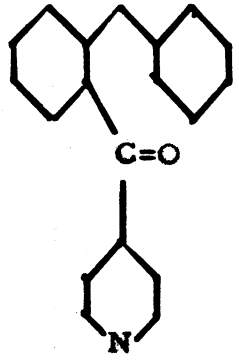
CHART VII



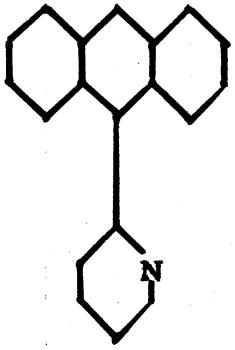
XXI



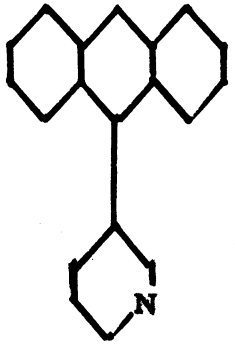
XLII



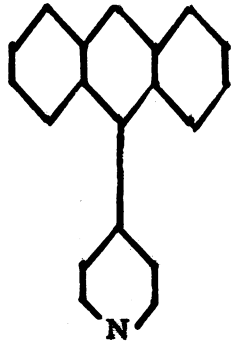
XLIII



XLIV



XLV



XLVI

ie. phenyl acid phosphate, and benzenesulfonic acid were also employed successfully.

The isolation of the pyridyl anthracenes (II) consisted in cooling the reaction mixture, neutralizing with dilute sodium carbonate or hydroxide solution and collecting the precipitate. The procedure was identical in all cases.

The ultraviolet spectra* of the three isomeric pyridyl anthracenes (II) are shown on Figures 4, 5, and 6**. Figure 4, indicates a similarity in spectrum between anthracene, 9-phenylanthracene (XLVII), and an example of II, 9-(4'-pyridyl)-anthracene (XLVI). No significant bathochromic or hypsochromic shift were noted. The strong similarity of the ultraviolet spectra served to support elemental analysis, and known intermediate structures as evidence for the proposed structures of the isomeric pyridyl anthracenes (II). Acceptable analytical data, well established chemical reactions, and known intermediate compounds served as evidence for the assigned structures of the isomeric pyridyl ketones (I).

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* The ultraviolet spectra of the pyridyl anthracenes were obtained using a Beckmann spectrophotometer (model DU, 1-cm., silica cell) at a concentration of 5 mg. per liter using 95% ethyl alcohol as the solvent.

** The ultraviolet spectra observed in Figures 4, 5, and 6 were measured on the pyridyl anthracenes which had been obtained via benzenesulfonic acid cyclization. The pyridyl anthracenes which had been obtained via other cyclodehydrating reagents yielded identical ultraviolet spectra.

Many cyclizations using a mixture of hydrobromic and acetic acids were undertaken in order to approximate the relative rates of cyclization of the isomeric pyridyl ketones (I). Table I, indicates a definite trend in which ketone XLIII appears to cyclize more rapidly than ketone XLII, which in turn, showed a more rapid rate of cyclization than ketone XXI.

TABLE I

YIELDS OF CYCLODEHYDRATION PRODUCTS USING A MIXTURE OF HYDROBROMIC AND ACETIC ACIDS

Heating Time (in hours)	% Yield of Products		
	XLIV	XLV	XLVI
1.0	0	14	62
2.0	9	31	97
3.5	--	--	100
5.0	40	89	91
10	50	93	--
22	--	93	--
44	--	92	--
52	92	--	--
63	84	87	100

However, in order to investigate the rates of cyclization of isomeric pyridyl ketones (I) a more quantitative study was undertaken. Using the specially prepared reaction vessels used by Van Oot (21) and other workers (6, 7) in their quantitative gravimetric studies, attempts were made to determine the rate constants for the cyclization of I $\longrightarrow$ II.

Several modifications of the original procedure were necessitated because of the basic nature of the pyridyl group. In the carbocyclic series, the solutions following their removal from the constant temperature bath were poured into a beaker and crystallization was induced by scratching the sides of the beaker. The pyridyl anthracenes, on the other hand, were neutralized with a control sodium hydroxide solution and precipitation was instantaneous.

An additional modification consisted of washing the precipitate with hot water to dissolve any sodium hydroxide which has crystallized from solution since these solutions had been kept in a cold room previous to their quantitative transfer. Errors became apparent in the quantitative transfer to the sintered glass funnel and since the organic compounds were in an aqueous media any unreacted ketone would usually appear as oil droplets which would be occluded by the precipitate and result in non-reproducible data.

In order to circumvent these errors, it became necessary to obtain a high percentage of reaction which would minimize the amount of unreacted ketone. However, Van Oot (21) suggested that yields in excess of 90% could not be considered accurate in view of the logarithmic nature of the equation which has been used to calculate the rate constants. This equation is given below where X = the yield of the reaction in percent, and t = reaction time in hours, and K = the rate constant x 10^{-2} $hours^{-1}$.

$$K = \frac{2.303}{t} \log \frac{100}{100 - X}$$

Examination of the logarithmic term in the equation indicates that yields in excess of 90% would result in a logarithm term of ten or more which would lead to a number greater than one. Such a high value would magnify the logarithmic portion of the equation and minimize the first term which includes the important function of t.

With these restrictions in mind the gravimetric determinations became tedious and their precision although sufficient for qualitative purposes did not warrant any further investigation.

The gravimetric rate constants for the cyclization of the isomeric pyridyl ketones (I) seemed to support the earlier view that hydrocarbon*XLVI was formed at a more rapid rate than XLV. Although the formation of XLV appeared to be more rapid than the formation of XLIV, a conclusive statement should be avoided on two counts. Firstly, the values were not too distant (26.99×10^{-2} hours^{-1} for XLV) as compared to (20.67×10^{-2} hours^{-1} for XLIV); secondly, only one value for the formation of XLIV was obtainable.

However, the gravimetric data (Tables II - V) suggest rather strongly that all of the isomeric pyridyl anthracenes (II) were cyclized at a more rapid rate than the conversion of o-benzylbenzophenone (XLVIII) to 9-phenylanthracene (XLVII). The rate constants for the conversion

* refer to a pyridyl anthracene

TABLE II*

Rate of Cyclization of o-Benzylbenzophenone to 9-Phenylanthracene

Run	Weight ketone (grams)	Weight anthracene (grams)	Time Hours	Yield %	K x 10^{+2} $hrs.^{-1}$
1	0.3475	0.0700	6.5	20.15	3.46
2	0.3785	0.1404	10.5	37.09	4.40
3	0.3864	0.2815	24.0	72.86	5.32
				Average	4.4
				Average Deviation	0.6

The solubility of the anthracene in 20 ml. of the acid mixture was 0.02 g. according to (6, 7, 21).

The rate constant reported by earlier workers (6, 7, 21) was $4.4 \pm 0.2 \times 10^{-2}$ $hrs.^{-1}$

* The gravimetric determinations of the rates of cyclization shown in Tables II - V were measured at $117.5 \pm 0.2^{\circ}$.

TABLE III

Rate of Cyclization of 2-Benzylphenyl-2'-pyridyl Ketone

9-(2'-Pyridyl)-anthracene

Run	Weight ketone (grams)	Weight anthracene (grams)	Time Hours	Yield %	$K \times 10^{+2}$ hrs.$^{-1}$
1	0.3633	0.2875	9.0	84.43	20.67
			Average		20.67
			Average Deviation		---

The solubility of the anthracene in 65 ml. of the neutral solution at room temperature was 0.0061 g.

TABLE IV

Rate of Cyclization of 2-Benzylphenyl-3'-pyridyl Ketone to 9-(3'-Pyridyl)-anthracene

Run	Weight ketone (grams)	Weight anthracene (grams)	Time Hours	Yield %	$K \times 10^{+2}$ $hrs.^{-1}$
1	0.4345	0.2951	5.0	72.5	25.81
2	0.3105	0.2217	5.5	75.98	25.93
3	0.3088	0.2392	6.0	82.68	29.25
			Average		26.99
			Average Deviation		1.5

The solubility of the anthracene in 65 ml. of the neutral solution at room temperature was 0.01 g.

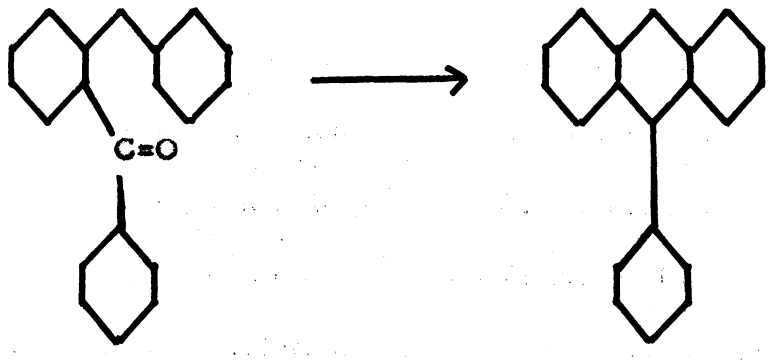
TABLE V

Rate of Cyclization of 2-Benzylphenyl-4'-pyridyl Ketone to 9-(4'-Pyridyl)-anthracene

Run	Weight ketone (grams)	Weight anthracene (grams)	Time Hours	Yield %	$K \times 10^{+2}$ $hrs.^{-1}$
1	0.3552	0.2443	2.0	73.41	66.25
2	0.3196	0.2390	2.5	80.47	65.34
			Average		65.80
			Average Deviation		0.46

The solubility of the anthracene in 65 ml. of the neutral solution at room temperature was 0.0026 g.

of XLVIII to XLVII were determined by earlier workers (6, 7, 21) and repeated in this investigation (Table II).



XLVIII XLVII

The rates of cyclization of the isomeric pyridyl ketones (I) were also determined spectrophotometrically using a method developed by R. D. Katstra*. The conversion of XLVIII to XLVII was also undertaken spectrophotometrically for comparison purposes.

Basically, the technique is a spectrophotometric determination of the product of a reaction which in this investigation was a pyridyl anthracene (II). By examining the ultraviolet spectra of the ketones (I) (Figures 7, 8, and 9) and the hydrocarbons (II) (Figures 4, 5, and 6) it can readily be seen that the ketone absorbance is small in the region of

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* For a detailed description of this technique see (22) Richard D. Katstra, M.S. Thesis, Virginia Polytechnic Institute, May, 1958.

maximum absorbance of the hydrocarbon.

The reaction mixtures were analyzed after definite time intervals and the hydrocarbon products determined by measuring the absorbance of the above reaction mixtures. The first order rate constants were evaluated by plotting the logarithm of the ketone concentration against time and multiplying the slope of this line by 2.303 (Figure 3*). The calculations of the ketone concentrations from the absorbance readings are shown in the sample calculation (35) in Table VI. The approximate percent of reaction was obtained by dividing the heat corrected reading by the extinction coefficient x 500 x 10^{-5}. The ketone correction was calculated by multiplying the heat corrected reading by the percent of ketone present. The final concentration of the hydrocarbon was obtained by dividing the final corrected reading by the extinction coefficient.**

Previous to the analysis of the reaction mixtures, the decomposition corrections and the extinction coefficients were measured. During the former measurements the plot of the absorbance values against

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* The straight line graphs (Figures 1, 2, and 3), and the sample calculation (Table VI) were intended for illustrative purposes, and 9-(3'-pyridyl)-anthracene at 368 mu was merely chosen as a random sample. However, all of the values for the decomposition data, and extinction coefficients were included in Tables VII - X for future reference.

** For a more detailed explanation of Table VI, see pp. 71-72.

TABLE VI

Sample Calculation for the Determination of the Ketone Concentrations of 2-Benzylphenyl-3'-pyridyl Ketone

Time Hours	Uncorrected* Reading (E)	E x 2.5	Decomposition Correction Factor	Heat Corrected Reading	Approx. % Reaction	Approx. % Ketone
0	0.045	0.1125	0.0000	0.1125	0.00	100
5	0.438	1.095	-0.0332	1.129	14.29	85.71
10	0.771	1.928	-0.0664	1.994	25.24	74.76
15	1.075	2.688	-0.0996	2.788	35.30	64.70
20	1.294	3.235	-0.1328	3.368	42.64	57.30
25	1.492	3.730	-0.1660	3.896	49.32	50.68

* Absorbance reading of the reaction mixture at 368 mu was obtained directly from the spectrophotometer.

TABLE VI (continued)

Time Hours	Ketone Correction	Corrected Reading (Final)	Hydrocarbon Concentration x 10^{-5}	Ketone Concentration x 10^{-5}	5 + logarithm Ketone Concentration
0	-0.1125	0.000	0.00	500	2.6990
5	-0.0969	1.032	65.32	434.7	2.6382
10	-0.0845	1.910	120.9	379.1	2.5787
15	-0.0731	2.715	171.2	328.8	2.5169
20	-0.0647	3.303	209.0	291.0	2.4639
25	-0.0573	3.839	242.9	257.1	2.4101

time did not yield a straight line in two cases, namely, hydrocarbons XLIV, and XLVII. As a result, the correction for decomposition due to heating was neglected in these two cases. The correction factors for both hydrocarbons XLV, and XLVI were calculated by multiplying the slope of the line (Figure 1) by t (the number of hours of heating). If the slope of the line was negative, the decomposition correction factor was added to the absorbance readings; however, a positive slope would necessitate subtracting this factor from the absorbance readings.

The determination of the extinction coefficients were made by plotting the absorbance values against varying concentrations of the hydrocarbon solutions. The hydrocarbon solutions were diluted with ethyl alcohol to a concentration which obeyed Beer's Law (Figure 2). A closer examination of Figure 2 reveals that the validity of Beer's Law beyond the approximate concentration of 115×10^{-5} molar cannot be substantiated. Therefore if the absorbance values of the reaction mixtures forming the hydrocarbon was in excess of that concentration (ie. greater than 1.9), then the plot of the logarithm of the ketone concentrations against time might not lead to a straight line similar to Figures 2 and 3 (36). This effect occured with all of the pyridyl ketones and resultant decreases* in concentration were made necessary.

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* Details concerning the decreases in concentration of the reaction mixtures are discussed in the Experimental section in a footnote.

The results of the spectrophotometric determinations (Tables VII - X) support to some degree some of the earlier assumptions. Firstly, all of the isomeric pyridyl ketones (I) appear to cyclize at a greater rate than o-benzylbenzophenone (XLVIII). Secondly, in considering only the isomeric pyridyl ketones (I), XLIII tends to cyclize at a more rapid rate than XLII. The rates of cyclization of XLII and XXI were found to be of the same order of magnitude while the gravimetric studies indicated a slight difference in their respective rates of cyclization. However, in considering that the spectrophotometric determinations were of a more precise nature than the gravimetric studies, it was felt that one could rely more heavily on the former measurements.

Current views (6) on the mechanism of the aromatic cyclodehydration reaction support the following equilibria shown in Chart VIII. Other workers (7, 21) have theorized that the "overall rate of reaction was controlled by two rate determining steps of opposing electrical requirements and that a decrease in the effectiveness in the positive character of the central carbon atom of the conjugate acid (L) would lead to a lower rate of cyclization of that acid" L $\longrightarrow$ LII.

An electron releasing group in the bottom ring (R) would effect such a decrease in the central carbon atom of XLIX; however, these electron releasing groups would also increase the electron density of

TABLE VII*

Rate of Cyclization of o-Benzylbenzophenone to 9-Phenylanthracene

Wavelength (mu)	Extinction Coefficient x 10^3	Heat Correction	K x 10^{+2} $hrs.^{-1}$
332	0.615	neglected	0.726
348	1.26	"	0.727
366	1.95	"	0.694
386	1.79	"	0.716
		Average	0.727
		Average Deviation	0.011

* The spectrophotometric determinations of the rates of cyclization shown in Tables VII - X were measured at 100 + 0.2°.

TABLE VIII

Rate of Cyclization of 2-Benzylphenyl-2'-pyridyl Ketone to 9-(2'-Pyridyl)-anthracene

Wavelength (mu)	Extinction Coefficient x 10^3	Heat Correction	K x 10^{+2} hrs.$^{-1}$
352	1.03	neglected	2.78
368	1.38	"	2.75
388	1.30	"	2.71
		Average	2.75
		Average Deviation	0.023

TABLE IX

Rate of Cyclization of 2-Benzylphenyl-3'-pyridyl Ketone to 9-(3'-Pyridyl)-anthracene

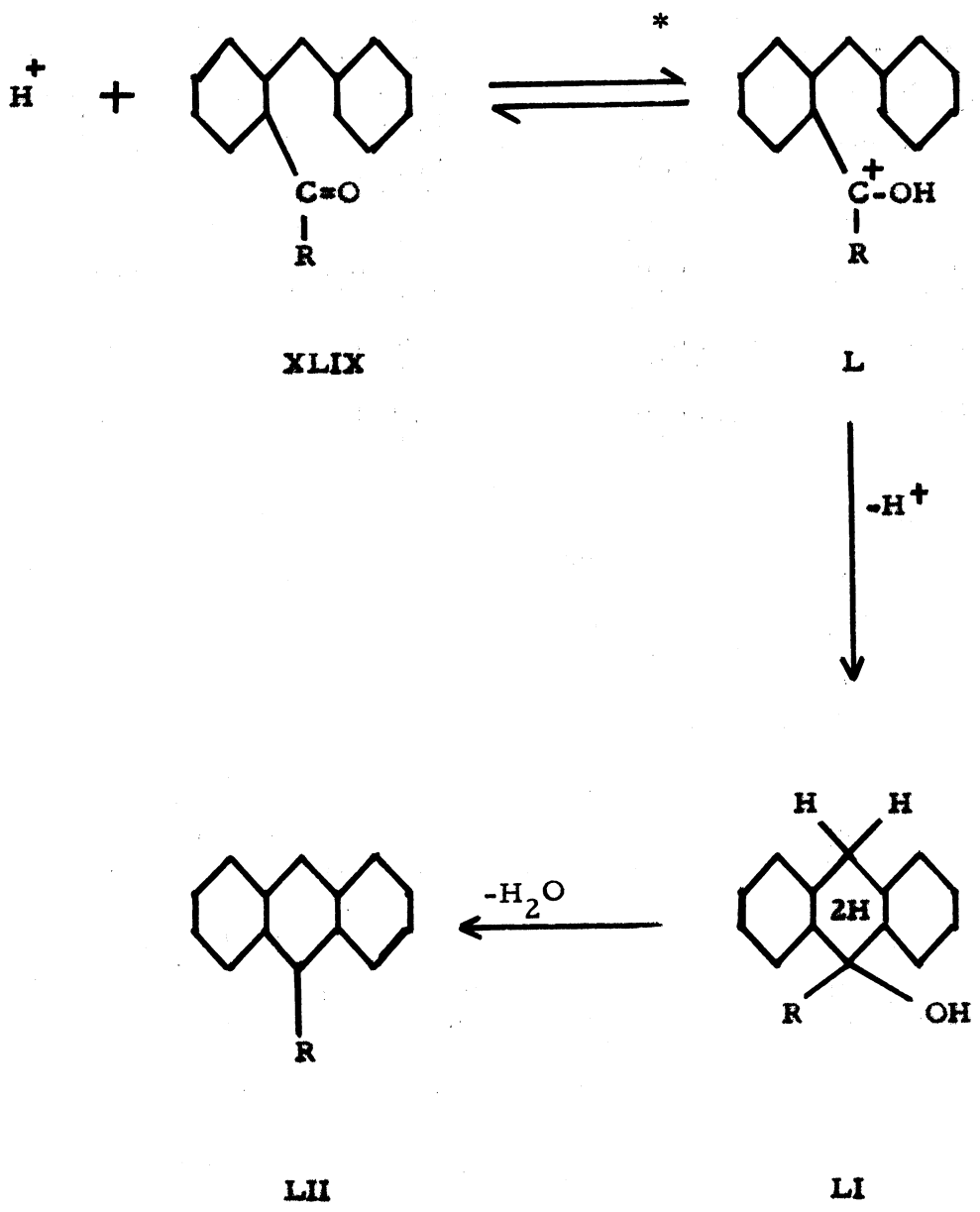
Wavelength (mu)	Extinction Coefficient x 10^3	Heat Correction Slope	K x 10^{+2} $hrs.^{-1}$
350	1.15	-0.00589	2.78
368	1.58	-0.00664	2.70
388	1.42	-0.00407	2.60
		Average	2.69
		Average Deviation	0.063

TABLE X

Rate of Cyclization of 2-Benzylphenyl-4'-pyridyl Ketone to 9-(4'-Pyridyl)-anthracene

Wavelength (mu)	Extinction Coefficient x 10^3	Heat Correction Slope	K x 10^{+2} $hrs.^{-1}$
350	0.840	0.00348	8.59
366	1.09	0.02090	8.36
386	1.13	0.00357	8.15
		Average	8.37
		Average Deviation	0.15

CHART VIII



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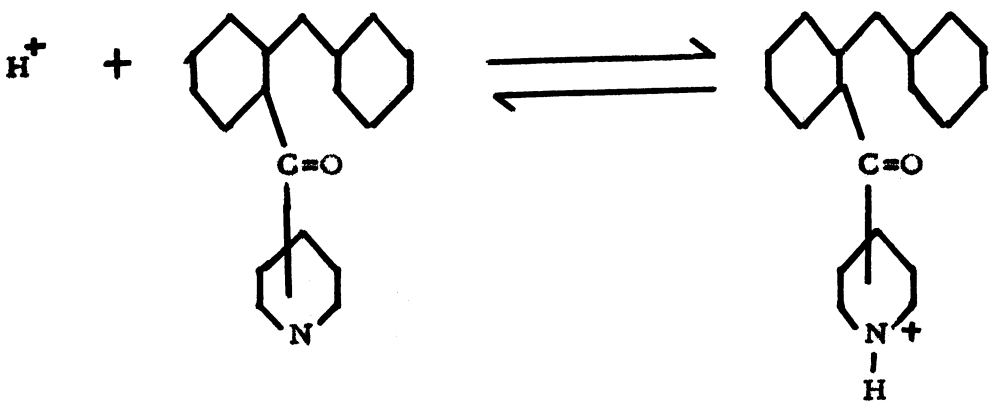
* The equal lengths of the respective arrows in all of the equilibria notations in this thesis are not indicative of the position of the equilibrium of the reactants in question.

the carbonyl oxygen thus shifting the equilibrium XLIX $\rightleftharpoons$ L to the right. This increase in electron density of the carbonyl oxygen would increase the concentration of the conjugate acid (L) and accelerate the overall rate of XLIX $\longrightarrow$ LII.

Other workers (37) in this field have substantiated that the overall rate of the reaction XLIX $\longrightarrow$ LII was dependent upon the position of the equilibrium XLIX $\rightleftharpoons$ L.

An electron attracting substituent in the bottom ring (R) would have the opposite effect, ie. shift the equilibrium XLIX $\rightleftharpoons$ L to the left and decrease the concentration of the conjugate acid (L), but simultaneously increase the positive nature of the carbonium ion in L and thus facilitate its attack on the ortho position in the benzene ring into which cyclization will occur.

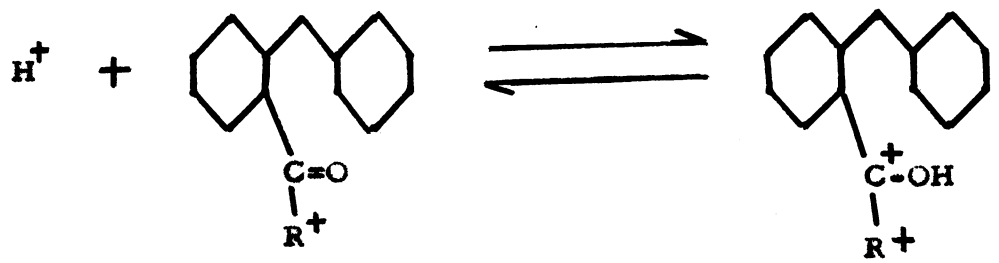
Turning our attention to the isomeric pyridyl ketones (I) it seems plausible to assume that in an acid environment the species will exist primarily as a pyridinium ion (LIII). If such is the case then an excess of the stoichiometric amount of acid would be necessary to effect cyclization since an equimolar amount of the acid would merely protonate the basic nitrogen center. This assumption was somewhat verified during this investigation when ketone XLII was heated under reflux for five hours with an equimolar amount of 48% hydrobromic acid in acetic acid and no hydrocarbon could be recovered. An excess of the cyclizing reagent



I LIII

in contact with XLII for five hours provided a yield of 88% of the corresponding hydrocarbon (XLV).

Thus the presence of a positive pole in LIV would give rise to very strong electron withdrawing properties of the lower ring (R) and the equilibrium may be more generally written as LIV ⇌ LV.



LIV LV

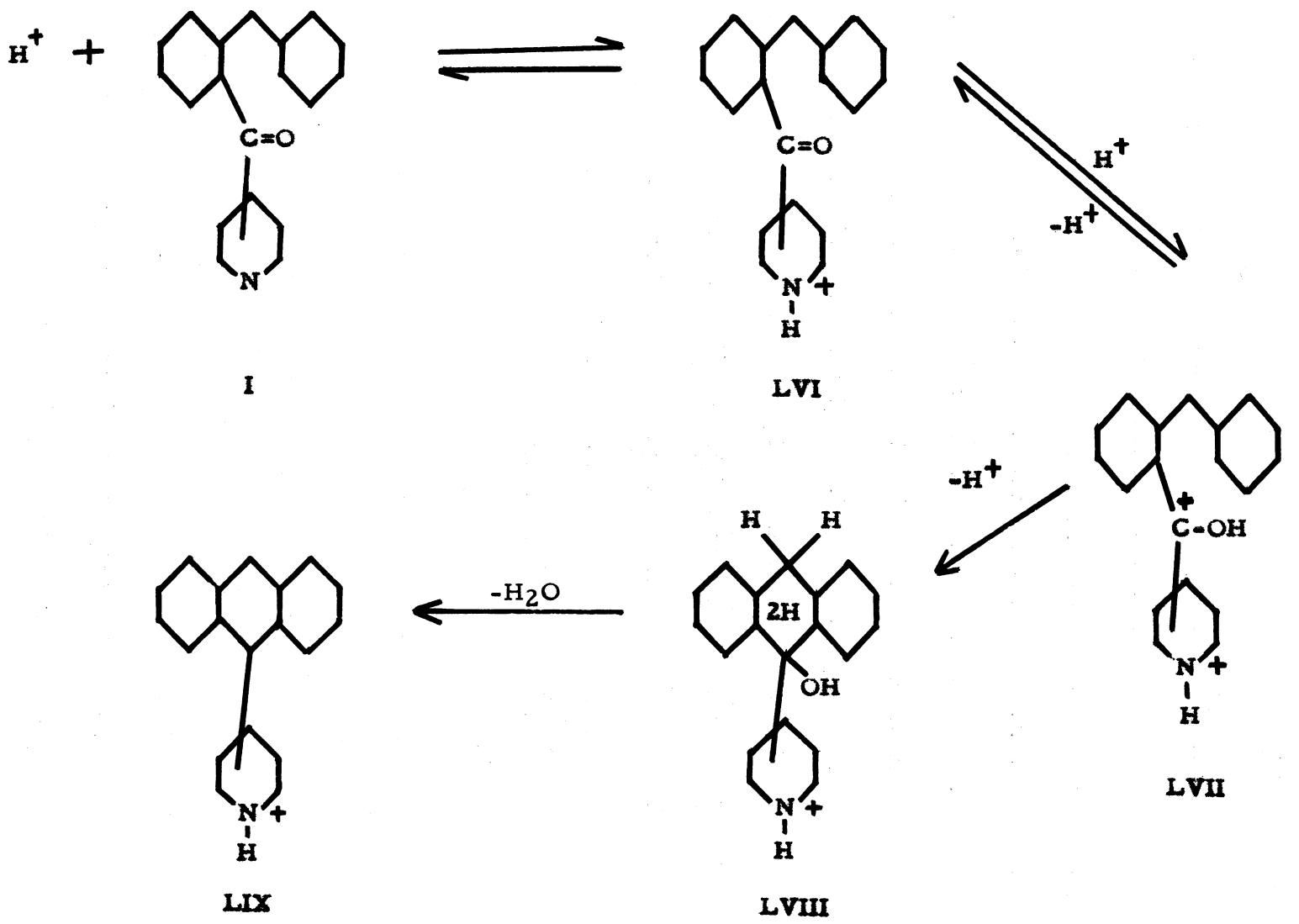
If electron withdrawing substituents have a tendency to decrease

the electron density of the carbonyl oxygen in XLIX and simultaneously increase the positive character of the carbonium ion in the conjugate acid (L) then it follows that this effect should be present to a greater extent in the equilibrium LIV $\rightleftharpoons$ LV.

As we have previously mentioned, studies (7, 21) have indicated that the more significant rate determining step was the position of the equilibrium of XLIX and the conjugate acid (L), and not the attack of the carbonium ion on the ortho position of the benzene ring into which cyclization will occur (L $\longrightarrow$ LII).

Considering the strong positive nature of the pyridinium ion, it appears that the decrease in electron density of the carbonyl oxygen would shift the equilibrium to the left in LVI $\rightleftharpoons$ LVII (Chart IX) thus decreasing the concentration of the conjugate acid (LVII) which would lead to a lower rate of cyclization. However, the gravimetric and particularly the spectrophotometric data suggest that the isomeric pyridyl ketones (I) cyclise at a more rapid rate than the carbocyclic analogs. With these facts in mind it might be feasible to argue that the other proposed rate determining step LVII $\longrightarrow$ LIX is the more significant one as regards the pyridyl ketones (I). Therefore the relative positive nature of the carbonium ion in LVII may be said to have the greater effect on the conversion LVII $\longrightarrow$ LIX and possibly be considered as the most significant single factor, in this series of ketones, in the overall cyclization I $\longrightarrow$ LIX.

CHART IX



Considering our present knowledge of electronic effects in organic chemistry, a clear explanation concerning the relative rates of cyclization of the isomeric pyridyl ketones (I) cannot be given at this time. The electron density of the ortho position of the benzene ring into which cyclization will occur is identical since no substituents are present in the aforementioned benzene ring. Hence, this concept would not be a differentiating factor. It is also felt that steric effects could be neglected in view of the relatively small size of the proton in comparison with larger groups, ie. methyl. However, by following the earlier line of reasoning, ie. if the positive nature of the carbonium ion in LVII tends to influence the rate determining step LVII $\longrightarrow$ LIX, then any factor which would alter the status of the carbonium ion may be said to effect the overall rate of cyclization. Possibly the effect of the strong electronic attraction of the pyridinium ion could alter the positive nature of the carbonium ion in LVII by virtue of its position in relation to the carbonium ion.

However, it would be difficult to see how this would account for the individual differences noted in the cyclization of the isomeric pyridyl ketones (I).

Admittedly this is probably a gross oversimplification in view of the heterogeneous and complex equilibria existing during the cyclization. However, a feasible and academic approach to the problem has been

suggested in light of the previous studies which have been undertaken in this field keeping in mind the results of this investigation.

A further complicating factor was the unavailability of data concerning electronic effects through a protonated pyridine ring as well as the lack of significant tautomeric effects in the protonated species.

Certainly, a completely different mechanism other than an aromatic cyclization may be postulated; however, it would be presumptuous even to attempt such a step in view of the extensive nature of the research which has proceeded this relatively brief investigation.

EXPERIMENTAL

EXPERIMENTAL[a, b]

o-Bromobensaldehyde (XXVI).

A. Via Chromic Acid Oxidation and Hydrolysis.

A solution of 238 g. (1.39 moles) of o-bromotoluene, 1700 ml. of acetic anhydride, 1000 ml. of glacial acetic acid, and 700 g. of concentrated sulfuric acid was placed in a five liter three-necked flask equipped with a mechanical stirrer and thermometer and cooled to 0° in an ice-salt mixture. A slurry of 475 g. (4.75 moles) of granular chromium trioxide and 1.5 liters of glacial acetic acid were added with stirring maintaining the reaction mixture from 0 - 10°. Upon completion of the addition (three hours), the partially solidified green solution was poured onto a large portion of cracked ice. The combined mixture was extracted several times with isopropyl ether, and the ethereal extracts were washed with dilute sodium carbonate solution, concentrated, and the semi-solid residue was placed in a 500 ml. round-bottomed flask with 250 ml. of concentrated hydrochloric acid and heated under reflux for six hours. The solution was cooled, diluted

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a All recorded melting points are uncorrected unless otherwise specified, and all temperature values are recorded on the centigrade scale.

b The microanalysis were carried out by the Geller Microanalytical Laboratories, West Englewood, New Jersey.

with 300 ml. of cold water, extracted several times with ethyl ether and dried over anhydrous magnesium sulfate. The dried ethereal solution was concentrated, the residue distilled, and the fraction distilling between 95 - 100° (9 mm.) [Lit. (38) 118 - 119° (12mm.)] was collected; yield 96 g. (39%).

B. Via Bromination and Hydrolysis.

A solution of 171 g. (one mole) of o-bromotoluene was placed in a 500 ml. three-necked flask equipped with a mechanical stirrer, reflux condenser, and a dropping funnel. The solution was heated to 130° with stirring and 160 g. (one mole) of bromine was added dropwise directly in front of a source of ultraviolet light. Upon the completion of the addition of one mole, a second mole of bromine was added at 165° and on completion the solution was heated for an additional hour at this temperature. The resulting brown solution was placed in a two liter round-bottomed flask containing 150 g. of calcium carbonate, and 500 ml. of water and the contents were heated under reflux for ten hours. The mixture was steam distilled and the distillate was extracted several times with ethyl ether. The ethereal solution was concentrated and the residual oil added to a solution of sodium bisulfite (175 g./500 ml. of water). The resultant white precipitate was collected, washed with ethyl ether, made alkaline with sodium carbonate solution and steam distilled. The distillate was extracted several times with ethyl ether and the extracts were

dried over anhydrous magnesium sulfate. The dried ethereal solution was concentrated and the residual oil distilled under reduced pressure. The fraction distilling between 84 - 87° (3 mm.) [Lit. (38) 118 - 119° (12 mm.)] was collected. The yield was 129 g. (70%) and the semicarbazone melted between 214 - 216° (corr.) [Lit. (37) m.p. 214°].

o-Bromodiphenylmethane (XXIX).

A Grignard reagent was prepared from 218 g. (1.4 moles) of bromobenzene and 33.9 g. (1.4 moles) of magnesium in 300 ml. of anhydrous ethyl ether in a three-necked one liter flask equipped with a mechanical stirrer, reflux condenser, and a dropping funnel. A solution of 128 g. (0.70 mole) of o-bromobenzaldehyde in 125 ml. of anhydrous ethyl ether was added with stirring over a period of several hours and the subsequent milky solution was heated under reflux for two hours. The complex was decomposed with an equivalent amount of 20% ammonium chloride solution and the ethereal solution was decanted and concentrated. The resultant oil was introduced into a three-necked two liter flask equipped with a mechanical stirrer, and a reflux condenser and 24.8 g. (0.80 mole) of red phosphorous, 24.8 g. of iodine, 1400 ml. of glacial acetic acid, and 200 ml. of water were added and the contents were heated under reflux for 30 hours. The resultant dark red solution was filtered while hot, and the filtrate was poured onto twice its volume of ice, neutralized with dilute sodium carbonate solution, and extracted several times with

ethyl ether. The combined ether extracts were washed with 10% sodium hydroxide solution, then with water and dried over anhydrous magnesium sulfate. The dried ethereal solution was concentrated, the resultant oil distilled, and 108 g. (63%) were collected between 177 - 182° (22 mm.) [Lit. (39) 180 - 183° (22 mm.)].

2-Cyanopyridine (XXXI).

A solution of 101 g. (0.64 mole) of 2-bromopyridine, 50 g. (0.57 mole) of cuprous cyanide, and a trace of anhydrous cupric sulfate were placed in a 250 ml. round-bottomed flask and heated cautiously with a free flame with vigorous shaking until the mixture barely fused. The flask was then equipped with an air-cooled condenser, placed in a metal bath maintained at ca. 180° and a vigorous reaction ensued during which time the reaction flask was intermittently cooled in an ice-water mixture. Immediately following the completion of the reaction (15 minutes) a von Braun distillation head was attached to the reaction flask and the contents were crudely distilled at 50 mm. using a free flame. The partially solidified distillate (ca. 50 ml.) was washed with dilute sodium hydroxide solution and the resultant yellow oil was extracted several times with ethyl ether and dried over "Drierite". The dried ethereal solution was concentrated and the yellow oil fractionated collecting the portion boiling between 121 - 133° (25 mm.) [Lit. (33) 118 - 120° (25 mm.)]; yield 33 g. (50%).

3-Cyanopyridine (XXXIII).

A mixture of 100 g. (0.82 mole) of nicotinic acid, 49.6 g. (0.82 mole) of glacial acetic acid, and 126 g. (1.64 moles) of ammonium acetate was placed in a 500 ml. round-bottomed flask equipped with a Vigreaux column, distillation head, thermometer, water-cooled condenser, Dean-Stark tube, and a receiver. The contents were heated, the distillates below 130° were discarded, and the water was drained from the condenser converting it to an air-cooled condenser. About 90 ml. of the distillate which boiled between 135 - 140° was collected, and a third fraction from 140 - 180°, consisting mainly of a white solid, was also collected and retained. The latter two fractions were made alkaline with ammonium hydroxide, the semi-solid material was extracted several times with ethyl ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. The dried ethereal solution was concentrated and the residual oil distilled. The fraction distilling between 101 - 104° (31 mm.) Lit. (32) 105° (30 mm.) was collected; yield 43 g. (50%).

Ethyl Isonicotinate (XXXV).

A solution of 102 g. (0.83 mole) of isonicotinic acid in ca. 200 g. of absolute ethyl alcohol, and ca. 200 g. of concentrated sulfuric acid was placed in a 500 ml. round-bottomed flask equipped with a water-cooled condenser and heated on a steam bath for a period of five hours.

The contents were cooled, poured over cracked ice, made alkaline with ammonium hydroxide, and extracted several times with ethyl ether. The combined ether extracts were dried over anhydrous potassium carbonate, and following concentration the resultant oil was distilled. The fraction containing 97 g. (78%) boiling between 114 - 115° (24 mm.) [Lit. (40) 118 - 119° (25 mm.)] was collected.

Isonicotinamide (XXXVI).

A solution containing 90 ml. (0.6 mole) of ethyl isonicotinate and 360 ml. of ethyl alcohol was placed in a three-necked one liter flask and heated under reflux for 12 hours during which time a stream of ammonia was bubbled through the reaction mixture. The ethyl alcohol was removed and the residue appeared to be unreacted ester. The oily residue was treated with 250 ml. of concentrated ammonium hydroxide at 0° for about 11 hours. Some solid material precipitated from solution and repetition of the process yielded 58 g. (75%) of the amide, m.p. 157-158° (corr.) [Lit. (40) m.p. 156°].

Attempted Preparation of 4-Cyanopyridine (XXXVII).

A mixture of 57 g. (0.47 mole) of isonicotinamide and 75 g. of phosphorous pentoxide was introduced into a 50 ml. round-bottomed flask equipped with a von Braun distillation head, and a receiver. The pressure was reduced to about 25 mm. and the reaction flask was placed in an oil bath maintained between 160 - 180° for a period of two and one-half

hours. The reaction flask was then heated with a free flame and very little material distilled before decomposition became evident. An unidentifiable material (5 g.) was isolated, m.p. 190 - 270° Lit. (40) 78.5 - 80° .

4-Cyanopyridine (XXXVII).

A mixture of 62 g. (0.5 mole) of isonicotinic acid, 30 g. (0.5 mole) of glacial acetic acid, and 77 g. (one mole) of ammonium acetate was placed in a 250 ml. round-bottomed flask equipped with a Vigreaux column, distillation head, water-cooled condenser, Dean-Stark tube, and a receiver. When the temperature reached 150° the water was drained from the condenser converting it to an air-cooled condenser. The fractions which distilled between 150 - 170° (ca. 65 ml.) and all of the solid material distilling over 170° were collected. The distillation was continued until the temperature of the distilling vapors fell below 150°, and the desired fractions were made alkaline with ammonium hydroxide and extracted several times with ethyl ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and the concentrate was crystallized. Recrystallization from benzene yielded 18 g. (35%) of white needles, m.p. 77 - 81° (corr.) Lit. (40) m.p. 78.5 - 80° .

2-Benzoylpyridine (XXVIII).

A Grignard reagent was prepared from 50.3 g. (0.32 mole) of bromobenzene in 100 ml. of anhydrous ethyl ether, and 8 g. (0.33 mole)

of magnesium in a three-necked 500 ml. flask. A solution of 31.2 g. (0.30 mole) of 2-cyanopyridine in 100 ml. of anhydrous ethyl ether was added dropwise over a period of two hours during which time the solution became progressively darker and thickened to such an extent that the stirrer stopped moving. About 100 - 150 ml. of solvent was added and the solution was stirred at room temperature for a period of seven to eight hours. The complex was decomposed with an ammonium chloride - hydrochloric acid solution (50 g. of ammonium chloride dissolved in 200 ml. of water and 50 ml. of concentrated hydrochloric acid), and the resultant two layer solution was stirred overnight. The organic layer was separated, and the aqueous portion was heated under reflux for two to three hours. The solution was cooled, neutralized with dilute sodium hydroxide solution, extracted several times with ethyl ether, and dried over anhydrous magnesium sulfate. The dried ethereal solution was concentrated and the residual black oil was distilled under reduced pressure. The fraction boiling between 155 - 159° (9 mm.) [Lit. (41) 170 - 172° (10 mm.)] was collected; yield 29 g. (53%). The picrate melted between 130 - 132.5° [Lit. (41) m.p. 128 - 129°]. An admixture of the picrate and picric acid (m.p. 123 - 125°) showed a depression to 105 - 110°.

Attempted Preparation of 2-Benzylphenyl-2'-pyridyl Ketone (XXI).

A Grignard reagent was prepared from 94.8 g. (0.6 mole) of redistilled 2-bromopyridine, 26.2 g. (0.24 mole) of ethyl bromide, and

20.4 g. (0.84 mole) of magnesium *via* the "entrainment" technique. The magnesium and a few crystals of iodine were placed in a 500 ml. three-necked flask and the iodine was sublimed. Following the addition of 100 - 150 ml. of anhydrous ethyl ether, 3 g. of ethyl bromide dissolved in *ca.* 5 ml. of solvent was added to initiate the reaction. After the reaction had begun, 2-bromopyridine and the remainder of the ethyl bromide in 125 ml. of the solvent were added dropwise over a period of three hours during which time the solution turned dark brown. The resultant solution was stirred overnight at room temperature and subsequently heated under a partial take-off until *ca.* 100 ml. of the solvent had been removed. After the flask had cooled somewhat, a solution of 58 g. (0.3 mole) of *o*-benzylbenzonitrile in 150 ml. of anhydrous toluene was added dropwise with stirring over a period of thirty minutes. The dark brown solution was heated under a partial take-off for two hours removing most of the ethyl ether, and the reaction mixture took on the appearance of a tar. Decomposition with 20% ammonium chloride solution, removal of the organic layer, and subsequent extraction with toluene yielded a red-brown semi-solid mixture, m.p. 130 - 160°. The liquid portion of this mixture was made alkaline with sodium hydroxide solution, extracted several times with ethyl ether, and the ethereal solutions were concentrated and distilled into two broad fractions. Fraction I (11 g.), a slightly viscous yellow oil, distilled between 140 - 170° (22 mm.) and yielded crystals, m.p. 50 - 62°.

These colorless prisms when treated with ferrous ion yielded an intense red color. Fraction II (26 g.) distilled between 190 - 210° (5 mm.) and partially solidified into a dark brown tar.

2-Benzylphenyl-2'-pyridyl Ketone (XXI).

A Grignard reagent was prepared from 21.1 g. (0.085 mole) of o-bromodiphenylmethane, and 2.1 g. (0.086 mole) of magnesium in ca. 75 ml. of anhydrous ethyl ether in a three-necked 250 ml. flask. A solution of 8 g. (0.084 mole) of 2-cyanopyridine in ca. 30 ml. of solvent was added dropwise over a period of ninety minutes and a slightly exothermic reaction was noticed. The resultant dark brown solution was heated under reflux for a period of seven to eight hours during which time small portions of the solvent were added to prevent the stirrer from stopping. The solution was decomposed with 60 ml. of a 20% ammonium chloride solution and 15 ml. of concentrated hydrochloric acid, and the two layer solution was then stirred at room temperature for a period of seven to eight hours. The organic layer was decanted, the aqueous portion heated under reflux for four hours and then made alkaline with dilute sodium hydroxide solution. The basic solution was extracted several times with an ethyl ether-acetone mixture, and the combined organic extracts were dried over anhydrous magnesium sulfate. Following concentration the black oil was distilled under reduced pressure. The fraction boiling between 208 - 211° (3 mm.) was collected.

The yield was 12 g. (59%) and ethyl alcohol recrystallizations of the solidified distillate yielded white prisms, m.p. 61 - 62°.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53.
Found: C, 83.26; H, 5.65.

2-Benzylphenyl-3'-pyridyl Ketone (XLII).

A Grignard reagent was prepared from 37 g. (0.15 mole) of o-bromodiphenylmethane in 100 ml. of anhydrous ether and 3.78 g. (0.16 mole) of magnesium in a 500 ml. flask. A solution of 15.5 g. (0.15 mole) of 3-cyanopyridine in 30 ml. of anhydrous ethyl ether was added dropwise over a period of three hours. The orange-red suspension was heated under reflux overnight and decomposed with 100 ml. of a 20% ammonium chloride solution and 25 ml. of concentrated hydrochloric acid. Following the removal of the organic layer, the water portion was heated under reflux for six hours, neutralized, and the product was isolated in the same manner as described above. The fraction distilling between 204 - 207° (3 mm.) containing 14 g. (33%) was collected. Poor analytical analysis, and a continued darkening of the yellow oil necessitated the preparation of a derivative for acceptable carbon and hydrogen analysis.

Picrate of 2-Benzylphenyl-3'-pyridyl Ketone.

A hot solution of 1 g. of ketone XLII in ca. 6 ml. of ethyl alcohol was added to a hot solution of 1 g. of picric acid in ca. 3 ml. of ethyl alcohol. The solution was then placed in a dry ice-acetone bath and the

resultant precipitate on recrystallization from ethyl alcohol yielded yellow flakes, m.p. 116 - 118°.

Anal. Calcd. for $C_{25}H_{18}N_4O_8$: C, 59.76; H, 3.61.
Found: C, 59.83; H, 3.71.

2-Benzylphenyl-4'-pyridyl Ketone (XLIII).

A Grignard reagent was prepared from 24.7 g. (0.10 mole) of o-bromodiphenylmethane in 70 ml. of anhydrous ethyl ether and 2.5 g. (0.10 mole) of magnesium in a 250 ml. flask. A solution of 10 g. (0.10 mole) of 4-cyanopyridine in 70 ml. of an anhydrous toluene-ethyl ether mixture was added dropwise over a period of one hour. The resultant dark brown solution was heated under reflux for seven hours, and decomposed with 64 ml. of an 20% ammonium chloride solution and 16 ml. of concentrated hydrochloric acid. The two layer solution was stirred for a period of five hours, the organic layer was removed, and following the heating and neutralization of the aqueous portion the isolation of the product was carried out in the same manner as described in the above experiments. The fraction distilling between 207 - 212° (3.5 mm.) containing 14 g. (53%) was collected. The preparation of a derivative was necessary for acceptable analysis for the same reasons mentioned in discussing ketone XLII.

Picrate of 2-Benzylphenyl-4'-pyridyl Ketone.

This compound was prepared using the same procedure as was

used in preparing its isomer. Recrystallization of the precipitate from an ethyl alcohol-benzene mixture yielded yellow needles, m.p. 165-167.5°.

Anal. Calcd. for $C_{25}H_{18}N_4O_8$: C, 59.76; H, 3.61.
Found: C, 59.53; H, 3.75.

9-(2'-Pyridyl)-anthracene (XLIV).

A. Via Hydrobromic and Acetic Acid Cyclization.

A mixture of 4.5 g. (0.017 mole) of ketone XXI, 25 ml. of 48% hydrobromic acid, and 50 ml. of glacial acetic acid was placed in a 100 ml. round-bottomed flask and heated under reflux for 52 hours. The solution was neutralized with dilute sodium hydroxide solution, and the resultant precipitate was collected, washed with water, and dried. The yield was 3.9 g. (92%) and recrystallization from an ethyl and methyl alcohol mixture afforded light yellow-green crystals, m.p. 163-165°.

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13.
Found: C, 89.04; H, 5.19.

B. Via Phenyl Acid Phosphate Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XXI and ca. 7 g. of phenyl acid phosphate was placed in a 50 m. round-bottomed flask and heated in an oil bath maintained at 190° for five hours. The dark oil was neutralized and the product was isolated in the same manner as the above experiment. The yield was quantitative and subsequent recrystallizations

from an ethyl and methyl alcohol mixture yielded light yellow-green crystals, m.p. 163 - 165°.

C. Via Benzenesulfonic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XXI, and ca. 5 g. of benzenesulfonic acid was placed in a 50 ml. round-bottomed flask and placed in an oil bath maintained at 150° for a period of five hours. The dark oil was treated in the usual manner and light yellow-green crystals, m.p. 162 - 165° were obtained upon recrystallization from ethyl and methyl alcohol. The yield was 0.58 g. (62%).

D. Via a Sealed Tube Hydrobromic and Acetic Acid Cyclization.

A mixture of 0.5 g. (0.0018 mole) of ketone XXI, 8 ml. of 48% hydrobromic acid, and 15 ml. of glacial acetic acid was placed in a Carius tube, sealed, and inserted into a Carius oven maintained at 180° for a period of six hours. The resultant black solution was treated in the usual manner and light yellow-green crystals, m.p. 162 - 164°, were obtained upon recrystallization from the usual medium. The yield was quantitative.

9-(3'-Pyridyl)-anthracene (XLV).

A. Via Hydrobromic and Acetic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLII, 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was heated under

reflux for 10 hours. The resultant solution was neutralized, and the product was isolated in the same manner as used for hydrocarbon XLIV. The yield was 0.87 g. (93%), and recrystallization from ethyl alcohol afforded very light greenish prisms, m.p. 197 - 198°.

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13.

Found: C, 89.52; H, 5.26.

B. Via Phenyl Acid Phosphate Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLII, and ca. 7 g. of phenyl acid phosphate was heated at 190° for a period of five hours. The dark oil was treated in the usual manner and 0.78 g. (83%) of the precipitate was recrystallized from ethyl alcohol yielding very light greenish prisms, m.p. 197 - 198°.

C. Via Benzenesulfonic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLII and ca. 5 g. of benzenesulfonic acid was heated at 150° for a period of five hours. The resultant dark oil was treated in the usual manner yielding 0.84 g. (90%) of a precipitate which was recrystallized from ethyl alcohol giving very light greenish prisms, m.p. 196 - 198°.

D. Via a Sealed Tube Hydrobromic and Acetic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLII, 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was placed in a

Carius tube, sealed, and inserted into a Carius oven maintained at 180° for a period of six hours. The resultant black solution was treated in the usual manner and 0.77 g. (82%) of a precipitate was obtained. Recrystallisation from ethyl alcohol afforded very light greenish prisms, m.p. 195 - 198°.

Attempted Preparation of 9-(3'-Pyridyl)-anthracene (XLV).

A mixture of 1 g. (0.0037 mole) of ketone XLII, 0.42 ml. (0.0037 mole) of 48% hydrobromic acid, and 5 ml. of glacial acetic acid was placed in a 10 ml. flask and heated in an oil bath which maintained the solution at reflux for a period of five hours. The resultant solution was neutralized and treated in the usual manner and no precipitate could be recovered while visual signs of oil droplets indicated unreacted ketone XLII.

9-(4'-Pyridyl)-anthracene (XLVI).

A. Via Hydrobromic and Acetic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLIII, 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was heated under reflux for two hours. The solution was neutralized and treated in the usual manner yielding 0.91 g. (97%) of a precipitate which was recrystallized from an ethyl alcohol-benzene mixture giving light yellow needles, m.p. 199 - 200°.

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13.

Found: C, 89.16; H, 5.18.

B. Via Phenyl Acid Phosphate Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLII, and ca. 7 g. of phenyl acid phosphate was heated at 190° for a period of five hours. The dark oil was treated in the usual manner yielding 0.79 g. (84%) of a precipitate which was recrystallized from an ethyl alcohol-benzene mixture giving light yellow needles, m.p. 198 - 200°.

C. Via Benzenesulfonic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLIII and ca. 5 g. of benzenesulfonic acid was heated at 150° for a period of three hours. The dark oil was treated in the usual manner yielding 0.81 g. (86%) of a precipitate which was collected and recrystallizedf from the usual medium giving light yellow needles, m.p. 198 - 200°.

D. Via a Sealed Tube Hydrobromic and Acetic Acid Cyclization.

A mixture of 1 g. (0.0037 mole) of ketone XLIII, 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was placed in a Carius tube, sealed, and inserted into a Carius oven maintained at 180° for a period of six hours. The resultant black solution was treated in the usual manner giving a quantitative yield of product which melted between 198 - 200° following recrystallization from an ethyl alcohol-benzene mixture.

Gravimetric Determination of the Rate Constants

A. o-Benzylbenzophenone to 9-Phenylanthracene.

A stock solution of a standard acid mixture was prepared by combining 700 ml. of redistilled glacial acetic acid, 166.4 ml. of redistilled 48% hydrobromic acid, and 43.6 ml. of redistilled water (6, 7, 21). The accurately weighed ketones (0.3 to 0.5 g.) were placed in specially prepared reaction tubes*, dissolved in 20 ml. of the stock acid solution, heated to a gentle boil, capped, and placed in a constant temperature bath** maintained at 117 $\pm$ 0.2° for varying periods of time. On removal from the bath, the contents of the tube were poured into a small beaker, allowed to cool, and the sides of the beaker were scratched to induce crystallization. When crystallization had begun the beakers were covered with a watch glass and placed in a cold room maintained at 15 $\pm$ 1° for at least five hours. The precipitates were quantitatively transferred to a previously weighed sintered glass funnel, sucked dry, washed three times with ten ml. portions of water, and dried to a constant weight in a calcium chloride

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* These tubes were described in (21) J. Van Oot, Ph.D. Thesis, V.P.I. (1950), pp. 93 as "Pyrex glass reaction tubes of about 18 mm. diameter and about 40 ml. capacity, equipped at the upper end with 24/40 standard taper female joint and two glass hooks, which could be used to secure (by means of rubber bands) a glass stopper similarly equipped".

** The author is indebted to R.D. Katstra for his assistance in preparing and maintaining the constant temperature bath.

desiccator (21). These weights were corrected for the solubility of the anthracene in the cyclizing medium by submitting a weighed portion (ca. 0.2 g.) to be same procedure, in triplicate, and determining the dissolved portion by difference. The rate constants were determined from the corrected weight of the anthracene using the equation shown on pp. 26 . The results are shown in Table II.

B. Isomeric Pyridyl Ketones to Pyridyl Anthracenes.

The above method was modified in this manner. Following the allotted reaction time in the constant temperature bath, the contents of the reaction tubes were transferred to small beakers and neutralized with 45 ml. of 20% sodium hydroxide solution. The beakers were subsequently placed in the previously mentioned cold room, and the precipitates following the quantitative transfer to the sintered glass funnel were washed with 200 ml. of hot water. The precipitates were sucked dry, and dried in the manner indicated in Part A. The resultant weights were corrected for the solubility of the anthracene in the neutral solution by putting a weighed portion (ca. 0.2 g.) through the same procedure and determining the dissolved portion by difference. From the corrected weight of the anthracene, the rate constants were determined from the equation on pp. 26 . The results are shown in Tables III - V.

Spectrophotometric Determination of the Rate Constants.

A. Isomeric Pyridyl Ketones to Pyridyl Anthracenes.

1. Determination of the Decomposition of the Hydrocarbons.** Due to Heating.

An approximately 100 x 10^{-5} molar solution of each hydrocarbon was prepared by quantitatively transferring 12.5 mg. of each of the hydrocarbons into a clean, dry 50 ml. volumetric flask. The hydrocarbons were dissolved and diluted to the mark with the stock acid solution. Two portions of the hydrocarbon solutions (10 ml. each) were transferred by means of a pipette to specially prepared reaction flasks*, sealed and inserted into a constant temperature bath maintained at 100 $\pm$ 0.2° for periods of five and ten hours. These two solutions along with a ten ml. portion of the unheated hydrocarbon solution were diluted as follows. Exactly five ml. of each of the three solutions were transferred by means of a pipette into a clean, dry 50 ml. Erlenmeyer flask and 25 ml. of redistilled 95% ethyl alcohol was added with swirling. The ultraviolet spectra of these solutions between the range of 300 - 400 mu was obtained

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* Thanks are extended to R. D. Katstra for his assistance in preparing the reaction flasks. The flasks were prepared by "sealing a 12 inch piece of pyrex tubing (inside diameter = 8 mm., outside diameter = 10 mm.) to a Pyrex test tube (inside diameter = 16 mm., outside diameter = 18 mm.) that had been narrowed at the mouth. The total length of each vessel was 15 inches". (22)

** refers to the isomeric pyridyl anthracenes

using the same spectrophotometer which was noted earlier in the thesis. The absorbance values of each of the peaks which were read directly from the spectrophotometer were plotted against time (ie. zero, five and ten hours of heating), and the slope of the resultant straight line (Figure 1) was used to calculate the heat correction due to decomposition by multiplying it by t (the number of hours of heating). If the slope of the line was negative, the decomposition correction factor was added to the absorbance reading; however, a positive slope would necessitate subtracting this factor from the absorbance reading.

2. Determination of the Extinction Coefficients of the Hydrocarbons*.

A 195.8×10^{-5} molar solution of each of the hydrocarbons was prepared by quantitatively transferring 50 mg. of the hydrocarbons to a clean, dry 100 ml. volumetric flask, dissolving the solid, and diluting to the mark with the stock acid solution. Hydrocarbon solutions of five other concentrations were prepared from the above solution, utilizing the following dilutions with the stock acid solution.

15 ml. of 195.8×10^{-5} M sol'n. diluted to 25 ml. = 117.5×10^{-5} M.

13 ml. " " " " = 101.8×10^{-5} M.

10 ml. " " " " = 78.34×10^{-5} M.

7 ml. " " " " = 54.64×10^{-5} M.

4 ml. " " " " = 31.34×10^{-5} M.

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* refers to the isomeric pyridyl anthracenes

Each of these solutions of varying concentrations (in five ml. portions) were transferred, by means of a pipette, to a clean , dry 25 ml. volumetric flask and diluted to the mark (with swirling) with redistilled 95% ethyl alcohol. The resultant absorbance values obtained from the spectrophotometer were plotted against concentration, and the slope of the straight line obtained was equal to the extinction coefficient (Figure 2). Regions of maximum absorbance for each of the hydrocarbons, ie. 345 mu, 365 mu, and 385 mu (Figures 4, 5, and 6) will yield different extinction coefficients as can be readily seen from Tables VII - X.

3. The Analysis of the Reaction Mixtures.

A 500 x 10^{-5} molar solution of each of the ketones was prepared by quantitatively transferring 273.3 mg. of the ketones to a clean, dry, 200 ml. volumetric flask. (If the ketone was an oil it was accurately weighed in a small beaker and rinsed at least six times directly into the volumetric flask with the stock acid solution). After the ketones has been transferred and dissolved, the solutions were diluted to the mark with the stock acid solution. Several portions (five) of these reaction mixtures (10 ml. each) were transferred to the specially prepared reaction flasks, sealed, and inserted in a constant temperature bath maintained at 100 $\pm$ 0.2° for periods of 5, 10, 15,

20, and 25 hours. Exactly five ml.* of each of the reaction mixtures along with a five ml.* portion of the unheated reaction mixture** were transferred, by means of a pipette, to a dry, clean 25 ml. volumetric flask and diluted with swirling to the mark with redistilled 95% ethyl alcohol. The absorbance values of the reaction mixtures (obtained directly from the spectrophotometer) at the regions of maximum absorbance were converted to the ketone concentrations (Table VI). The multiplication of the uncorrected absorbance readings (E) by 2.5 shown in Table VI was explained in the footnote on pp. 71 . The heat corrected readings were obtained by adding the decomposition correction factors to (E x 2.5), and the approximate percent of reaction was obtained by dividing the heat corrected readings by the extinction coefficient x 500 x 10^{-5}. The approximate percent of ketone present was calculated by subtracting the approximate percent of reaction from 100.

The product of the heat corrected readings and the percent of ketone present yielded the ketone corrections. The final corrected readings were calculated by algebraically adding the ketone corrections

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* The necessary dilutions consisted in using only two ml. of the reaction mixture of ketone XXI, and XLII, and one ml. of the reaction mixture of ketone XLIII. These dilutions necessitated multiplying the uncorrected absorbance readings by the appropriate number to total five, ie. the absorbance reading of XXI, and XLII by 2.5 and the absorbance reading of XLIII by 5.0.

** The absorbance reading of the unheated reaction mixture was determined to allow for the ketone correction (Table VI).

to the heat corrected readings, and the hydrocarbon concentrations were obtained by dividing the final corrected readings by extinction coefficient. Subtraction of the hydrocarbon concentrations from 500 yielded the ketone concentrations which were converted to their logarithms and plotted against heating time. The slope of this line (Figure 3) x 2.303 yielded the first order rate constant. The individual rate constants along with their respective extinction coefficients at particular regions of maximum absorbance are indicated in Tables VII - X.

B. o-Benzylbenzophenone to 9-Phenyl anthracene.

1. Determination of the Decomposition of the Hydrocarbons Due to Heating.

The method was identical with that of Part A.

2. Determination of the Extinction Coefficients of the Hydrocarbons.

A 196.2×10^{-5} molar solution of each hydrocarbons was prepared by quantitatively transferring 50 mg. of each of the hydrocarbons to a clean, dry 100 ml. volumetric flask, dissolving the solid and diluting to the mark with the stock acid solution. Hydrocarbon solutions of five other concentrations were prepared from the above solution utilizing the following dilutions with the stock acid solution.

15 ml. of 196.2 x 10^{-5} M sol'n. diluted to 25 ml. = 118.0 x 10^{-5} M.

13 ml. " " " " = 102.2 x 10^{-5} M.

10 ml. " " " " = 78.64 x 10^{-5} M.

7 ml. " " " " = 55.05 x 10^{-5} M.

4 ml. " " " " = 31.46 x 10^{-5} M.

The remainder of the procedure was identical with Part A.

3. The Analysis of the Reaction Mixtures.

The procedure was identical with that in Part A except that 272.3 mg. instead of 273.3 mg. was quantitatively transferred.

CONCLUSION

CONCLUSION

Three new isomeric pyridyl ketones (XXI), (XLII), and (XLIII) have been synthesized and their cyclizations to the three corresponding isomeric pyridyl anthracenes (XLIV), (XLV), and (XLVI) have been effected by the utilization of hydrobromic and acetic acids, phenyl acid phosphate, and benzenesulfonic acid.

Acceptable analytical data have been obtained for all six new compounds, and the ultraviolet spectra of the pyridyl anthracenes have been observed and found to be almost identical with anthracene, and particularly 9-phenylanthracene.

Since the synthesis of the ketones (I) occured from known intermediate products, one may conclude that the suggested structures for the ketones (I) and the hydrocarbons (II) are valid. This is by no means an implication that a rigorous proof of structure has been established; however, it is felt that the elemental carbon and hydrogen analysis and ultraviolet spectra support the assigned structures.

Gravimetric and spectrophotometric rate studies were conducted to contrast the rates of cyclization of the isomeric pyridyl ketones (I) with that of o-benzylbenzophenone (XLVI). In all cases, the data indicated that all of the isomeric pyridyl ketones (I) cyclized at a more rapid rate than XLVI.

Assuming that the mechanism of cyclization proceeded via the

Bradsher-type aromatic cyclodehydration reaction it was thought that the more significant rate determining step might be the attack of the carbonium ion on the ortho position of the benzene ring into which cyclization will occur. A consideration of the other postulated rate determining step, ie. the position of the equilibrium of the ketone and the conjugate acid, would lead to a lower rate of cyclization. These conclusions were considered in light of the fact that a diprotonated species was the postulated active entity.

The gravimetric and spectrophotometric studies support earlier views that a difference existed in the rates of cyclization among the isomeric pyridyl ketones (I). The spectrophotometric measurements, which were thought to be more precise than the gravimetric studies, implied that the ketone XLIII cyclized more rapidly than ketones XLII, and XXI. Furthermore, ketone XXI and XLII were observed to have essentially the same rate constant.

The similarity of the rates of cyclization of ketones XXI and XLII and the individual differences in the rate of cyclization of XXI, XLII, and XLIII are not clearly understood at this time.

SUGGESTIONS FOR FUTURE INVESTIGATIONS

It is felt that the synthesis of the isomeric pyridyl ketones (I) and their subsequent conversion to the corresponding pyridyl anthracenes (II) may be made more general than this brief investigation has indicated.

Pyridyl derivatives of 1, 2-benzanthracene or possibly quinolyl derivatives of anthracene and 1, 2-benzanthracene might be capable of synthesis by analagous procedures. An added feature particularly when considering quinolyl substituted ketones would be the possibility of two products upon loss of water.

The synthesis of compounds with functional group positioned in the benzene ring into which cyclization will occur and/or in the hetero nucleus in the pyridyl anthracene series might prove extremely helpful in studies of the aromatic cyclodehydration reaction, in the presence of a nitrogen moiety, by observing the effect of the electron withdrawing and releasing properties of these functional groups.

Other studies using a fully hydrogenated species, ie. piperidino derivatives might be of synthetic as well as theoretical interest.

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LITERATURE CITED

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VITA

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APPENDIX

Absorption Maxima of the Hydrocarbons Prepared

(Wavelength in mu)

9-Phenylanthracene*	9-(2'-Pyridyl)-anthracene
224	
254	254
330	330
350	345
365	365
385	380

9-(3'-Pyridyl)-anthracene	9-(4'-Pyridyl)-anthracene
254	254
330	330
345	345
365	365
385	385

*The absorption maxima for 9-phenylanthracene was included for comparison purposes.

Absorption Maxima of the Ketones Prepared

(Wavelength in mu)

2-Benzylphenyl-2'-pyridyl Ketone	2-Benzylphenyl-3'-pyridyl Ketone	2-Benzylphenyl-4'-pyridyl Ketone
235	232	---
270	270	270

FIGURE 1

Decomposition curve for 9-(3'-pyridyl)-anthracene at 368 mu

Decomposition correction factor = slope x t (heating time of reaction mixtures)

= -0.0064 x t

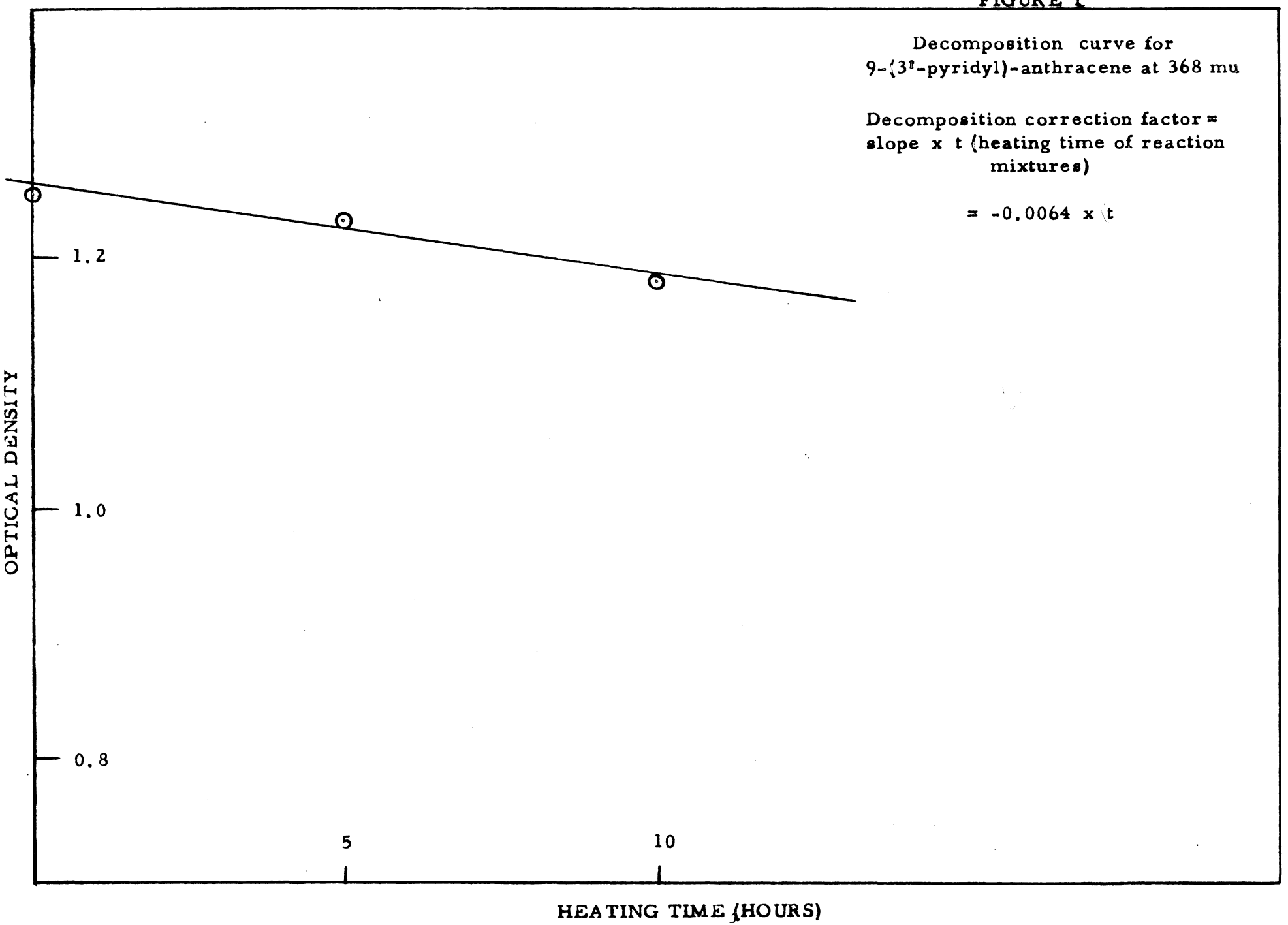


FIGURE 2

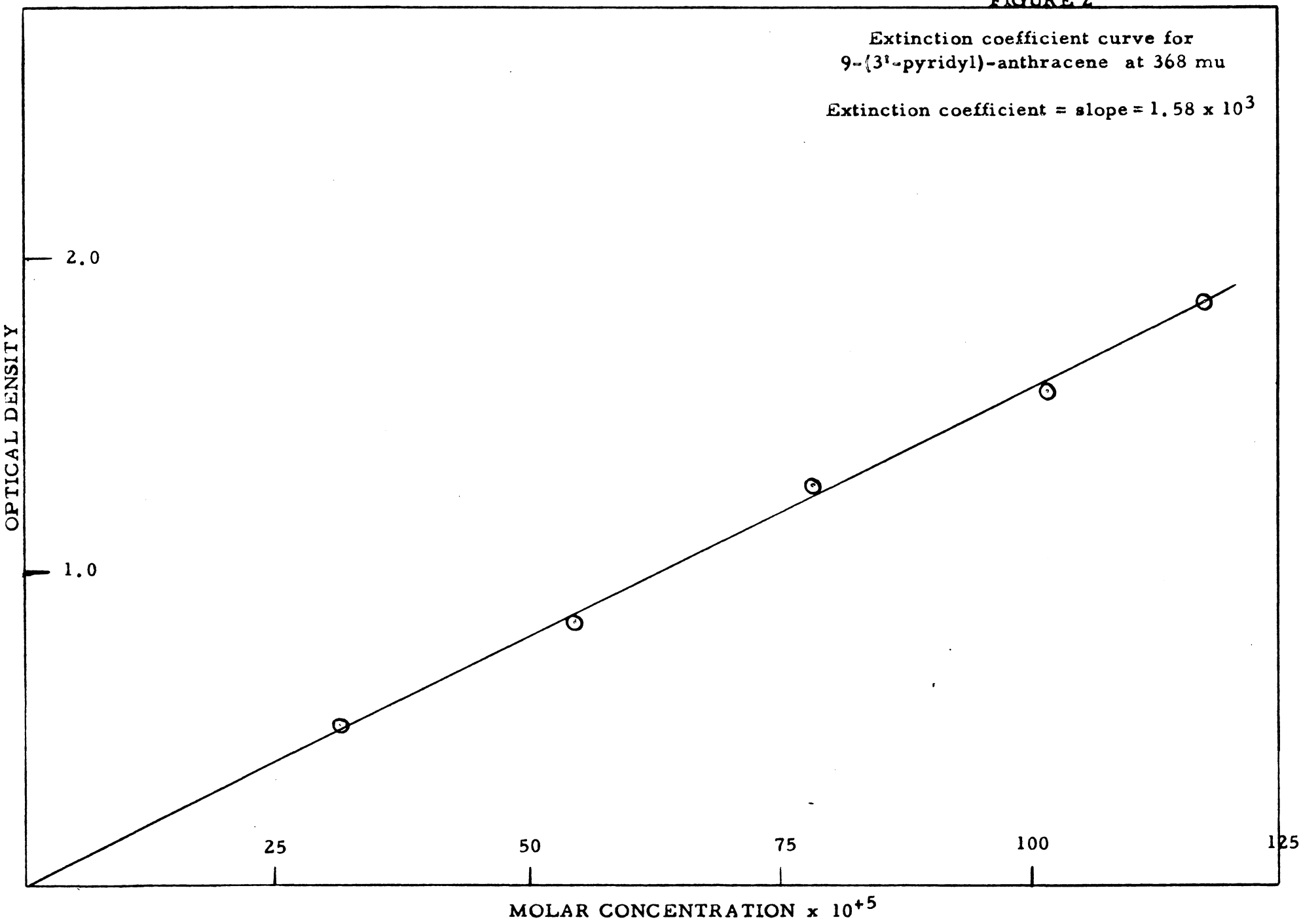

Extinction coefficient curve for
9-(3'-pyridyl)-anthracene at 368 mu
Extinction coefficient = slope = 1.58 x 10^3
OPTICAL DENSITY
2.0
1.0
25
50
75
100
125
MOLAR CONCENTRATION x 10^+5

FIGURE 3

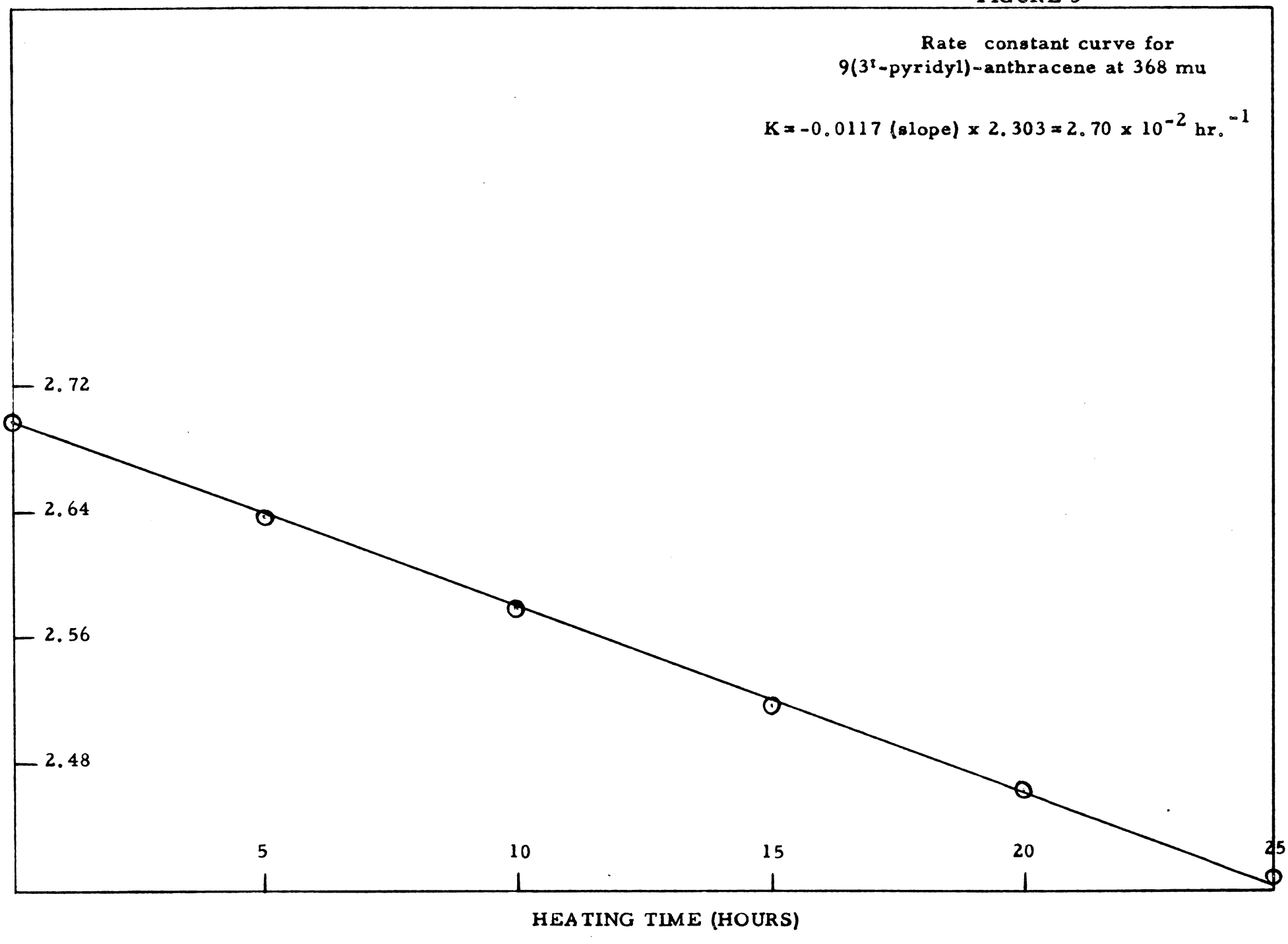

Rate constant curve for
9(3'-pyridyl)-anthracene at 368 mu
K = -0.0117 (slope) x 2.303 = 2.70 x 10^-2 hr.^-1
5 + LOGARITHM OF KETONE CONCENTRATION
2.72
2.64
2.56
2.48
5
10
15
20
25
HEATING TIME (HOURS)

FIGURE 4

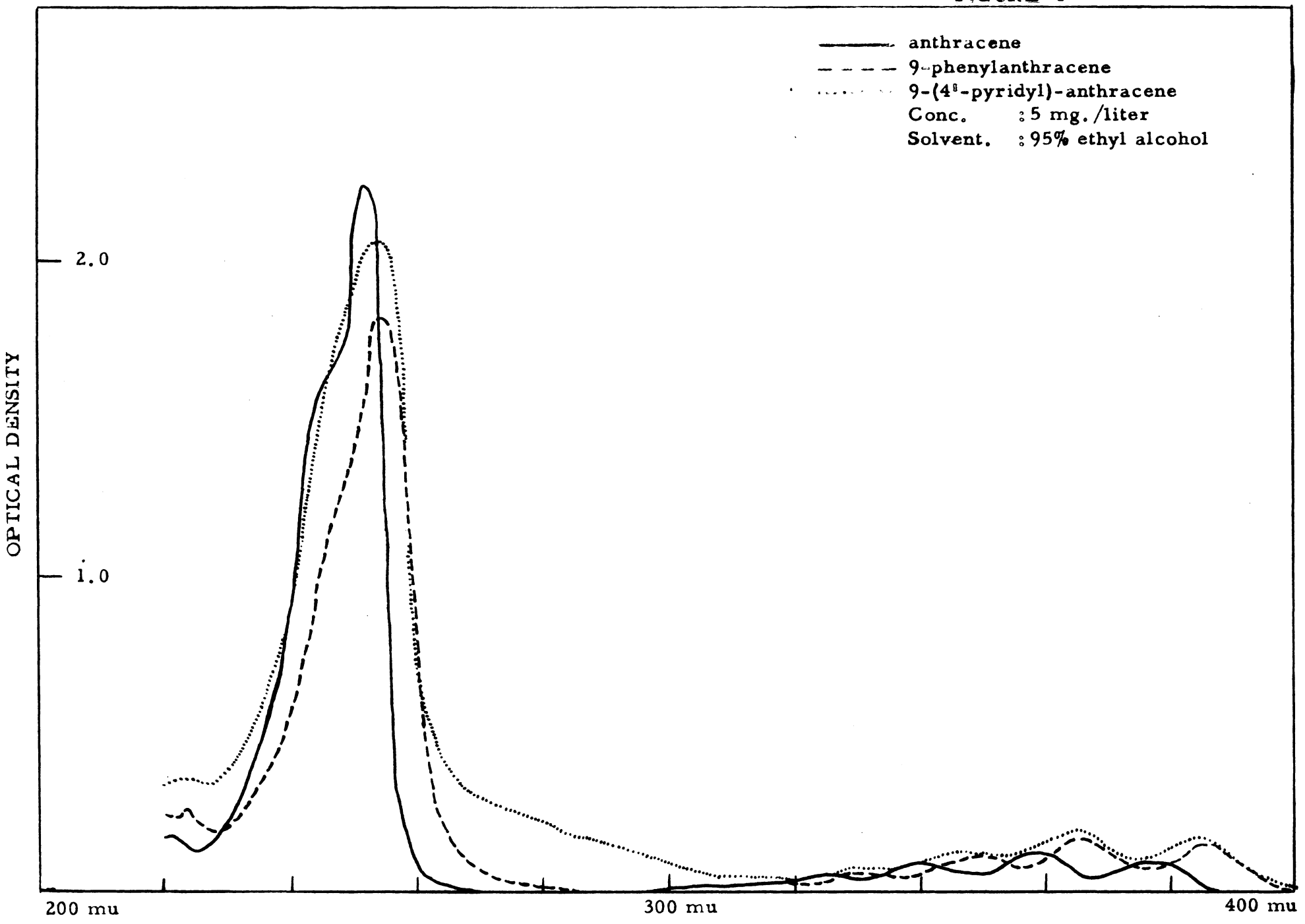

anthracene
9-phenylanthracene
9-(4'-pyridyl)-anthracene
Conc. : 5 mg./liter
Solvent. : 95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu

FIGURE 5

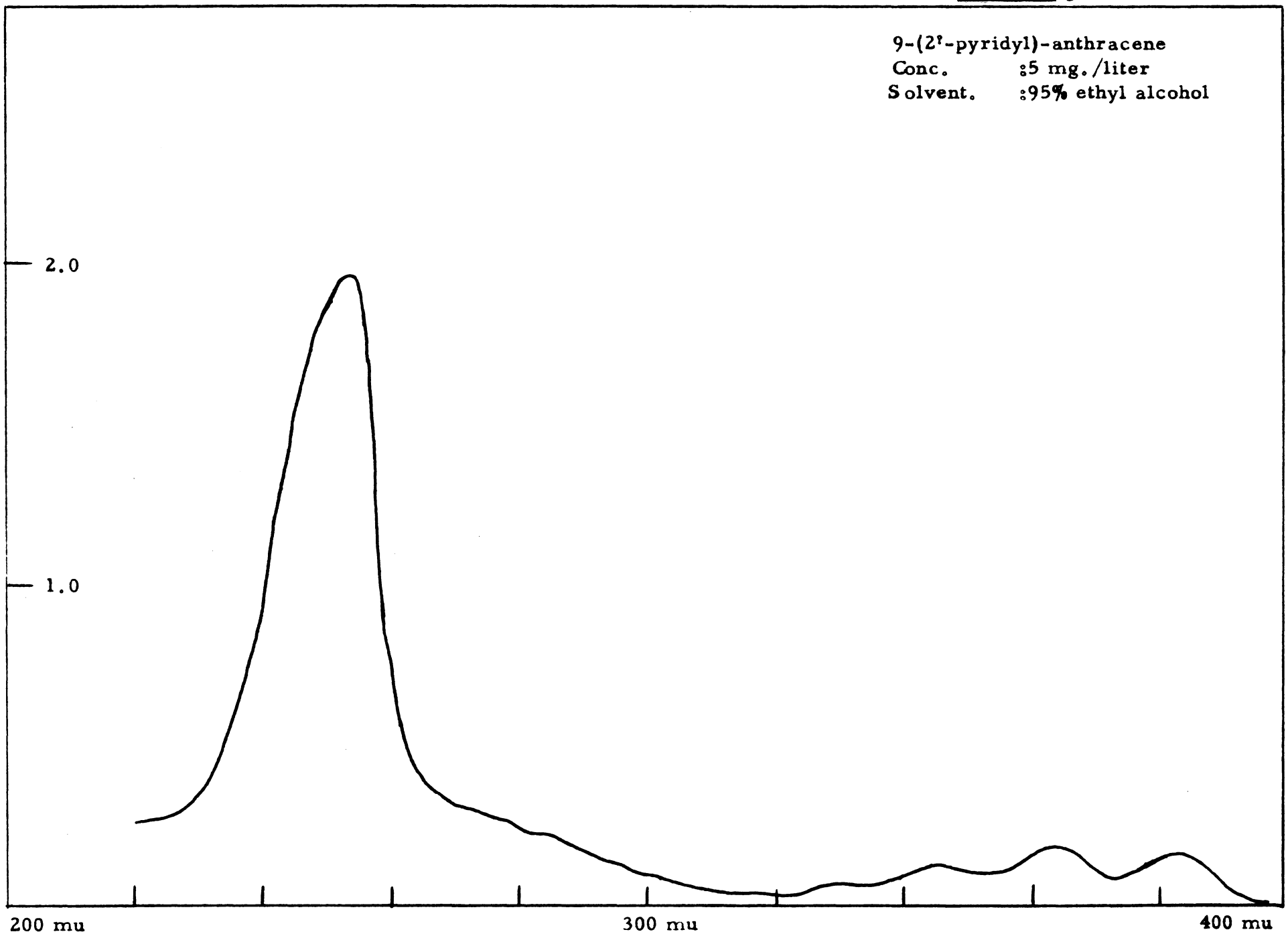

9-(2'-pyridyl)-anthracene
Conc. :5 mg./liter
Solvent. :95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu

FIGURE 6

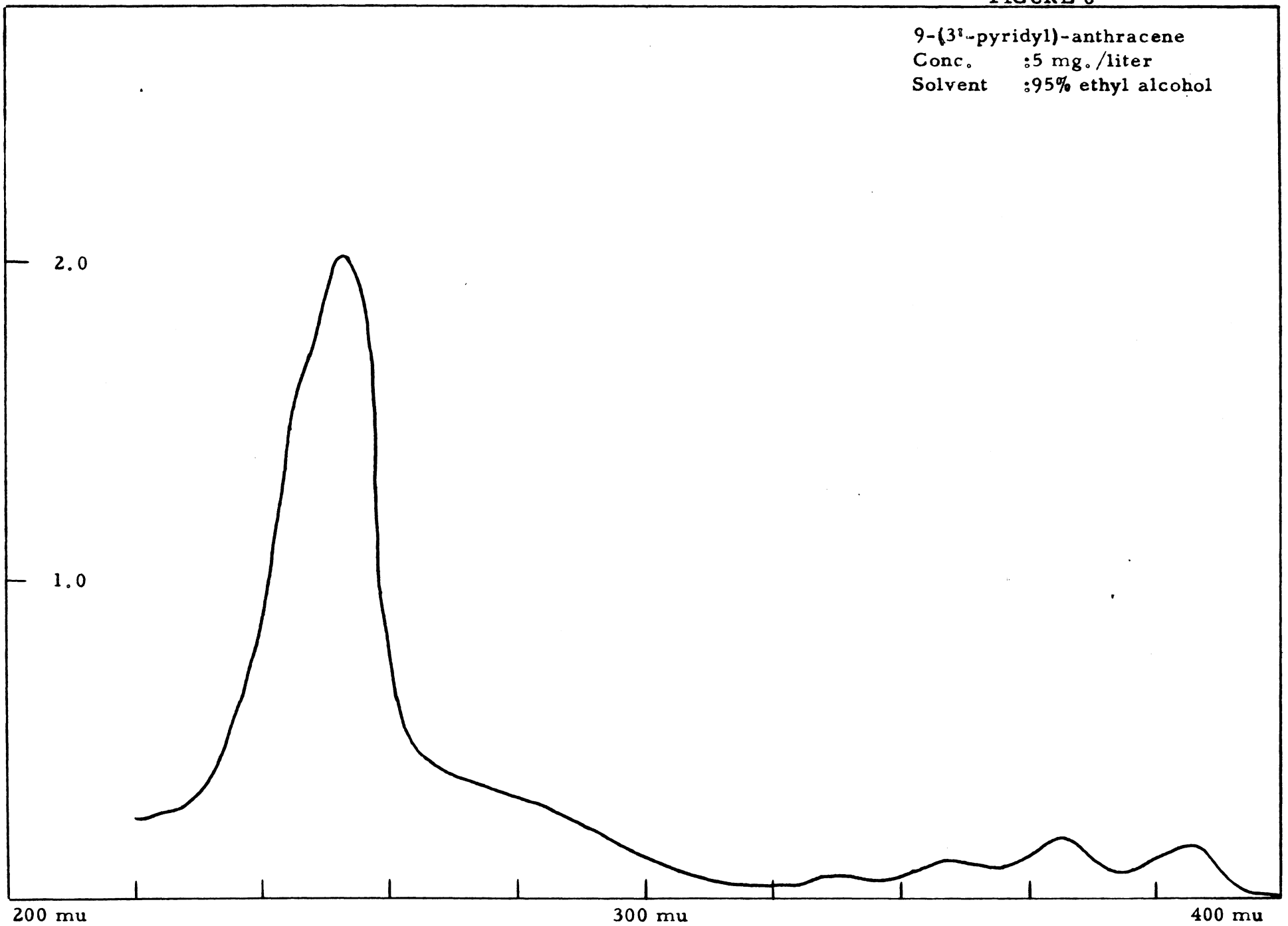

9-(3'-pyridyl)-anthracene
Conc. :5 mg./liter
Solvent :95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu

FIGURE 7

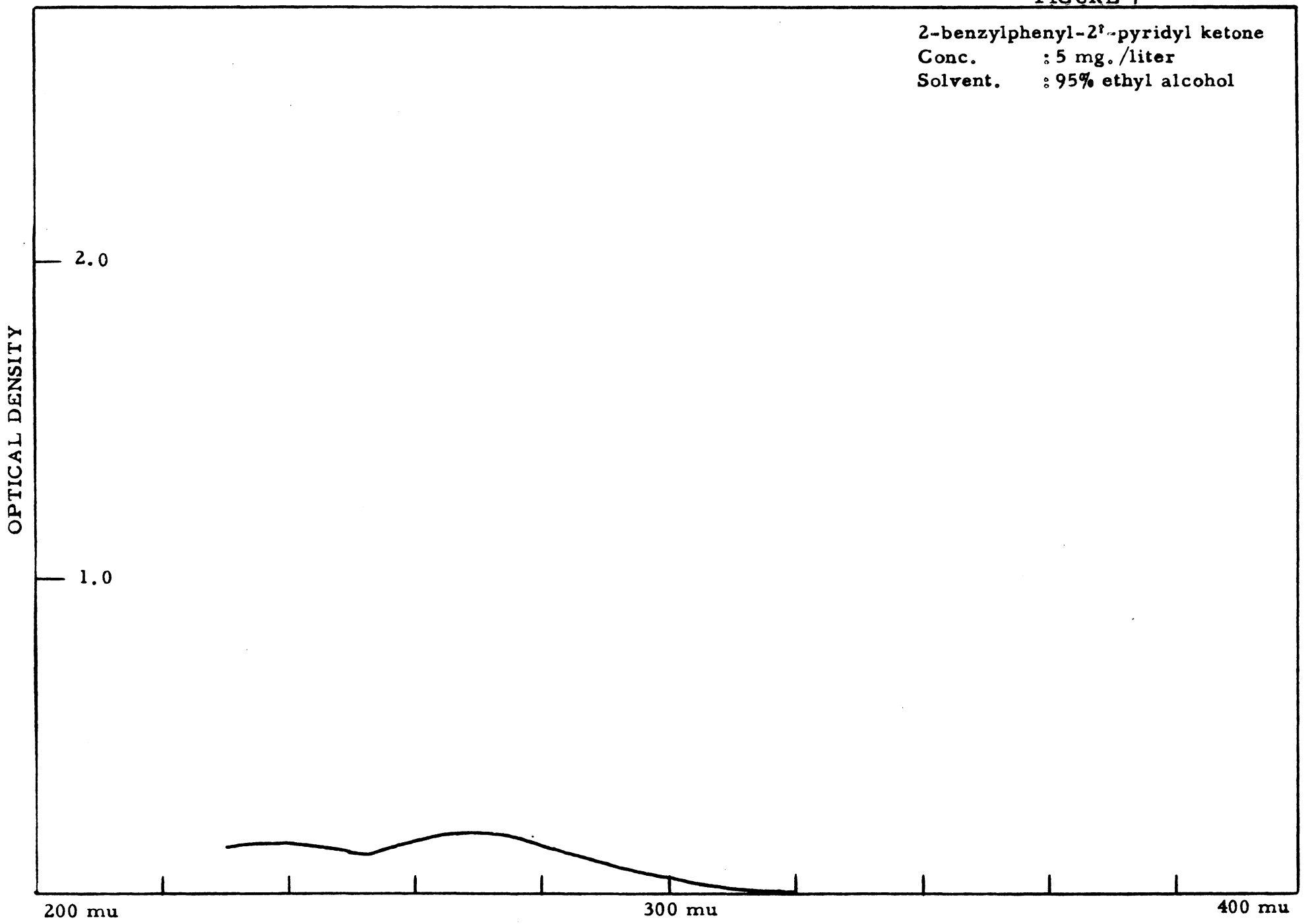

2-benzylphenyl-2'-pyridyl ketone
Conc. : 5 mg./liter
Solvent. : 95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu

FIGURE 8

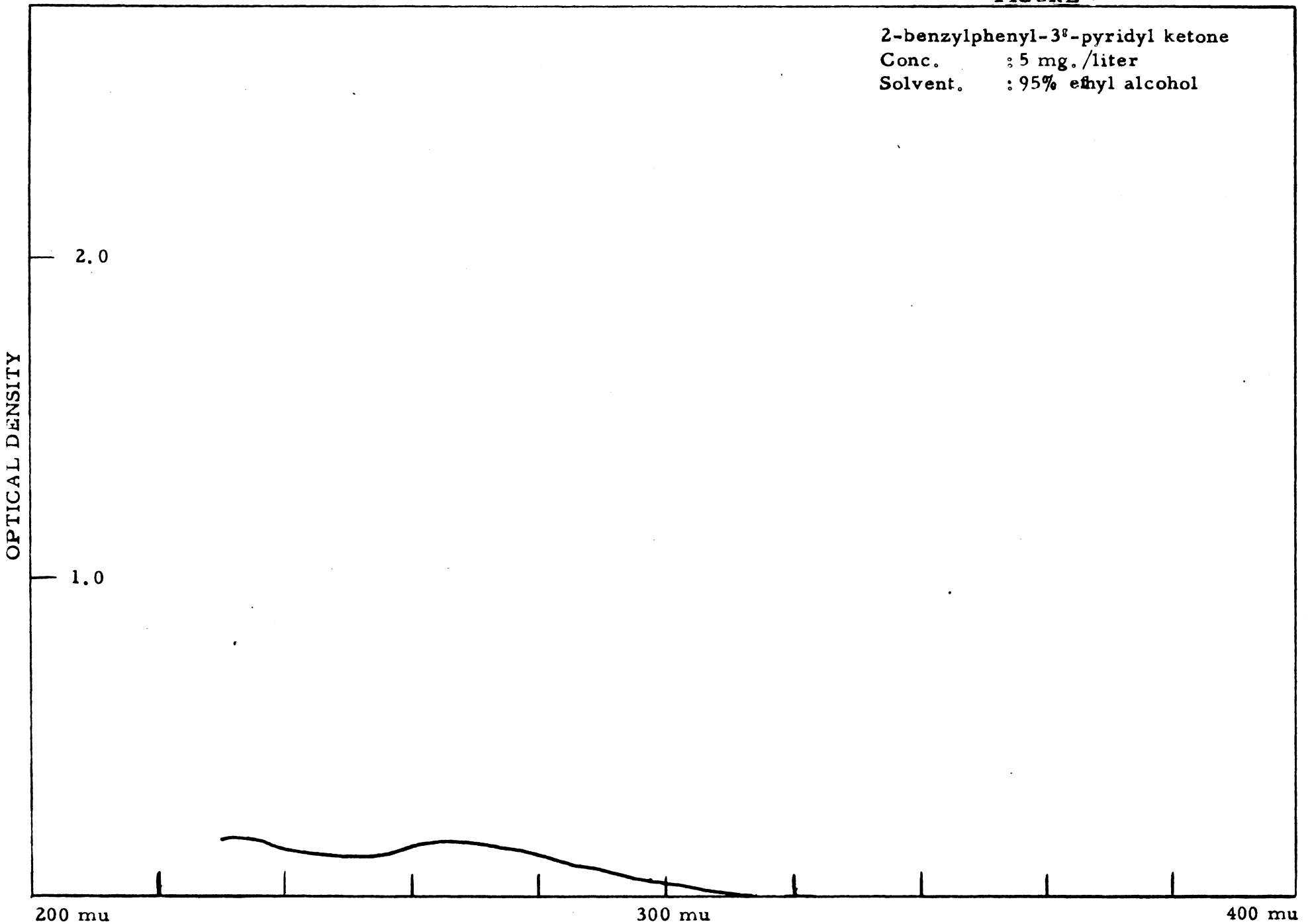
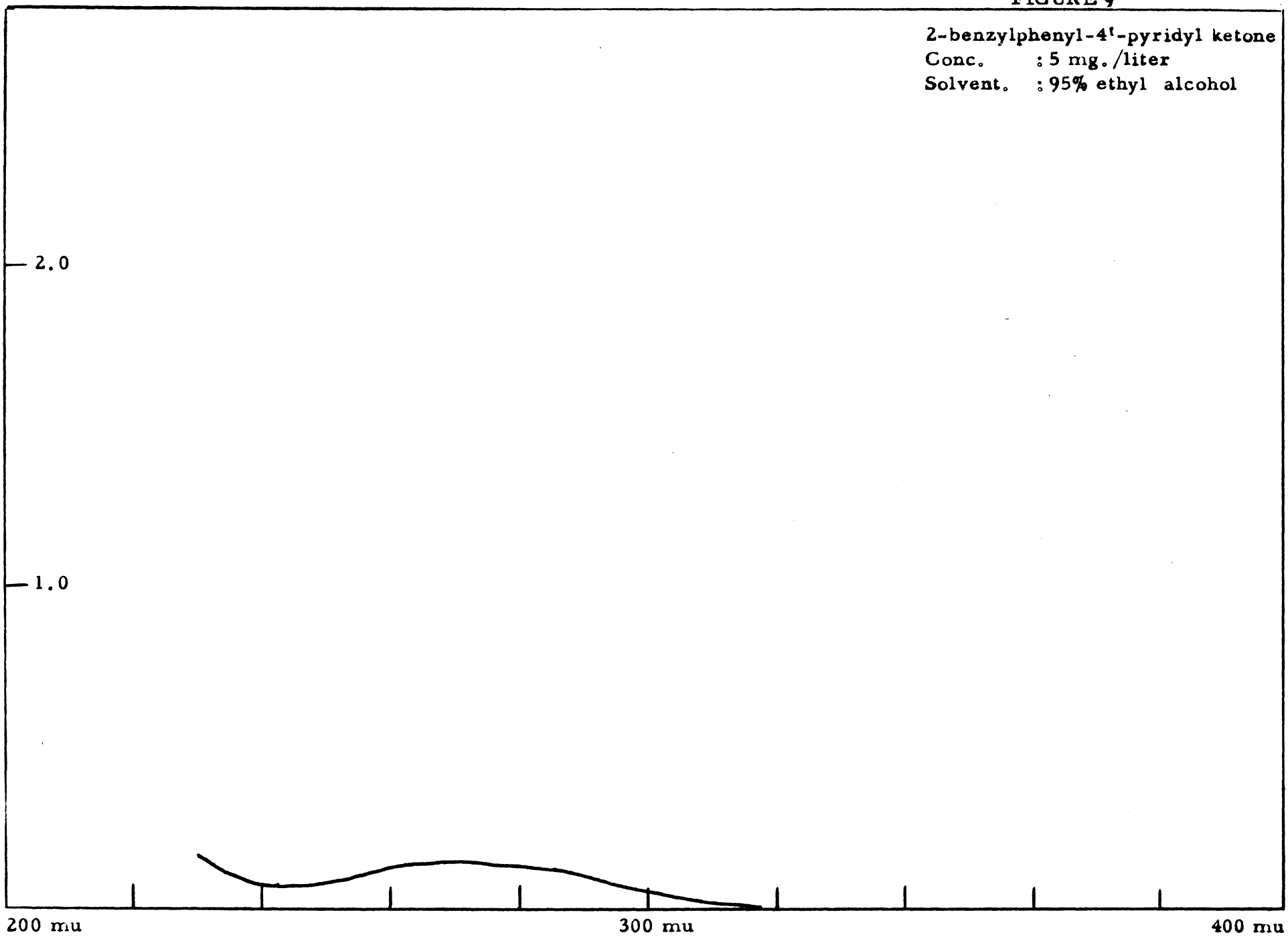

2-benzylphenyl-3'-pyridyl ketone
Conc. : 5 mg./liter
Solvent. : 95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu

FIGURE 9


2-benzylphenyl-4'-pyridyl ketone
Conc. : 5 mg./liter
Solvent. : 95% ethyl alcohol
OPTICAL DENSITY
2.0
1.0
200 mu
300 mu
400 mu